

PHYSICAL PROPERTIES OF POLYMERS

The third edition of this well-known textbook discusses the diverse physical states and associated properties of polymeric materials. The contents of the book have been conveniently divided into two general parts, “Physical states of polymers” and “Some characterization techniques.”

This third edition, written by seven leading figures in the polymer-science community, has been thoroughly updated and expanded. As in the second edition, all of the chapters contain general introductory material and comprehensive literature citations designed to give newcomers to the field an appreciation of the subject and how it fits into the general context of polymer science.

The third edition of *Physical Properties of Polymers* provides enough core material for a one-semester survey course at the advanced undergraduate or graduate level.

Professor James E. Mark is a consultative editor for the Cambridge polymer science list.

PHYSICAL PROPERTIES OF POLYMERS

Third Edition

JAMES MARK
KIA NGAI
WILLIAM GRAESSLEY
LEO MANDELKERN
EDWARD SAMULSKI
JACK KOENIG
GEORGE WIGNALL



PUBLISHED BY THE PRESS SYNDICATE OF THE UNIVERSITY OF CAMBRIDGE
The Pitt Building, Trumpington Street, Cambridge, United Kingdom

CAMBRIDGE UNIVERSITY PRESS
The Edinburgh Building, Cambridge CB2 2RU, UK
40 West 20th Street, New York, NY 10011-4211, USA
477 Williamstown Road, Port Melbourne, VIC 3207, Australia
Ruiz de Alarcón 13, 28014 Madrid, Spain
Dock House, The Waterfront, Cape Town 8001, South Africa
<http://www.cambridge.org>

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Jack Koenig and George Wignall 2003

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Publication Date 2004 for the 3rd edition

- 1st edition published 1984 American Chemical Society
- 2nd edition published 1993 by American Chemical Society – Distributed by OUP.

Printed in the United Kingdom at the University Press, Cambridge

Typeface Times 11/14 pt *System* L^AT_EX 2_ε [TB]

A catalog record for this book is available from the British Library

Library of Congress Cataloging in Publication data

Physical properties of polymers / James Mark . . . [*et al.*].— 3rd edn.
p. cm.

Includes bibliographical references and index

ISBN 0 521 82317 X – ISBN 0521 53018 0 (pb.)

1. Polymers. 2. Chemistry, Physical and theoretical. I. Mark, James E., 1934–
TA455.P58P474 2003
620.1'92–dc21 2003048466

ISBN 0 521 82317 X hardback

ISBN 0 521 53018 0 paperback

The authors wish to dedicate this volume to the memory of Paul J. Flory, whose intuitive grasp of the fundamentals of polymer science predicted and integrated much of the research described in their various contributions. Paul was an inspiring colleague to those of us who were fortunate enough to know him, and one whose influence is still very much in evidence in the field.

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JACK L. KOENIG, born on February 12, 1933, is one of the most cited polymer spectroscopists in the world. He has written seven monographs on spectroscopy, including the ACS Monograph *Spectroscopy of Polymers*, which was one of the most popular books of its kind published by the ACS. Dr Koenig has published over 650 papers in the fields of infrared and Raman spectroscopy, solid-state NMR, and infrared and NMR imaging, so he is truly an expert among polymer spectroscopists, and his chapter is an important addition to the book.

GEORGE D. WIGNALL received his Ph.D. in physics from Sheffield University, UK, in 1966, and specialized in neutron- and X-ray-scattering techniques during postdoctoral fellowships at the Atomic Energy Research Establishment (Harwell, UK) and the California Institute of Technology. While he was working with Imperial Chemical Industries (1969–1979), he initiated small-angle-neutron-scattering (SANS) studies of polymers and used deuterium-labeling techniques to provide the first direct information on polymer-chain configurations in the condensed state. In 1979 he joined the Oak Ridge National Laboratory (ORNL) and helped construct a 30-meter SANS facility, which was one of the first such instruments available to the US scientific community. He has collaborated with many visiting scientists in studies of polymer structure, thermodynamics, and phase behavior, and has over 200 publications to his name, including reviews of neutron scattering from polymers for the *Encyclopedias of Materials Science and Technology* and *Polymer Science and Engineering*. He has received several honors for his research, including Lockheed-Martin-Marietta Awards for the elucidation of isotope-driven phase separation in polymer blends (1987), and for sustained achievement and pioneering research on polymer structures by SANS (1996). He shared the Arnold Beckman Prize (1999) for the development of ultra-small-angle-scattering instrumentation and was given the Paul W. Schmidt Memorial Award (1999) for major contributions to the SANS field. He is a Senior Research Scientist in the ORNL Condensed Matter Sciences Division and a Fellow of the American Physical Society, and is currently responsible for the design and construction of two new user-dedicated state-of-the-art SANS facilities, which are being built at the ORNL High Flux Isotope Reactor.

Preface

The first two editions of this book found considerable use either as a supplementary text or as sole textbook in introductory polymer courses, or simply as a book for self-study. It was therefore decided to bring out an expanded third edition. As before, all of the chapters contain general introductory material and comprehensive literature citations designed to give newcomers to the field an appreciation of the subject and how it fits into the general context of polymer science. All chapters have been extensively updated and expanded. The authors are the same as those for the second edition, except for the authorship of the chapter “The glass transition and the glassy state” by Kia L. Ngai. For pedagogical purposes, the contents have been subdivided into two parts, “Physical states of polymers” and “Some characterization techniques.”

This expanded edition should provide ample core material for a one-term survey course at the graduate or advanced-undergraduate level. Although the chapters have been arranged in a sequence that may readily be adapted to the classroom, each chapter is self-contained and may be used as an introductory source of material on the topics covered.

Part I

Physical states of polymers

1

The rubber elastic state

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1.1 Introduction

1.1.1 Basic concepts

The elastic properties of rubber-like materials are so strikingly unusual that it is essential to begin by defining rubber-like elasticity, and then to discuss what types of materials can exhibit it. Accordingly, this type of elasticity may be operationally defined as very large deformability with essentially complete recoverability. In order for a material to exhibit this type of elasticity, three molecular requirements must be met: (i) the material must consist of polymeric chains, (ii) the chains must have a high degree of flexibility and mobility, and (iii) the chains must be joined into a network structure [1–5].

The first requirement arises from the fact that the molecules in a rubber or elastomeric material must be able to alter their arrangements and extensions in space dramatically in response to an imposed stress, and only a long-chain molecule has the required very large number of spatial arrangements of very different extensions. This versatility is illustrated in Fig. 1.1 [3], which depicts a two-dimensional projection of a random spatial arrangement of a relatively short polyethylene chain in the amorphous state. The spatial configuration shown was computer generated, in as realistic a manner as possible. The correct bond lengths and bond angles were employed, as was the known preference for *trans* rotational states about the skeletal bonds in any n-alkane molecule. A final feature taken into account is the fact that rotational states are interdependent; what one rotational skeletal bond does depends on what the adjoining skeletal bonds are doing [6–8]. One important feature of this typical configuration is the relatively high spatial extension of some parts of the chain. This is due to the preference for the *trans* conformation, as has already been mentioned, which is essentially a planar zig-zag and thus of high extension. The

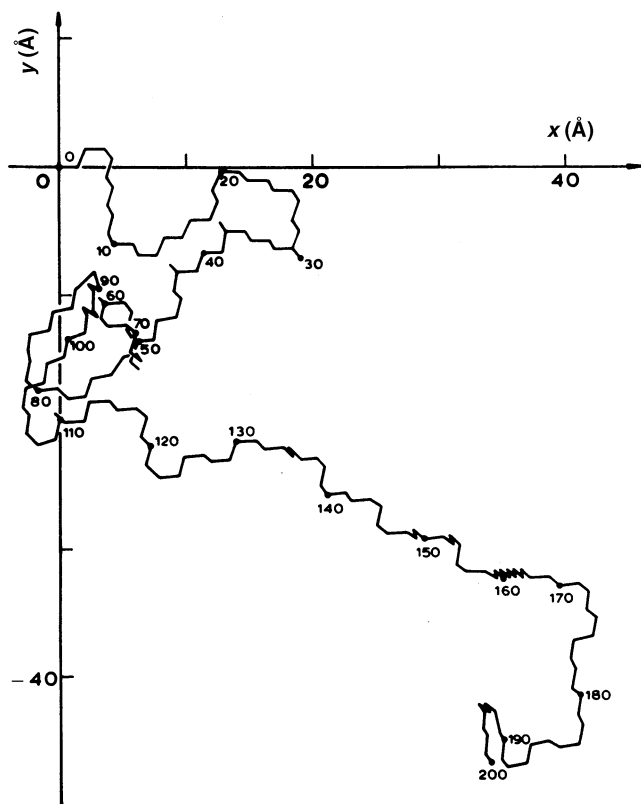


Fig. 1.1. A two-dimensional projection of an n-alkane chain having 200 skeletal bonds [3]. The end-to-end vector starts at the origin of the coordinate system and ends at carbon atom number 200.

second important feature is the fact that, in spite of these preferences, many sections of the chain are quite compact. Thus, the overall chain extension (measured in terms of the end-to-end separation) is quite small. Even for such a short chain, the extension could be increased approximately four-fold by simple rotations about skeletal bonds, without any need for distortions of bond angles or increases in bond lengths.

The second characteristic required for rubber-like elasticity specifies that the different spatial arrangements be *accessible*, i.e. changes in these arrangements should not be hindered by constraints such as might result from inherent rigidity of the chains, extensive chain crystallization, or the very high viscosity characteristic of the glassy state [1, 2, 9].

The last characteristic cited is required in order to obtain the elastomeric recoverability. It is obtained by joining together or “cross-linking” pairs of segments, approximately one out of a hundred, thereby preventing stretched polymer chains

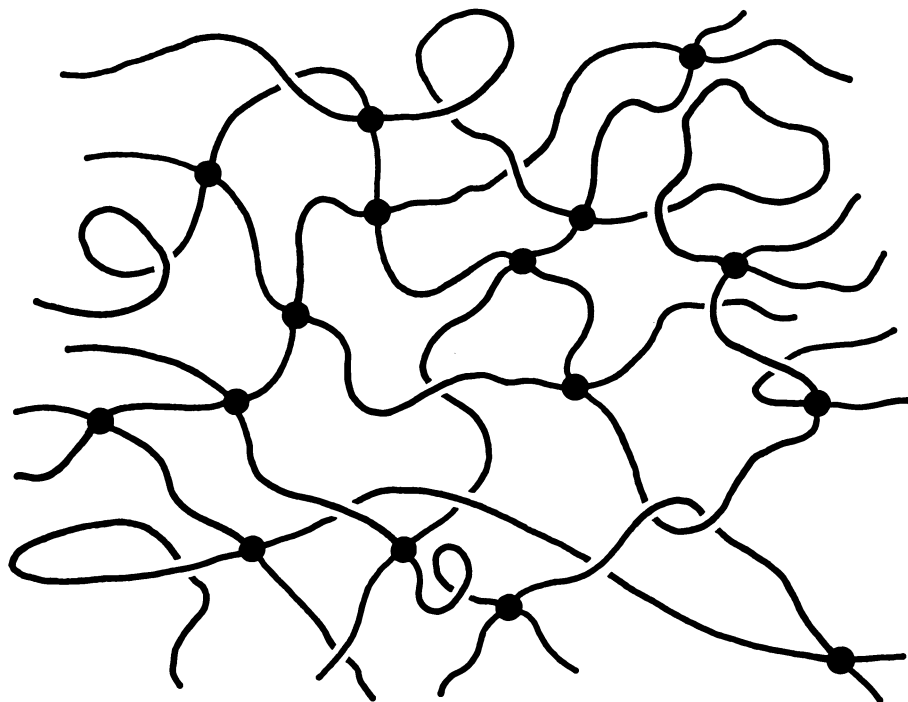


Fig. 1.2. A sketch of an elastomeric network, with the cross-links represented by dots [3].

from irreversibly sliding by one another. The network structure thus obtained is illustrated in Fig. 1.2 [9], in which the cross-links may be either chemical bonds (as would occur in sulfur-vulcanized natural rubber) or physical aggregates, for example the small crystallites in a partially crystalline polymer or the glassy domains in a multiphase block copolymer [3]. Additional information on the cross-linking of chains is given in Section 1.1.6.

1.1.2 The origin of the elastic retractive force

The molecular origin of the elastic force f exhibited by a deformed elastomeric network can be elucidated through thermoelastic experiments, which involve the temperature dependence of either the force at constant length L or the length at constant force [1, 3]. Consider first a thin metal strip stretched with a weight W to a point short of that giving permanent deformation, as is shown in Fig. 1.3 [3]. An increase in temperature (at constant force) would increase the length of the stretched strip in what would be considered the “usual” behavior. Exactly the opposite, a *shrinkage*, is observed in the case of a stretched elastomer! For purposes

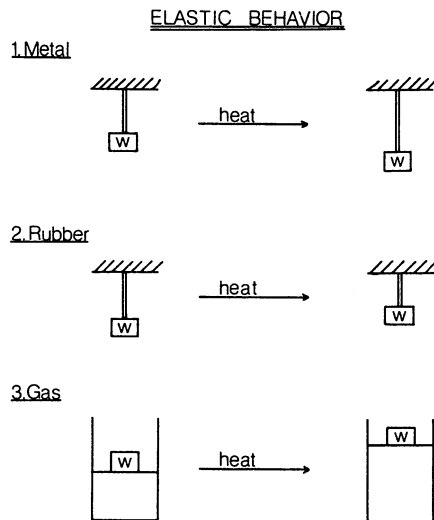


Fig. 1.3. Results of thermoelastic experiments carried out on a typical metal, rubber, and gas [3].

of comparison, the result observed for a gas at constant pressure is included in Fig. 1.3. Raising its temperature would of course cause an increase in volume V , as exemplified by the ideal-gas law.

The explanation for these observations is given in Fig. 1.4 [3]. The primary effect of stretching the metal is the increase ΔE in energy caused by changing the separation d between the metal atoms. The stretched strip retracts to its original length upon removal of the force since this is associated with a decrease in energy. Similarly, heating the strip at constant force causes the usual expansion arising from an increase in oscillations about the minimum in the asymmetric potential-energy curve. In the case of the elastomer, however, the major effect of the deformation is the stretching out of the network chains, which substantially reduces their entropy [1–3]. Thus, the retractive force arises primarily from the tendency of the system to increase its entropy toward the (maximum) value it had in the undeformed state. An increase in temperature increases the magnitude of the chaotic molecular motions of the chains and thus increases the tendency toward this more random state. As a result, there is a decrease in length at constant force, or an increase in force at constant length. This is strikingly similar to the behavior of a compressed gas, in which the extent of deformation is given by the reciprocal volume $1/V$. The pressure of the gas is also largely entropically derived, with an increase in deformation (i.e. an increase in $1/V$) also corresponding to a decrease in entropy. Heating the gas increases the driving force toward the state of maximum entropy (infinite volume or zero deformation). Thus, increasing the temperature

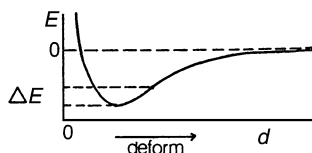
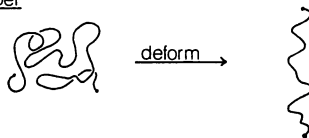
ORIGINS OF ELASTICITY1. Metal2. Rubber3. Gas

Fig. 1.4. Sketches explaining the observations described in Fig. 1.3 in terms of the molecular origin of the elastic force or pressure [3].

increases the volume at constant pressure, or increases the pressure at constant volume.

This surprising analogy between a gas and an elastomer (which is a condensed phase) carries over into the expressions for the work dw of deformation. In the case of a gas, dw is of course $-p dV$. For an elastomer, however, this pressure–volume term is generally essentially negligible. For example, network elongation is known to take place at very nearly constant volume [1, 3]. The corresponding work term now becomes $+fdL$, where the difference in sign is due to the fact that positive dw corresponds not to a decrease in volume of a gas but to an increase in length of an elastomer. Adiabatically stretching an elastomer increases its temperature in the same way that adiabatically compressing a gas (for example in a diesel engine) will increase its temperature. Similarly, an elastomer cools on adiabatic retraction, just as a compressed gas cools during the corresponding expansion. The basic point here is the fact that the retractive force of an elastomer and the pressure of a gas are both primarily entropically derived and, as a result, the thermodynamic and molecular descriptions of these otherwise dissimilar systems are very closely related.

1.1.3 Some historical high points

The simplest of the thermoelastic experiments described above were first carried out many years ago, by J. Gough, back in 1805 [1, 2, 9, 10]. Gough was a clergyman,

who also practiced botany, but had to do it through his sense of touch since he was blind. This is presumably the reason some of his experiments involved sensing the increase in temperature of a rubber strip rapidly stretched while it was in contact with his lips. Particularly important in this regard was the discovery of vulcanization or curing of rubber into network structures by C. Goodyear and N. Hayward in 1839; it permitted the preparation of samples that could be investigated in this regard with much greater reliability. Specifically, the availability of such cross-linked samples led to the more quantitative experiments carried out by J. P. Joule, in 1859. This was, in fact, only a few years after the entropy had been introduced as a concept in thermodynamics in general! Another important experimental fact relevant to the development of these molecular ideas was the fact that deformations of rubber-like materials generally occurred essentially at constant volume, so long as crystallization was not induced [1]. (In this sense, the deformation of an elastomer and that of a gas are very different.)

A molecular interpretation of the fact that rubber-like elasticity is primarily entropic in origin had to await H. Staudinger's much more recent demonstration, in the 1920s, that polymers were covalently bonded molecules, rather than being some type of association complex best studied by the colloid chemists [1]. In 1932, W. Kuhn used this observed constancy in volume to point out that the changes in entropy must therefore involve changes in orientations or spatial configurations of the network chains. These basic qualitative ideas are shown in the sketch in Fig. 1.5 [9], where the arrows represent some typical end-to-end vectors of the network chains.

Later in the 1930s, W. Kuhn, E. Guth, and H. Mark first began to develop quantitative theories based on this idea that the network chains undergo configurational changes, by rotations of skeletal bonds, in response to an imposed stress [1, 2]. More rigorous theories began with the development of the "phantom-network" theory by H. M. James and E. Guth in 1941, and the "affine-model" theory by F. T. Wall, and by P. J. Flory and J. Rehner Jr in 1942 and 1943.

These theories, and some of their modern-day refinements, are described in the following sections.

1.1.4 Basic postulates

There are several important postulates that have been used in the development of the molecular theories of rubber-like elasticity [9].

The first is that, although intermolecular interactions are certainly present in elastomeric materials, they are independent of chain configuration and are therefore also independent of deformation. In effect, the assumption is that rubber-like elasticity is entirely of *intramolecular* origin.

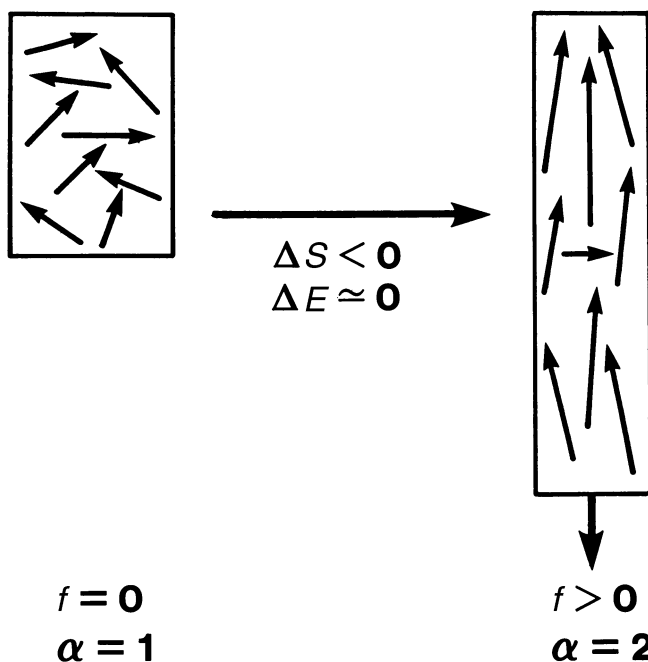


Fig. 1.5. A sketch showing changes in length and orientation of network end-to-end vectors upon elongation of a network [9]. Note that vectors lying approximately perpendicular to the direction of stretching (i.e. horizontally) become *compressed*.

The second postulate states that the free energy of the network is separable into two parts, a liquid-like part and an elastic part, with the former not depending on deformation. This permits the elasticity to be treated independently of other properties characteristic of solids and liquids in general.

In some of the theories it is further assumed that the deformation is affine, i.e. that the network chains move in a simple linear fashion with the macroscopic deformation. Most theories invoke a Gaussian distribution. Non-Gaussian theories have, however, been developed for network chains that are unusually short or stretched close to the limits of their extensibility [2].

1.1.5 Some rubber-like materials

Since high flexibility and mobility are required for rubber-like elasticity, elastomers generally do not contain groups such as ring structures and bulky side chains [2, 9]. These characteristics are evidenced by the low glass-transition temperatures T_g exhibited by these materials. (The structural features of a polymeric chain conducive to low values of T_g are discussed by K. L. Ngai in Chapter 2.) These polymers also tend to have low melting points, if any, but some do undergo crystallization upon being

subjected to sufficiently large deformations. Examples of typical elastomers include natural rubber and butyl rubber (which do undergo strain-induced crystallization), and poly(dimethylsiloxane) (PDMS), poly(ethyl acrylate), styrene–butadiene copolymer, and ethylene–propylene copolymer (which generally do not). The crystallization of polymers in general is discussed by L. Mandelkern in Chapter 4.

Some polymers are not elastomeric under normal conditions but can be made so by raising the temperature or adding a diluent (“plasticizer”). Polyethylene is in this category because of its high degree of crystallinity. Polystyrene, poly(vinyl chloride), and the biopolymer elastin are also of this type, but because of their relatively high glass-transition temperatures [9].

A final class of polymers is inherently non-elastomeric. Examples are polymeric sulfur, because its chains are too unstable, poly(*p*-phenylene), because its chains are too rigid, and thermosetting resins because their chains are too short [9].

There is currently much interest in designing network chains of controlled stiffness. The primary aim here is to increase the melting point of an elastomer such as PDMS so that it undergoes strain-induced crystallization. This crystallization is the origin of the superb mechanical properties of natural rubber, and it results from the reinforcing effects of the crystallites. One way of stiffening elastomeric chains such as PDMS is to put a *meta*- or *para*-phenylene group in the backbone, in an attempt to increase the melting point by bringing about a decrease in the entropy of fusion [9, 11].

Also of interest are fluorosiloxane elastomers. Placing fluorine atoms into siloxane repeat units can be useful for increasing the solvent resistance, thermal stability, and surface-active properties of a polysiloxane [12–14].

One example of another interesting elastomeric material is a new hydrogenated nitrile rubber with good oil resistance and a wide service-temperature range [15]. Another is a type of “*baroplastic*” elastomer, which parallels *thermoplastic* elastomers in that an increase in pressure instead of the usual increase in temperature gives the desired softening required for processing [16].

1.1.6 Preparation of networks

One of the simplest ways to introduce the cross-links required for rubber-like elasticity is to carry out a copolymerization in which one of the comonomers has a functionality ϕ of three or higher [9, 17]. This method, however, has been used primarily to prepare materials so heavily cross-linked that they are in the category of relatively hard thermosets rather than elastomeric materials [18].

A sufficiently stable network structure can also be obtained by physical aggregation of some of the chain segments onto filler particles, by formation of microcrystallites, by condensation of ionic side chains onto metal ions, by chelation of ligand

side chains to metal ions, and by microphase separation of glassy or crystalline end blocks in a triblock copolymer [9]. The main advantage of these materials is the fact that the cross-links are generally only temporary, which means that such materials frequently exhibit reprocessability. This temporary nature of the cross-linking can, of course, also be a disadvantage since the materials are rubber-like only so long as the aggregates are not broken up by high temperatures, the presence of diluents or plasticizers, etc.

1.1.7 Gelation

The formation of network structures necessary for rubber-like elasticity has been studied extensively by a number of groups [19–21]. One approach is to carry out random end linking of functionally terminated precursor chains with a multifunctional reagent, and then to examine the sol fraction with regard to amounts and types of molecules present, and the gel fraction with regard to its structure and mechanical properties. One of the systems most studied in this regard [20] involves chains of PDMS having end groups X that are either hydroxyl or vinyl groups, with the corresponding Y groups on the end-linking agents then being OR alkoxy groups in an organosilicate, or H atoms in a multifunctional silane [22].

In a study of this type, the Monte Carlo method was used to simulate these reactions and thus generate information on the vinyl–silane end linking of PDMS [23, 24]. The simulations gave a very good account of the extent of reaction at the gelation points, but overestimated the maximum extent attainable. The discrepancy may be due to experimental difficulties in taking a reaction close to completion within a highly viscous, entangled medium.

1.1.8 Structures of networks

Before commenting further on such experiments, however, it is useful to digress briefly to establish the relationship among the three most widely used measures of the cross-link density. The first involves the number (or number of moles) of network chains ν , with a network chain defined as one that extends from one cross-link to another. This quantity is usually expressed as the chain density ν/V , where V is the volume of the (unswollen) network [1]. A second measure, directly proportional to it, is the density μ/V of cross-links. The relationship between the number of cross-links μ and the number of chains ν must obviously depend on the cross-link functionality. The two most important types of networks in this regard are the tetrafunctional ($\phi = 4$), almost invariably obtained upon joining two segments from different chains, and the trifunctional, obtained, for example, on forming a polyurethane network by end-linking hydroxyl-terminated chains

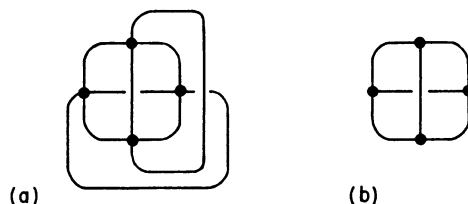


Fig. 1.6. Sketches of some simple, perfect networks having (a) tetrafunctional and (b) trifunctional cross-links (both of which are indicated by the dots) [25]. (Reproduced with permission; copyright 1982, *Rubber Chem. Technol.*)

with a triisocyanate. The relationship between μ and ν is illustrated in Fig. 1.6 [25], which consists of sketches of two simple, perfect network structures, the first tetrafunctional and the second trifunctional. They are simple in the sense of having small enough values of μ and ν for them to be easily counted, and perfect in the sense of not having any dangling ends or elastically ineffective loops (chains with both ends attached to the same cross-link). As can be seen, the tetrafunctional network yields $\mu/\nu = 4/8$ or $1/2$, and the trifunctional one $4/6$ or $2/3$.

In general, for a perfect ϕ -functional network the number $\phi\mu$ of cross-link attachment points equals the number 2ν of chain ends, thus giving the simple relationship $\mu = (2/\phi)\nu$ [1]. Another (inverse) measure of the cross-link density is the molecular weight M_c between cross-links. This is simply the density (ρ , in g cm^{-3}) divided by the number of moles of chains (ν/V , in mol cm^{-3}): $M_c = \rho/(\nu/V)$ [1]. A related structural quantity that is important in the more modern theories is the cycle rank ξ , which denotes the number of chains that have to be cut in order to reduce the network to a tree with no closed cycles at all. It is given by $\xi = (1 - 2/\phi)\nu$ [9].

1.2 Theory

1.2.1 Phenomenological

The phenomenological approach to rubber-like elasticity is based on continuum mechanics and symmetry arguments rather than on molecular concepts [2, 17, 26, 27]. It attempts to fit stress-strain data with a minimum number of parameters, which are then used to predict other mechanical properties of the same material. Its best-known result is the Mooney-Rivlin equation, which states that the modulus of an elastomer should vary linearly with reciprocal elongation [2].

1.2.2 The affine model

This theory, like any other molecular theory of rubber-like elasticity, is based on a chain-distribution function, which gives the probability of any end-to-end

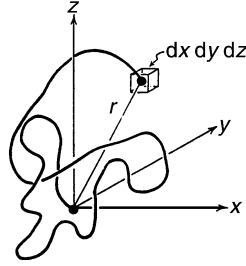


Fig. 1.7. A spatial configuration of a polymer chain, with some quantities used in the distribution function for the end-to-distance r [1]. (Reproduced with permission; copyright 1953, Cornell University Press.)

separation r . The characteristics of this type of distribution function are given in Fig. 1.7 [1]. What is required is a function that answers the question “If a chain starts at the origin of the coordinate system shown, what is the probability that the other end will be in an infinitesimal volume $dV = dx dy dz$ around some specified values of x , y , and z ?”

The simplest molecular theories of rubber-like elasticity are based on the Gaussian distribution function

$$w(r) = \left(\frac{3}{2\pi \langle r^2 \rangle_0} \right)^{3/2} \exp \left(-\frac{3r^2}{2\langle r^2 \rangle_0} \right) \quad (1.1)$$

for the end-to-end separations of the network chains (i.e. chain sequences extending from one cross-link to another) [1–3]. In this equation, $\langle r^2 \rangle_0$ represents the dimensions of the free chains as unperturbed by excluded-volume effects [1]. These excluded-volume interactions arise from the spatial requirements of the atoms making up the polymeric chain and are thus similar to those occurring in gases. They are more complex, however, in that they have an intramolecular as well as intermolecular origin. If they are present, they increase the dimensions of a polymer chain in the same way as that in which they can increase the pressure of a gas. The Gaussian distribution function in which $\langle r^2 \rangle_0$ resides is applied to the network chains both in the stretched state and in the unstretched state. The Helmholtz free energy of such a chain is given by the simple variant of the Boltzmann relationship shown in the first part of the equation

$$F(T) = -kT \ln w(r) = C(T) + \frac{3kT}{2\langle r^2 \rangle_0} r^2 \quad (1.2)$$

where $C(T)$ is a constant at a specified absolute temperature T . Consider now the process of stretching a network chain from its random undeformed state with r components of x , y , z , to the deformed state with r components of $\alpha_x x$, $\alpha_y y$, $\alpha_z z$, (where the α s are molecular deformation ratios). The change in free energy for a

single network chain is then simply

$$\Delta F = \frac{3kT}{2\langle r^2 \rangle_0} [(\alpha_x^2 x^2 + \alpha_y^2 y^2 + \alpha_z^2 z^2) - (x^2 + y^2 + z^2)] \quad (1.3)$$

Since the elastic response is essentially entirely intramolecular [1–3], the change in free energy for ν network chains is just ν times the above result:

$$\Delta F = \frac{3\nu kT}{2\langle r^2 \rangle_0} [(\alpha_x^2 - 1)\langle x^2 \rangle + (\alpha_y^2 - 1)\langle y^2 \rangle + (\alpha_z^2 - 1)\langle z^2 \rangle] \quad (1.4)$$

where the angle brackets around x^2 , y^2 , and z^2 specify their averages over the ν chains. In this model, it is now assumed that the strain-induced displacements of the cross-links or junction points are *affine* (i.e. linear) in the macroscopic strain. In this case, the deformation ratios are obtained directly from the dimensions of the sample in the strained state and in the initial, unstrained state:

$$\alpha_x = L_x/L_{xi} \quad \alpha_y = L_y/L_{yi} \quad \alpha_z = L_z/L_{zi} \quad (1.5)$$

The dimensions of the cross-linked chains in the undeformed state are given by the Pythagorean theorem:

$$\langle r^2 \rangle_i = \langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle \quad (1.6)$$

Also, the isotropy of the undeformed state requires that the average values of x^2 , y^2 , and z^2 , be the same, i.e.

$$\langle x^2 \rangle = \langle y^2 \rangle = \langle z^2 \rangle \quad (1.7)$$

Thus, the chain dimensions are given by

$$\langle r^2 \rangle_i = 3\langle x^2 \rangle = 3\langle y^2 \rangle = 3\langle z^2 \rangle \quad (1.8)$$

and the elastic free energy of deformation by

$$\Delta F = \frac{\nu kT}{2} \frac{\langle r^2 \rangle_i}{\langle r^2 \rangle_0} (\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3) \quad (1.9)$$

In the simplest theories [1–3], $\langle r^2 \rangle_i$ is assumed to be identical to $\langle r^2 \rangle_0$; i.e. it is assumed that the cross-links do not significantly change the chain dimensions from their unperturbed values. Equation (1.9) may then be approximated by

$$\Delta F \cong \frac{\nu kT}{2} (\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3) \quad (1.10)$$

Equations (1.9) and (1.10) are basic to the molecular theories of rubber-like elasticity and can be used to obtain the elastic equations of state for any type of deformation [1–3], i.e. the equations interrelating the stress, strain, temperature, and number or number density of network chains. Their application is best illustrated

for the case of elongation, which is the type of deformation used in the great majority of experimental studies [1–3]. This deformation occurs at essentially constant volume and thus a network stretched by the amount $\alpha_x = \alpha > 1$ would have its perpendicular dimensions compressed by the amounts

$$\alpha_y = \alpha_z = \alpha^{-1/2} < 1 \quad (1.11)$$

Accordingly, for elongation, one obtains the first part of the equation

$$\Delta F = \frac{\nu k T}{2}(\alpha^2 + 2\alpha^{-1} - 3) = f dL \quad (1.12)$$

Since the Helmholtz free energy is the “work function” and the work of deformation is $f dL$ (where $L = \alpha L_i$), as shown in the second equality, the elastic force may be obtained by differentiating Eq. (1.12), giving

$$f = (\partial \Delta F / \partial L)_{T,V} = \frac{\nu k T}{L_i}(\alpha - \alpha^{-2}) \quad (1.13)$$

The nominal stress $f^* \equiv f/A^*$, where A^* is the undeformed cross-sectional area, is then given by

$$f^* \equiv f/A^* = (\nu k T / V)(\alpha - \alpha^{-2}) \quad (1.14)$$

where ν/V is the density of network chains, i.e. their number per unit volume V , which is equal to $L_i A^*$.

The elastic equation of state in the form given in Eq. (1.14) is strikingly similar to the molecular form of the equation of state for an ideal gas:

$$p = N k T (1/V) \quad (1.15)$$

where the stress has replaced the pressure and the number density of network chains has replaced the number N of gas molecules. Similarly, since the stress was assumed to be entirely entropic in origin, f^* is predicted to be directly proportional to T at constant α (and V), as is predicted for the pressure of the ideal gas at constant $1/V$. The strain function $(\alpha - \alpha^{-2})$ is somewhat more complicated than is $1/V$ since the near incompressibility of the elastomeric network superposes compressive effects (given by the term $-\alpha^{-2}$) on the simple elongation (α) being applied to the system. This is illustrated by the approximately horizontal end-to-end vector shown schematically in Fig. 1.5.

Also frequently employed in elasticity studies is the “reduced stress” or modulus defined in the first part of the equation

$$[f^*] \equiv f^* v_2^{1/3} / (\alpha - \alpha^{-2}) = \nu k T / V \quad (1.16)$$

Its definition includes a factor that makes it applicable to networks that have been swelled with a low molecular weight diluent, which is frequently done in order to facilitate the approach to elastic equilibrium. This factor, which is the cube root of the volume fraction of polymer in the network, takes into account the fact that a swollen network has fewer chains passing through unit cross-sectional area, and that the chains are stretched due to the presence of the diluent [1].

1.2.3 The phantom model

In this model, the chains are viewed as having zero cross-sectional area, and can pass through one another as “phantoms” [2, 9, 28, 29]. The cross-links undergo considerable fluctuations in space, and in the deformed state these fluctuations occur in an asymmetric manner so as to reduce the strain below that imposed macroscopically. The deformation thus viewed is very non-affine. Because of this reduction in the strain sensed by the network chains, the modulus is predicted to be diminished relative to that in Eq. (1.16) by incorporation of the factor $A_\phi < 1$:

$$[f^*] = A_\phi \nu kT / V \quad (1.17)$$

In the limit of the very non-affine deformation which would be exhibited by a “phantom” network, A_ϕ is given by

$$A_\phi = 1 - 2/\phi \quad (1.18)$$

For a trifunctional network ($\phi = 3$), A_ϕ is $\frac{1}{3}$ and for a tetrafunctional one, it is $\frac{1}{2}$; it approaches unity in the limit of very high cross-link functionality (as might occur for example in the case of crystallites acting as physical cross-links) [9].

Some of the most interesting advances in the theory of rubber elasticity are the various approaches being developed to take better account of chain entanglements [22, 30]. In the “constraint” theories, the focus is on the way the constraints are placed within the network structure, as discussed in the following section.

1.2.4 The constrained-junction model

Experimental results indicate that the response to deformation of a network generally falls between the affine and phantom limits [31–34]. At low deformations, chain-junction entangling suppresses the fluctuations of the junctions and the deformation is relatively close to the affine limit. This is illustrated in Fig. 1.8, which shows schematically some of the results of the “constrained-junction” theory based on this qualitative idea [32–34]. In the case of the two limits, the affine deformation and the non-affine deformation in the phantom-network limit, the reduced stress should be independent of α . Because of junction fluctuations, the value for the

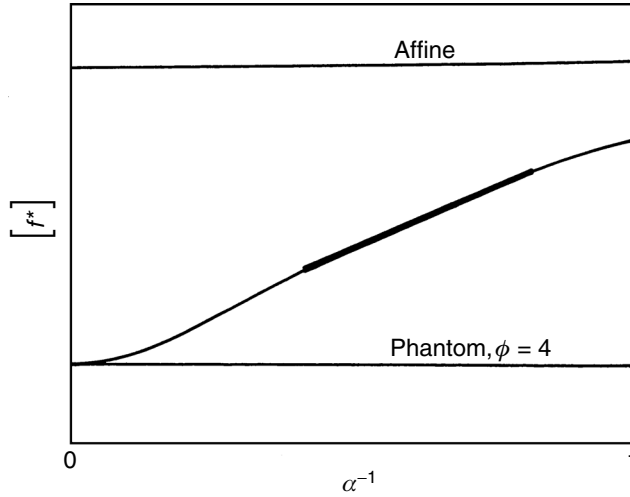


Fig. 1.8. A schematic diagram qualitatively showing theoretical predictions [32–34] for the reduced stress as a function of the reciprocal elongation α^{-1} .

phantom limit should be reduced, however, by the factor $1 - 2/\phi$ in the case of a ϕ -functional network, as is illustrated for the case $\phi = 4$. The experimentally observed decreases in reduced stress with increasing α are shown as the heavier portion of the theoretical curve. An increase in elongation disentangles the chains somewhat from the junctions and the fluctuations increase in magnitude, most markedly in the direction of the deformation. This causes the chains to sense a smaller deformation than that imposed macroscopically, making the deformation more non-affine. The modulus thus decreases until phantom-like behavior is reached in the limit of very high elongations. The extent to which the fluctuations are constrained is described by a constraint parameter κ , which is essentially infinite in the affine limit and zero in the phantom limit. One great success of this type of theory is the explanation [32–34] it provides for the previously puzzling decrease in modulus which is almost always observed with increasing elongation (for low and moderate elongations), and represented by the Mooney–Rivlin equation [2]. The increases in modulus frequently observed at very high deformations have to be dealt with separately, as described in Section 1.6.

1.2.5 The constrained-chain model

This refinement of the constrained-junction model is based on re-examination of the constraint problem and evaluation of some neutron-scattering estimates of actual junction fluctuations [35, 36]. It was concluded that the suppression of the fluctuations was over-estimated in the theory, presumably because the entire effect of

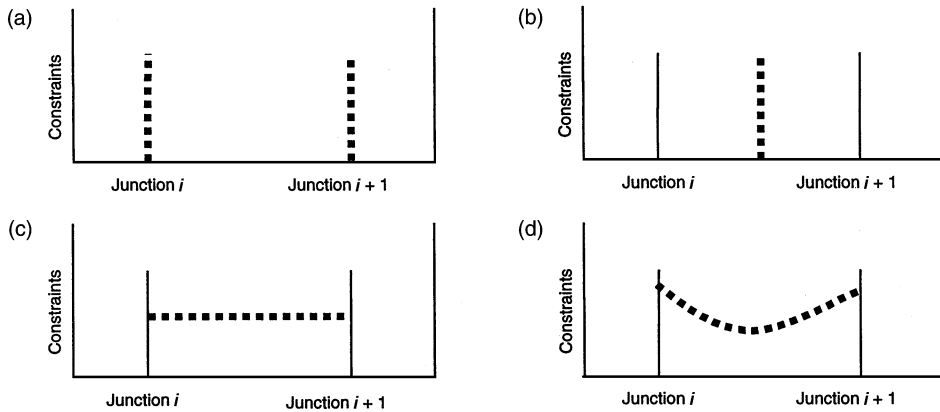


Fig. 1.9. Sketches of various choices for the locations of entanglement constraints.

the inter-chain interactions was arbitrarily placed on the junctions. The theory was therefore revised to make it more realistic by spreading the effects of the constraints along the network-chain contours [37]. This also improved the agreement between theory and experiment.

1.2.6 The diffused-constraints theory

This theory attempts even greater realism, by distributing the constraints continuously along the network chains. In its application to stress-strain isotherms in elongation [38], it has the advantage of having only a single constraint parameter and the values it exhibits upon comparing theory and experiment seem more reasonable than those obtained with the earlier models. Applications to strain birefringence [39], on the other hand, yield values of the birefringence that are much larger than those in the constrained-junction and constrained-chain theories.

These possibilities for placing the constraints within an elastomeric network are illustrated in parts (a), (b), and (c) of Fig. 1.9. Included is an additional possibility that might be suggested by additional experimental information, for example junction-fluctuation amplitudes from additional scattering results, preferably on networks having higher-functionality cross-links.

1.2.7 Some other general models

One of the most interesting alternative approaches is the “slip-link” model, which incorporates the effects of entanglements [40, 41] along the network chains directly into the elastic free energy [42]. Still other approaches are the “tube” model [43] and the van der Waals model [44].

1.2.8 Rotational-isomeric-state representation of the network chains

An approach [45–48] that takes direct account of the structural differences between chemically different elastomers is based on the rotational-isomeric-state representation of the chains [6–8]. In it, all of the structural features which distinguish one type of elastomeric chain from another are taken into account, as was done in the generation of the spatial configuration shown in Fig. 1.1. The required bond lengths, skeletal bond angles, locations of rotational states, and rotational-state energies are obtained from data on small molecules, and then used in a Monte Carlo method to generate a large number of spatial configurations, which are representative of the specified chain structure, at the specified chain length and temperature. The values of the end-to-end separation r for these various configurations are then calculated and, in effect, put into boxes corresponding to different ranges of r . Representation of the number of chains in a given range by the height of a bar and displaying these bars as a function of r then gives the usual type of bar graph. A smooth curve put through the levels of this bar graph then represents the distribution of r which can be used to replace the approximate Gaussian distribution. Such distributions are particularly useful for chains that are known to be non-Gaussian, for example because of their shortness or because of their being stretched close to the limits of their extensibility.

Going from the usual “structureless” molecular theories of rubber-like elasticity to ones taking into account the structural features that distinguish one type of polymer from another [17] parallels going from the theory of ideal gases to the van der Waals theory of non-ideal gases. The advantage in both cases is a more realistic portrayal of the system, but at the loss of universality (in that additional information specific to the chosen system is required). Useful theories for liquid-crystalline polymers [49, 50] may be particularly important in this regard.

Some of the elastic equations of state resulting from these various approaches are discussed further in subsequent sections.

1.3 Some experimental details

1.3.1 Mechanical properties

The great majority of studies of mechanical properties of elastomers involved elongation, because of the simplicity of this type of deformation [9]. The apparatus typically used to measure the force required to give a specified elongation of a rubber-like material is indeed very simple, as can be seen from its schematic description in Fig. 1.10 [3]. The elastomeric strip is mounted between two clamps, the lower one fixed and the upper one attached to a movable force gauge. A recorder is used to monitor the output of the gauge as a function of time in order to obtain equilibrium values of the force suitable for comparisons with theory. The sample is

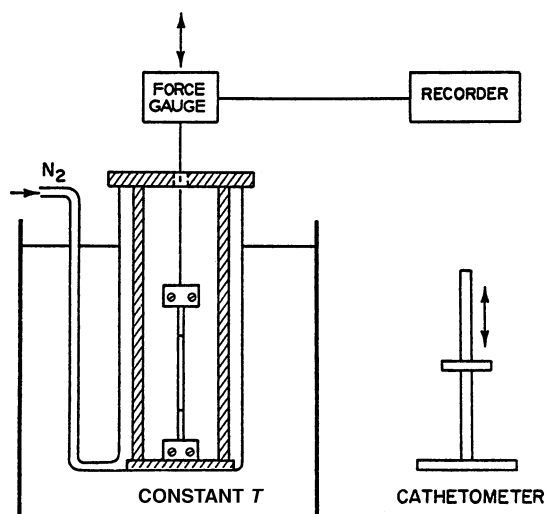


Fig. 1.10. Apparatus for carrying out stress-strain measurements on an elastomer in elongation [3].

generally protected with an inert atmosphere, such as nitrogen, to prevent degradation, particularly in the case of measurements carried out at elevated temperatures. Both the sample cell and the surrounding constant-temperature bath are glass, thus permitting use of a cathetometer or traveling microscope to obtain values of the strain, by measurements of the distance between two lines marked on the central portion of the test sample.

Some typical studies using other types of deformation, namely biaxial extension or compression, shear, and torsion, are described in Section 1.7.

1.3.2 Swelling

This nonmechanical property is also much used to characterize elastomeric materials [1, 2, 9, 17]. It is an unusual deformation in that changes in volume are of central importance, rather than being negligible. It is a three-dimensional dilation in which the network absorbs solvent, reaching an equilibrium degree of swelling at which the decrease in free energy due to the mixing of the solvent with the network chains is balanced by the increase in free energy accompanying the stretching of the chains. In this type of experiment, the network is typically placed into an excess of solvent, which it imbibes until the dilational stretching of the chains prevents further absorption. This equilibrium extent of swelling can be interpreted to yield the degree of cross-linking of the network, provided that the polymer-solvent-interaction parameter χ_1 is known. Conversely, if the degree of cross-linking is known from an independent experiment, then the interaction parameter can be determined. The

equilibrium degree of swelling and its dependences on various parameters and conditions provide, of course, additional tests of the theory.

The classic theory of swelling developed by Flory and Rehner gives the relationship [1]

$$\nu/V = -[\ln(1 - v_{2m}) + v_{2m} + \chi_1 v_{2m}^2]/[A'_\phi V_1 v_{2S}^{2/3} (v_{2,m}^{1/3} - \omega v_{2m})] \quad (1.19)$$

where ν/V is the cross-link density, v_{2m} the volume fraction of polymer at swelling equilibrium, χ_1 the already-mentioned free-energy-of-interaction parameter [1], A'_ϕ a structure factor equal to unity in the affine limit, V_1 the molar volume of the solvent, v_{2S} the volume fraction of polymer present during cross-linking, and ω an entropic volume factor equal to $2/\phi$.

In a refined theory developed by Flory [51], the extent to which the swelling deformation is non-affine depends on the looseness with which the cross-links are embedded in the network structure. This depends in turn both on the structure of the network and on its degree of equilibrium swelling. In one version of this theory, the resulting equation is

$$\nu/V = -[\ln(1 - v_{2m}) + v_{2m} + \chi_1 v_{2m}^2]/[F_\phi V_1 v_{2,S}^{2/3} v_{2,m}^{1/3}] \quad (1.20)$$

The factor F_ϕ characterizes the extent to which the deformation during swelling approaches the affine limit, and is given by

$$F_\phi = (1 - 2/\phi)[1 + (\mu/\xi)K] \quad (1.21)$$

where ξ is the cycle rank of the network mentioned earlier and $K = f(v_{2m}, \kappa, p)$ [51], where κ is a parameter specifying constraints on cross-links, and p a parameter specifying the dependence of cross-link fluctuations on the strain [51]. This theory is somewhat more difficult to apply since it contains parameters not present in the simpler theory. Their values not always available, even in the case of some relatively common and important elastomers.

1.3.3 Optical and spectroscopic properties

An example of a relevant optical property is the birefringence of a deformed polymer network [17]. This strain-induced birefringence can be used to characterize segmental orientation and both Gaussian and non-Gaussian elasticity, and to obtain new insights into the network-chain orientation necessary for strain-induced crystallization [2, 9, 52, 53]. Other optical and spectroscopic techniques are also important, particularly with regard to segmental orientation. Some examples are fluorescence polarization, deuterium NMR, and polarized infrared spectroscopy [9, 17, 54]. The application of spectroscopy to the characterization of polymers in general is covered by J. L. Koenig, in Chapter 6.

Also of importance are atomic-force microscopy, Brillouin scattering [55, 56], and pulse-propagation measurements [55, 57]. In the last of these techniques, the delay in pulses passing through the network is used to obtain information on the network structure.

1.3.4 Scattering

The technique of this type of greatest utility in the study of elastomers is small-angle neutron scattering; for example, from deuterated chains in a nondeuterated host [58–60]. One application has been the determination of the degree of randomness of the chain configurations in the undeformed state, which is an issue of importance with regard to the basic postulates of elasticity theory. Of even greater importance is determination of the manner in which the dimensions of the chains follow the macroscopic dimensions of the sample, i.e. the degree of affineness of the deformation. This relationship between the microscopic and macroscopic levels in an elastomer is one of the central problems in rubber-like elasticity. The use of neutron-scattering measurements in the characterization of polymers in general is discussed by G. D. Wignall, in Chapter 7.

Some small-angle-X-ray-scattering techniques have also been applied to elastomers. Examples are the characterization of fillers precipitated into elastomers, and the corresponding incorporation of elastomers into ceramic matrices, in both cases in order to improve mechanical properties [9, 61].

1.3.5 Pulse-propagation measurements and Brillouin scattering

One example of a relatively new technique for the non-invasive, nondestructive characterization of network structures involves pulse-propagation measurements [57, 62]. The goal is the rapid determination of the spacings between junctions and between entanglements in a network structure. Another example is really a resurrection of the Brillouin-scattering method [63], which should be quite useful for looking at glassy-state properties of elastomers at very high frequencies [64].

1.4 Comparisons between theory and experiment

1.4.1 The dependence of the stress on deformation

The great majority of experimental results used to evaluate theory came from experiments in which elongation was used. Correspondingly, these results will be

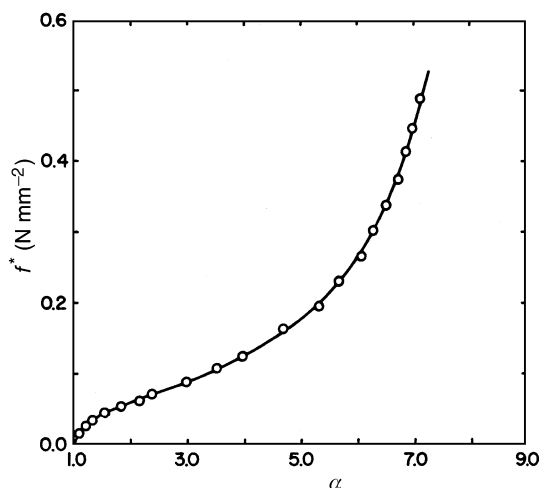


Fig. 1.11. The stress–elongation curve for natural rubber in the vicinity of room temperature [2, 3].

emphasized here, but some results on other deformations will be discussed briefly in Section 1.7.

A typical stress–strain isotherm obtained for a strip of cross-linked natural rubber as described above is shown in Fig. 1.11 [1–3]. The units for the force are generally newtons, and the curves obtained are usually checked for reversibility. In this type of representation, the area under the curve is frequently of considerable interest since it is proportional to the work of deformation $w = \int f \, dL$. Its value up to the rupture point is thus a measure of the toughness of the material.

The initial part of the stress–strain isotherm shown in Fig. 1.11 is of the expected form in that f^* approaches linearity with α as α becomes sufficiently large to make the α^{-2} term in Eq. (1.14) negligibly small. The large increase in f^* at high deformation in the case of natural rubber is due largely, if not entirely, to strain-induced crystallization, as is described in Section 1.6 on non-Gaussian effects. The melting point of the polymer is inversely proportional to the entropy of fusion, which is significantly diminished when the chains in the amorphous network remain stretched out because of the applied deformation. The melting point is thereby increased and it is in this sense that the stretching “induces” the crystallization of some of the network chains. This is shown schematically in Fig. 1.12 [65]. Removal of the force generally reduces the elevated melting point back to its original reference value. The effect is qualitatively similar to the increase in melting point generally observed upon an increase in pressure on a low molecular weight substance in the crystalline state. In any case, the crystallites thus formed act as physical cross-links, increasing the modulus of the network. The properties both of

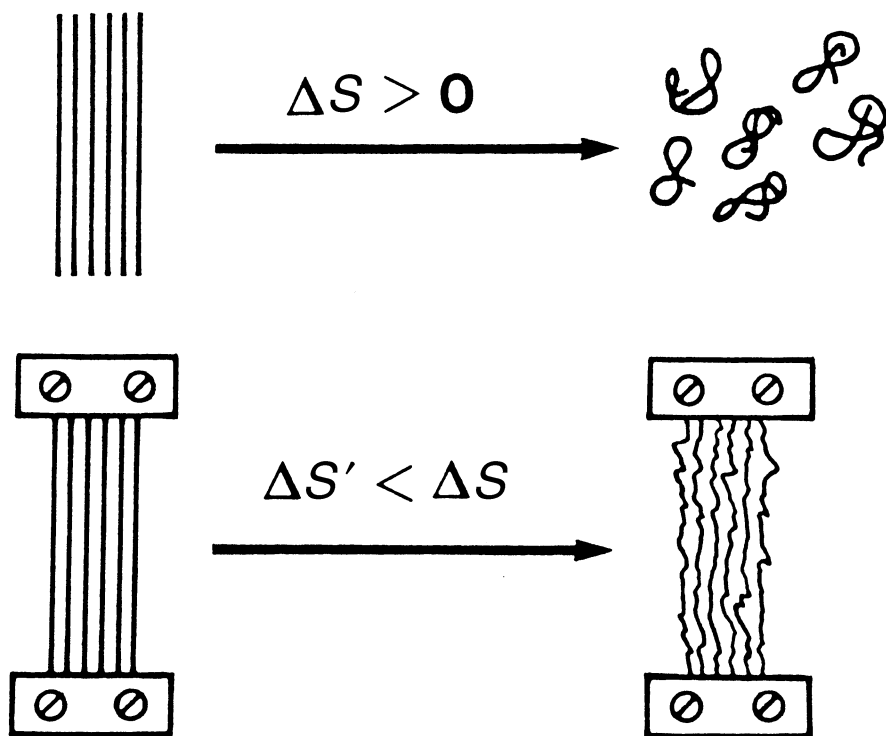


Fig. 1.12. A sketch explaining the increase in melting point with elongation in the case of a crystallizable elastomer [65].

crystallizable and of noncrystallizable networks at high elongations are discussed further in Section 1.6.

Additional deviations from theory are found in the region of moderate deformation upon examination of the usual plots of modulus against reciprocal elongation [2, 66]. Although Eq. (1.16) predicts the modulus to be independent of elongation, it generally decreases significantly upon an increase in α , as has already been mentioned. Typical results, obtained for swollen and unswollen networks of natural rubber, are shown in Fig. 1.13 [66]. The intercepts and slopes of such linear plots are generally called the Mooney–Rivlin constants $2C_1$ and $2C_2$, respectively, in the semi-empirical relationship $[f^*] = 2C_1 + 2C_2\alpha^{-1}$. It is interesting to note that the slope $2C_2$, a measure of the discrepancy from the predicted behavior, decreases to an essentially negligible value as the degree of swelling of the network increases. As described above, the more refined molecular theories of rubber-like elasticity [31–34] explain this decrease by invoking the gradual increase in the non-affineness of the deformation as the elongation increases toward the phantom limit, as is shown schematically in Fig. 1.8.

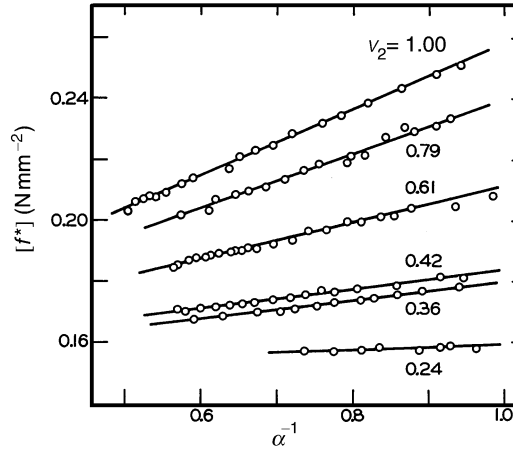


Fig. 1.13. The modulus shown as a function of the reciprocal elongation as suggested by the semi-empirical Mooney–Rivlin equation $[f^*] = 2C_1 + 2C_2\alpha^{-1}$ [2, 66]. The elastomer is natural rubber, both unswollen and swollen with n-decane [66]. Each isotherm is labeled with the volume fraction of polymer in the network.

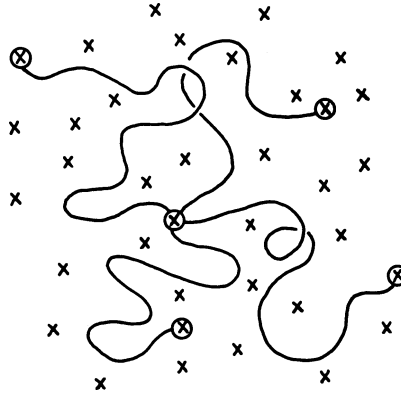


Fig. 1.14. Typical configurations of four chains emanating from a tetrafunctional cross-link in a polymer network prepared in the undiluted state [67].

In these theories, the degree of entangling around the cross-links is of primary importance, since this will determine the firmness with which the cross-links are embedded in the network structure. This type of chain–cross-link entangling is illustrated in Fig. 1.14 [67]. For a typical degree of cross-linking, there are 50–100 cross-links closer to a given cross-link than those directly joined to it through a single network chain. The configurational domains thus generally overlap severely. The degree of overlapping is a measure of the firmness with which the cross-links are embedded, and thus of the extent to which the idealized, affine deformation is approached. As already mentioned, stretching out the network chains decreases

this degree of entangling, thereby permitting an increase in magnitude of cross-link fluctuations, which are then asymmetric. The modulus thus decreases, approaching the value predicted for a phantom network, in which entangling is impossible and cross-link fluctuations are unimpeded. This concept also explains the essentially constant modulus at high degrees of swelling illustrated in Fig. 1.13. Large amounts of diluent “loosen” the cross-links so that the deformation is highly non-affine even at low deformations, and thus the modulus changes relatively little upon an increase in elongation.

1.4.2 The dependence of the stress on temperature

As mentioned above, the assumption of a purely entropic elasticity leads to the prediction, Eq. (1.14), that the stress should be directly proportional to the absolute temperature at constant α (and V). The extent to which there are deviations from this direct proportionality may therefore be used as a measure of the thermodynamic non-ideality of an elastomer [9, 68–74]. In fact, the definition of ideality for an elastomer is that the energetic contribution f_e to the elastic force f be zero. This quantity is defined by

$$f_e \equiv (\partial E / \partial L)_{V,T} \quad (1.22)$$

which is a definition closely paralleling the requirement that $(\partial E / \partial V)_T$ be zero for ideality in a gas.

Force–temperature (“thermoelastic”) measurements may therefore be used to obtain experimental values of the fraction f_e/f of the force which is energetic in origin. Such experiments carried out at constant volume are the most direct, and can be interpreted through use of the purely thermodynamic relationship

$$f_e/f = -T[\partial \ln(f/T)/\partial T]_{V,L} \quad (1.23)$$

Since, however, it is very difficult to maintain constant volume in these experiments, they are usually carried out at constant pressure instead. They are then interpreted using the equation

$$f_e/f = -T[\partial \ln(f/T)/\partial T]_{p,L} - \beta T/(\alpha^3 - 1) \quad (1.24)$$

in which β is the coefficient of thermal expansion for the network. This relationship was obtained by using the Gaussian elastic equation of state to correct the data to constant volume [68, 69, 71, 72].

These changes in energy are intramolecular [68, 69, 71, 72] and arise from transitions of the chains from one spatial configuration to another (since different configurations generally correspond to different intramolecular energies) [6]. They are thus obviously related to the temperature coefficient of the unperturbed

A. RESULTS

$$\frac{f_e}{f} = T \frac{d \ln \langle r^2 \rangle_0}{dT} = -0.45$$

B. INTERPRETATION

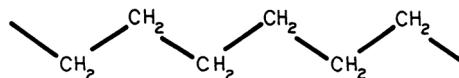


Fig. 1.15. Thermoelastic results on (amorphous) polyethylene networks and their interpretation in terms of the preferred, all-*trans* conformation of the chain [3, 6].

dimensions, the quantitative relationship

$$f_e/f = T d \ln \langle r^2 \rangle_0 / dT \quad (1.25)$$

being obtained by keeping the $\langle r^2 \rangle_i$ factor in Eq. (1.9) distinct from $\langle r^2 \rangle_0$. It is interesting to note that, since this type of non-ideality is intramolecular, it is not removed by diluting the chains (swelling the network) or by increasing the lengths of the network chains (decreasing the degree of cross-linking). In this respect, elastomers are rather different from gases, which can be made to behave ideally by decreasing the pressure to a sufficiently low value.

Typical thermoelastic data, obtained for amorphous polyethylene [69, 72], were interpreted using Eq. (1.24) in order to establish that the energetic contribution to the elastic force is large and negative. These results on polyethylene [69] may be understood using the information given in Fig. 1.15. The preferred (lowest-energy) conformation of the chain is the all-*trans* form, since *gauche* states (at rotational angles of $\pm 120^\circ$) cause steric repulsions between CH_2 groups [6]. Since this conformation has the highest possible spatial extension, stretching a polyethylene chain requires switching some of the *gauche* states (which are of course present in the higher-entropy randomly coiled form) to the alternative *trans* states [6, 69, 71, 72]. These changes decrease the conformational energy and are the origin of the negative type of ideality represented in the experimental value of f_e/f . (This physical picture also explains the decrease in unperturbed dimensions upon an increase in temperature. The additional thermal energy causes an increase in the number of the higher-energy *gauche* states, which are more compact than the *trans* ones.)

The opposite behavior is observed in the case of poly(dimethylsiloxane), as is shown in Fig. 1.16. The all-*trans* form is again the preferred conformation; the relatively long Si—O bonds and the unusually large Si—O—Si bond angles reduce steric repulsions in general, and the *trans* conformation places CH_3 side groups at separations at which they are strongly attractive [6, 71, 72]. Because of the inequality of the Si—O—Si and O—Si—O bond angles, however, this conformation is of very low spatial extension, approximating a closed polygon. Stretching

A. Results

$$\frac{f_e}{f} = T \frac{d \ln \langle r^2 \rangle_0}{dT} = 0.25$$

B. Interpretation

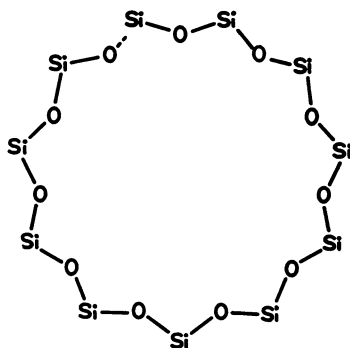
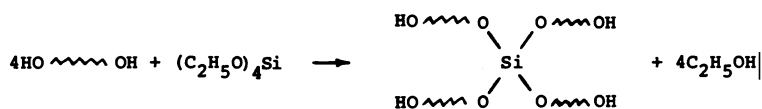


Fig. 1.16. Thermoelastic results on poly(dimethylsiloxane) networks and their interpretation in terms of the preferred, all-*trans* conformation of the chain [3, 6]. For purposes of clarity, the two methyl groups on each silicon atom have been deleted.

a poly(dimethylsiloxane) chain therefore requires an increase in the number of *gauche* states. Since these are of higher energy, this explains the fact that deviations from ideality for these networks are found to be positive [6, 71, 72].

Thermoelasticity results are also used to test some of the assumptions used in the development of the molecular theories. The results [72] indicate that the ratio f_e/f is essentially independent of the degree of swelling of the network, and this supports the postulate made in Section 1.1.4 that intermolecular interactions do not contribute significantly to the elastic force. The assumption is further supported by results [72] showing that the values of the temperature coefficients of the unperturbed dimensions obtained from thermoelasticity experiments are in good agreement with those obtained from viscosity-temperature measurements on the isolated chains in dilute solution.

Also, since intermolecular interactions do not affect the force, they must be independent of the extent of the deformation and thus independent of the spatial configurations of the chains. This in turn indicates that the spatial configurations must be independent of intermolecular interactions, i.e. the amorphous chains must be in random, unordered configurations, the dimensions of which should be the unperturbed values [1]. This conclusion has now been verified amply, in particular by

Preparation of End-Linked PDMS Networks

where $\text{HO} \sim \text{OH}$ represents a hydroxyl-terminated PDMS chain.

Known $\bar{M}_n \rightarrow$ known $\bar{M}_c$. Known M_n distribution $\rightarrow$ known M_c distribution.

Fig. 1.17. A typical synthetic route for preparing elastomeric networks of known structure by end linking of hydroxyl-terminated chains by a condensation reaction [75].

neutron-scattering studies on undiluted amorphous polymers by numerous research groups [72].

1.4.3 The dependence of the stress on network structure

Until recently, there was relatively little reliable quantitative information on the relationship of stress to structure, primarily because of the uncontrolled manner in which elastomeric networks were generally prepared [1–3, 9]. Segments close together in space were linked irrespective of their locations along the chain trajectories, thus resulting in a highly random network structure in which the number and locations of the cross-links were essentially unknown. Such a structure is shown in Fig. 1.2. New synthetic techniques for the preparation of “model” polymer networks of known structure are now available, however [25, 75–82]. An example is the reaction shown in Fig. 1.17, in which hydroxyl-terminated chains of PDMS are end linked using tetraethyl orthosilicate. Characterizing the uncross-linked chains with respect to the molecular weight M_n and the relative-molecular-mass distribution and then running the specified reaction to completion gives elastomers in which the network chains have these characteristics, in particular a molecular weight M_c between cross-links equal to M_n , and cross-links having the functionality of the end-linking agent.

Trifunctional and tetrafunctional PDMS networks prepared in this way have been used to test the molecular theories of rubber elasticity with regard to the increase in non-affineness of the network deformation with increasing elongation. The ratio $2C_2/(2C_1)$ was found to decrease with increasing cross-link functionality from three to four [77] because cross-links connecting four chains are more constrained than those connecting only three. There is therefore less of a decrease in modulus brought about by the fluctuations which are enhanced at high deformation and give the deformation its non-affine character. There is also a decrease in $2C_2/(2C_1)$ with

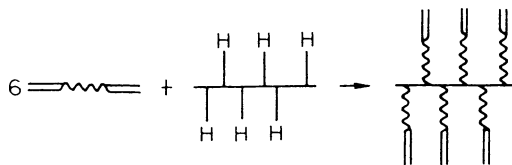


Fig. 1.18. A typical reaction in which vinyl-terminated PDMS chains are end linked with a multifunctional silane.

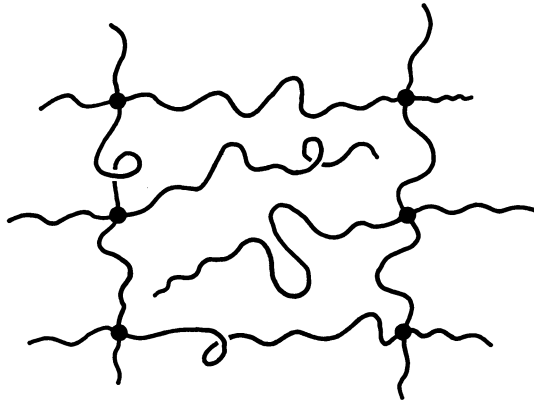
decreasing network-chain molecular weight, which is due to the fact that there is less configurational interpenetration in the case of short network chains. This decreases the firmness with which the cross-links are embedded and thus the deformation is already highly non-affine even at relatively small deformations.

A more thorough investigation of the effects of cross-link functionality requires use of the more versatile chemical reaction illustrated in Fig. 1.18. Specifically, vinyl-terminated PDMS chains were end linked using a multifunctional silane [78]. This reaction was used to prepare PDMS model networks having functionalities ranging from three to 11, with a relatively unsuccessful attempt to achieve a functionality of 37. The modulus $2C_1$ increased with increasing functionality, as expected from the increase in constraints on the cross-links, and as predicted in Eqs. (1.17) and (1.18). Similarly, $2C_2$ and its value relative to $2C_1$ both decreased, for reasons that have already been mentioned.

Such model networks may also be used to provide a direct test of molecular predictions of the modulus of a network of known degree of cross-linking. Some experiments on model networks [75, 77, 78] have given values of the elastic modulus in good agreement with theory. Others [79, 81] have given values significantly larger than predicted, and the increases in modulus have been attributed to contributions from “permanent” chain entanglements of the type shown in the lower-right-hand portion of Fig. 1.2. There are disagreements, and the issue has not yet been resolved. Since the relationship of modulus to structure is of such fundamental importance, there is currently a great deal of research activity in this area [22].

The same very specific chemical reactions can also be used to prepare networks containing known numbers and lengths of dangling-chain irregularities. This is illustrated in Fig. 1.19 [83]. If more chain ends are present than reactive groups on the end-linking molecules, then dangling ends will be produced and their number is directly determined by the extent of the stoichiometric imbalance. Their lengths, however, are of necessity the same as those of the elastically effective chains, as shown in the upper sketch in Fig. 1.19. This constraint can be removed by separately preparing monofunctionally terminated chains of the desired lengths and attaching them as shown in the lower sketch. Results from some studies of this type are presented below.

(a) Excess difunctional chains



(b) Monofunctional chains

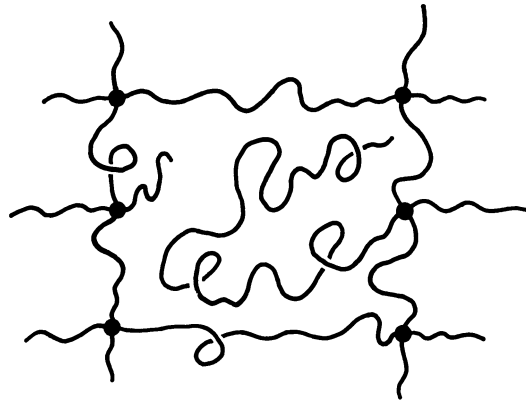


Fig. 1.19. Two end-linking techniques for preparing networks with known numbers and lengths of dangling chains [83].

1.5 Some unusual networks

1.5.1 Networks prepared in solution or in a state of strain

Two techniques that may be used to prepare networks having simpler topologies are illustrated in Fig. 1.20 [84, 85]. Basically, they involve separating the chains prior to their cross-linking by either stretching or dissolution. After the cross-linking, the stretching force or solvent is removed and the network is studied (unswollen) with regard to its stress-strain properties in elongation. Some results obtained on PDMS networks cross-linked in solution by means of γ radiation [85, 86] showed that there were continual decreases in the time required to reach elastic equilibrium

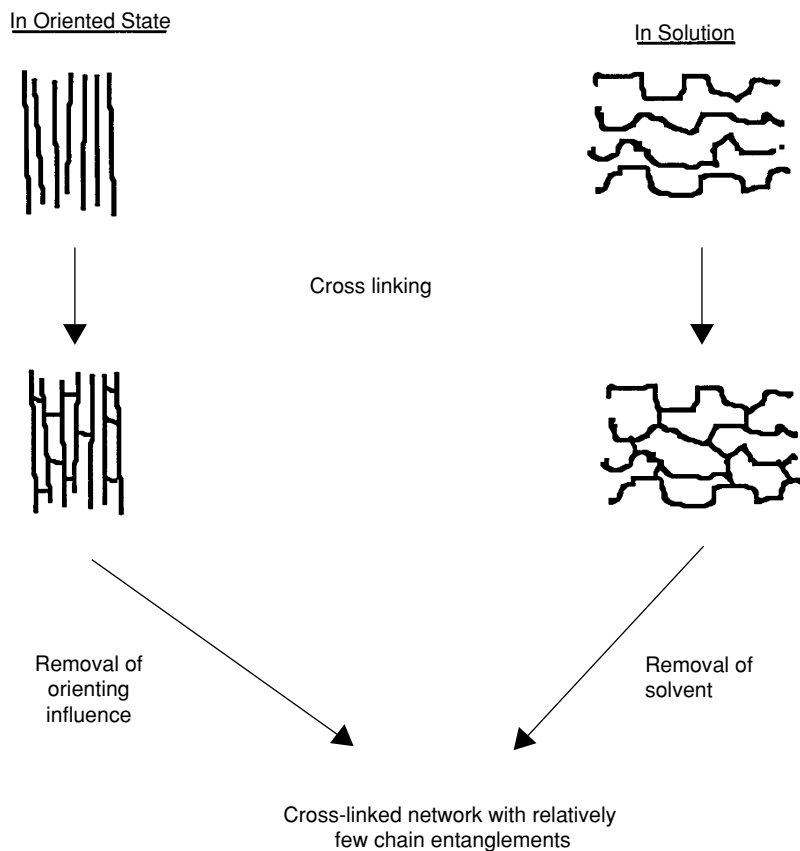


Fig. 1.20. Two techniques that may be used to prepare networks of simpler topology [84, 85].

and in the extent of relaxation of stress upon decreasing the volume fraction of polymer present during the cross-linking. Also, at higher dilutions there was a decrease in the Mooney–Rivlin $2C_2$ constant as well. Such networks are also of interest with regard to their “super extensibility” [87, 88] and crystallizability upon elongation [89, 90].

These observations are qualitatively explained in Fig. 1.21. If a network is cross-linked in solution and the solvent then removed, the chains collapse in such a way that there is a decrease in overlap in their configurational domains. It is primarily in this regard, namely a decrease in chain-junction entangling, that solution-cross-linked samples have simpler topologies, with correspondingly simpler elastomeric behavior. The fact that the chains are now supercompressed upon drying is the origin of their unusually high extensibilities.

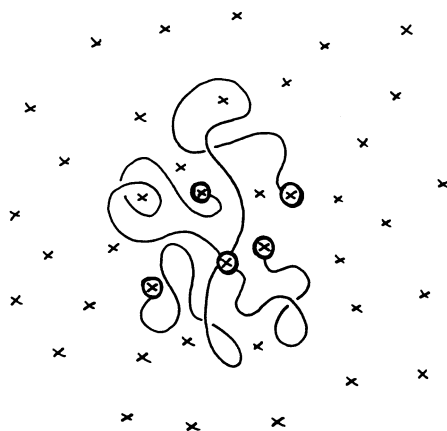


Fig. 1.21. Typical configurations of four chains emanating from a tetrafunctional cross-link in a (dried) polymer network that had been prepared in solution.

It is appropriate to comment at this point on the opposite sort of experiment, cross-linking a network in the undiluted state and then studying its stress–strain isotherms in the swollen state. Such a diluent might be introduced to suppress crystallization or to facilitate the approach to elastic equilibrium. There is a complication, however, which can occur in the case of networks of polar polymers at relatively high degrees of swelling [86, 91]. The observation is that different solvents, at the same degree of swelling, can have significantly different effects on the elastic force. This is apparently due to a “specific-solvent effect” on the unperturbed dimensions which appear in the basic relationship given in Eq. (1.9). Although it is frequently observed in studies of the solution properties of uncross-linked polymers, the effect is not yet well understood. It is apparently partly due to the effect of the solvent’s dielectric constant on the Coulombic interactions between parts of a chain, but probably also to solvent–polymer-segment interactions that change the conformational preferences of the chain backbone [91].

1.5.2 Unusual diluents

End linking functionally terminated chains in the presence of chains whose ends are inert yields networks through which the unattached chains *reptate* [92]. Networks of this type have been used to determine the efficiency with which unattached chains can be extracted from an elastomer as a function of their lengths and the degree of cross-linking of the network [9, 93]. The efficiency is found to decrease with increasing molecular weight of the diluent and with increasing degree of cross-linking, as expected. It has also been found to be more difficult to extract diluents

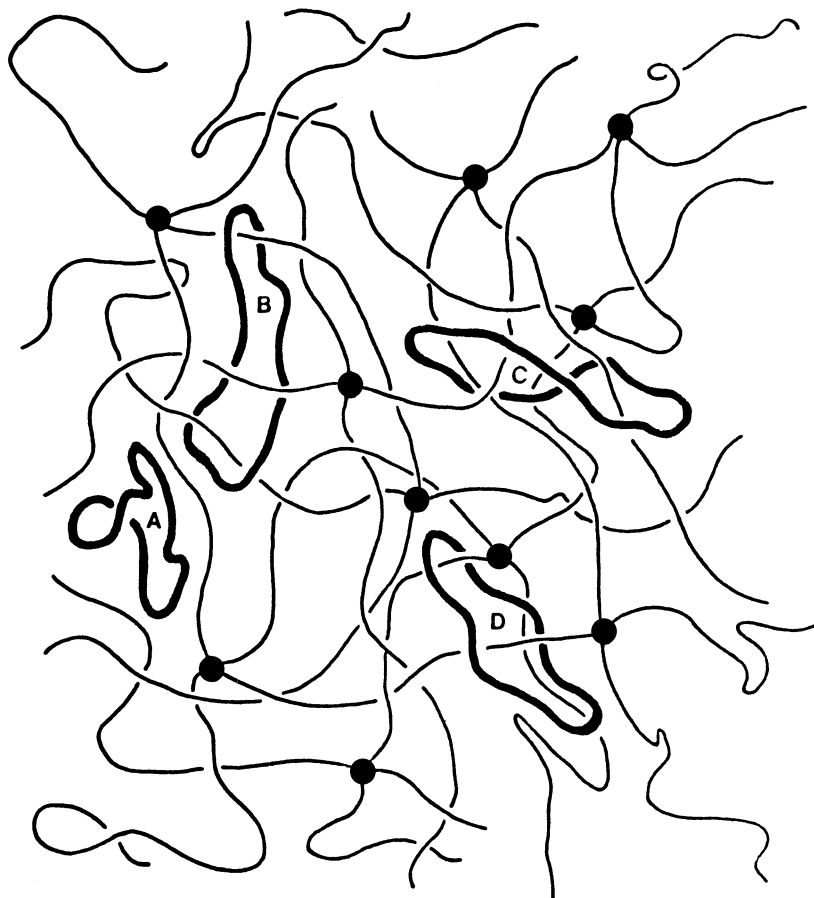


Fig. 1.22. Trapping of cyclic molecules during end-linking preparation of a network [94].

present during the cross-linking than to extract the same diluents once they have been absorbed into the network after cross-linking. Such comparisons can provide valuable information on the arrangements and transport of chains within complex network structures.

It has also been found that, if relatively large PDMS cyclics are present when linear PDMS chains are end linked, then some can be permanently trapped by one or more network chains threading through them, as is shown by cyclics B, C, and D in Fig. 1.22 [94]. The amount trapped ranges from 0% for cyclics with fewer than approximately 30 skeletal bonds, to essentially 100% for those having more than approximately 300 skeletal bonds [95]. It is possible to interpret these results in terms of the effective “hole” sizes of the cyclics, which can be estimated from Monte Carlo simulations of their spatial configurations. The agreement between theory and experiment was found to be very good [94].

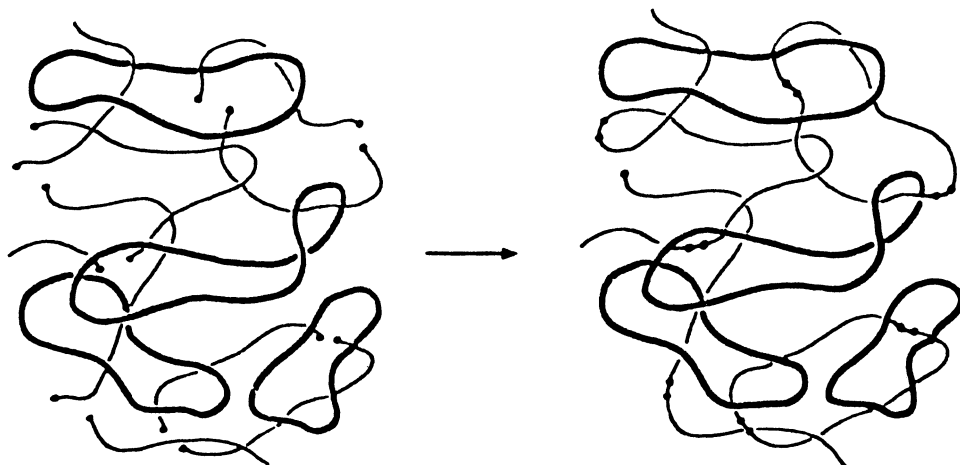


Fig. 1.23. Preparation of a “chain-mail” or “Olympic” network consisting entirely of interlooped cyclic molecules [96].

It may also be possible to use this technique to form a network having no cross-links whatsoever. Mixing linear chains with large amounts of cyclics and then *difunctionally* end linking them could give sufficient cyclic interlooping to yield a “chain-mail” or “Olympic” network as depicted in Fig. 1.23 [96]. Such materials could have very unusual stress–strain isotherms [97].

1.5.3 Bimodal networks

The end-linking reactions described above can also be used to make networks having unusual chain-length distributions [98–102]. Those having a bimodal distribution are of particular interest with regard to their ultimate properties, and are discussed in the following section.

1.6 Networks at very high deformations

1.6.1 Non-Gaussian effects

As has already been shown in Fig. 1.11 [1–3], some (unfilled) networks exhibit a large and rather abrupt increase in modulus at high elongations. This increase, which is further illustrated for natural rubber in Fig. 1.24 [103, 104], is very important since it corresponds to a significant toughening of the elastomer. Its molecular origin, however, has been the source of considerable controversy [2, 9, 103, 105–111]. It had been widely attributed to the “limited extensibility” of the network chains, i.e. to an inadequacy in the Gaussian distribution function. This potential inadequacy is readily evident in the exponential in Eq. (1.1), specifically from the fact that this

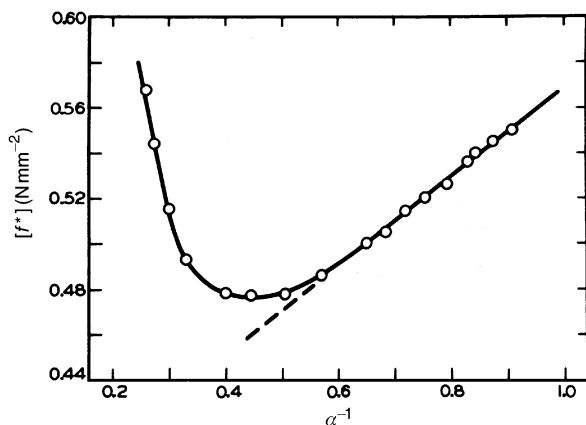


Fig. 1.24. The stress–strain isotherm for an unfilled rubber network at 25 °C [104], showing the anomalous increase in modulus at high elongation [103]. (Reproduced with permission; copyright 1976, John Wiley & Sons, Inc.)

function does not assign a zero probability to a configuration unless its end-to-end separation r is infinite. This explanation in terms of limited extensibility was viewed with skepticism by some workers since significant increases in modulus were generally observed only in networks that could undergo strain-induced crystallization. Such crystallization in itself could account for the increase in modulus, primarily because the crystallites thus formed would act as additional cross-links in the network structure.

Attempts to clarify the problem by using noncrystallizable networks [104] were not convincing since such networks were incapable of the large deformations required to distinguish between the two possible interpretations. The issue was resolved [75, 109, 112–114], however, by the use of end-linked, noncrystallizable model PDMS networks. These networks have high extensibilities, presumably because of their very low incidence of dangling-chain network irregularities. They have particularly high extensibilities when they are prepared from mixtures of very short chains (around a few hundred g mol^{-1}) with relatively long chains (around 18 000 g mol^{-1}), as discussed below. Apparently the very short chains are important because of their limited extensibilities, and the relatively long chains because of their ability to retard rupture.

Stress–strain measurements on such bimodal PDMS networks exhibited upturns in modulus which were much less pronounced than those for crystallizable polymer networks such as natural rubber and *cis*-1,4-polybutadiene, and they are independent of temperature, as would be expected in the case of limited chain extensibility [86, 109]. For a crystallizable network, the upturns diminish and eventually disappear upon an increase in temperature [112, 114]. Similarly, swelling has relatively little

effect on the upturns in the case of PDMS [86, 109], and can even make the upturns more pronounced through the dilation-causing effects of the solvent. In contrast, the upturns in modulus of crystallizable polymer networks disappear upon sufficient swelling, because of the loss of the reinforcing effects of the crystallites [113, 114].

Two other results of swelling a network capable of undergoing strain-induced crystallization merit additional comments. First, the initiation of the strain-induced crystallization (evidenced by departure of the isotherm from linearity) is facilitated by the presence of the low molecular weight diluent. Thus, in a sense this kinetic effect acts in opposition to the thermodynamic effect, which is primarily the depression of the melting point of the polymer by the diluent. The second interesting point has to do with the frequently observed decrease in the modulus prior to its increase. This is probably due to the fact that the crystallites are oriented along the direction of stretching, and the chain sequences within a crystallite are in regular, highly extended conformations. The straightening and aligning of portions of the network chains thus decreases the deformation in the remaining amorphous regions, with an accompanying decrease in the stress [67, 114].

In summary, the anomalous upturn in modulus observed for crystallizable polymers such as natural rubber and *cis*-1,4-polybutadiene is largely, if not entirely, due to strain-induced crystallization. In the case of the noncrystallizable PDMS model networks it is clearly due to the limited chain extensibility, and thus the results on this system will be extremely useful for reliable evaluation of the various non-Gaussian theories of rubber-like elasticity.

There is now considerable interest in using simulations for characterizing crystallization in copolymeric elastomers. In particular, Windle and co-workers [115] have developed models capable of simulating chain ordering in copolymers composed of two comonomers, at least one of which is crystallizable. Typically, the chains are placed in parallel, two-dimensional arrangements. Neighboring chains are then searched for like-sequence matches in order to estimate extents of crystallinity. Chains stacked in arbitrary registrations are taken to model quenched samples. Annealed samples, on the other hand, are modeled by sliding the chains past one another longitudinally to search for the largest possible matching densities. The longitudinal movement of the chains relative to one another, out of register, approximately models the lateral searching of sequences in copolymeric chains during annealing [116, 117].

1.6.2 Ultimate properties

This section continues the discussion of unfilled elastomers at high elongations, but with an emphasis on ultimate properties, namely the ultimate strength and maximum extensibility.

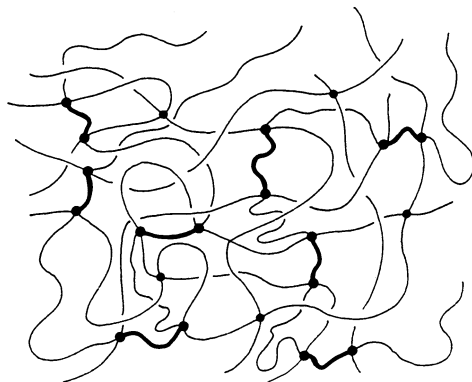


Fig. 1.25. A portion of a network that is compositionally heterogeneous with respect to chain length. The very short and relatively long chains are arbitrarily shown by the thick and thin lines, respectively [75]. (Reproduced with permission; copyright 1979, Huthig & Wepf Verlag, Basel.)

Some relevant results on the effects of strain-induced crystallization on ultimate properties have been obtained for *cis*-1,4-polybutadiene networks [112]. As has already been mentioned, the higher the temperature, the lower the extent of crystallization and, correspondingly, the lower the ultimate properties. The effects of increasing swelling parallel those for increasing temperature, since diluent also suppresses crystallization of the network. For noncrystallizable networks such as those of PDMS, however, neither change is found to be very important [118].

In the case of such noncrystallizable, unfilled elastomers, the mechanism for rupture of the network has been elucidated to a great extent by studies of model networks similar to those described in the preceding section. For example, values of the moduli of bimodal networks formed by end linking mixtures of very short and relatively long chains as illustrated in Fig. 1.25 [75] were used to test the “weakest-link” theory, in which rupture was thought to be initiated by the shortest chains (because of their very limited extensibility). It was observed that increasing the number of very short chains did *not* significantly decrease the ultimate properties. The reason, shown schematically in Fig. 1.26 [109], is the very non-affine nature of the deformation at such high elongations. The network simply reapportions the increasing strain among the polymer chains until no further reapportioning is possible. It is generally only at this point that chain scission begins, leading to rupture of the elastomer. The weakest-link theory implicitly assumes that an affine deformation occurs, which leads to the prediction that the elongation at which the modulus increases should be independent of the number of short chains in the network. This assumption is contradicted by relevant experimental results, which reveal very different behavior [109]; the smaller the number of short chains, the

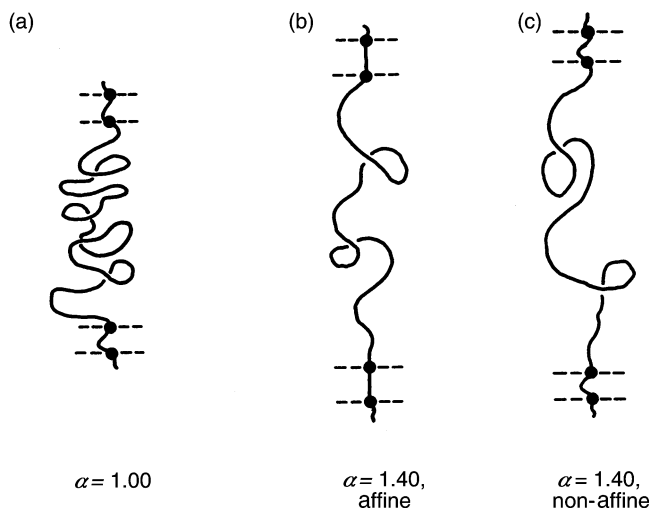


Fig. 1.26. The effect of deformation on an idealized network segment consisting of a relatively long chain bracketed by two very short chains [109]. (Reproduced with permission; copyright 1980, American Institute of Physics.)

easier the reappportioning and the higher the elongation required to bring about the upturn in modulus.

There turns out to be an exciting bonus if one puts a very large number of short chains into the bimodal network. The ultimate properties are then actually improved! This is illustrated in Fig. 1.27 [119], in which data on PDMS networks are plotted in such a way that the area under a stress–strain isotherm corresponds to the energy required to rupture the network. If the network is all short chains, it is brittle, which means that the maximum extensibility is very small. If the network is entirely long chains, the ultimate strength is very low. In neither case is the material a tough elastomer. As can readily be seen from Fig. 1.27, the bimodal networks are much improved elastomers in that they can have high ultimate strengths without the usual decreases in maximum extensibility.

A series of experiments was carried out in an attempt to determine whether this reinforcing effect in bimodal PDMS networks could possibly be due to some intermolecular effect such as strain-induced crystallization. In the first such experiment, temperature was found to have little effect on the shape of the isotherms [100]. This strongly argues against the presence of any crystallization or other type of intermolecular ordering. So also do the results of stress–temperature and birefringence–temperature measurements [100]. In a final experiment, the short chains were pre-reacted in a two-step preparative technique in the hope of possibly being able to segregate them in the network structure [86, 98], as might occur in a network cross-linked by an incompletely soluble peroxide. This had very little

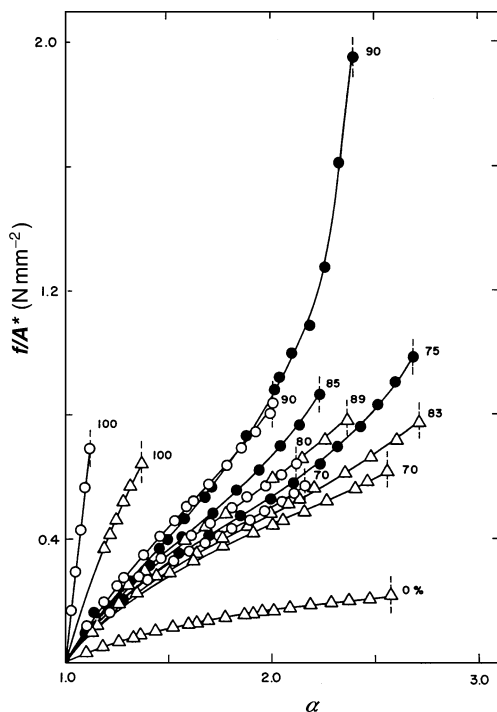


Fig. 1.27. Typical plots of nominal stress against elongation for (unswollen) bimodal PDMS networks consisting of relatively long chains ($M_c = 18\,500 \text{ g mol}^{-1}$) and very short chains ($M_c = 1100$ (Δ), 660 ($\circ$), and 220 ($\bullet$)). Each curve is labeled with the mole percentage of short chains it contains, and the area under each curve represents the rupture energy (a measure of the “toughness” of the elastomer) [119]. (Reproduced with permission; copyright 1981, John Wiley & Sons, Inc.)

effect on elastomeric properties, again arguing against the hypothesis of any type of intermolecular organization as the origin for the reinforcing effects. Apparently, the observed increases in modulus are due to the limited extensibility of the short chains, with the long chains serving to retard rupture.

The molecular origin of the unusual properties of bimodal PDMS networks having been elucidated at least to some extent, it is now possible to utilize these materials in a variety of applications. The first involves the interpretation of the limited chain extensibility in terms of the configurational characteristics of the PDMS chains making up the network structure [6–8].

The first important characteristic of limited chain extensibility is the elongation α_u at which the increase in modulus first becomes discernible. Although the deformation is non-affine in the vicinity of the upturn, it is possible to provide at least a semiquantitative interpretation of such results in terms of the dimensions of the network chains [6, 109]. At the beginning of the upturn, the average extension r of a network chain having its end-to-end vector along the direction of stretching is

simply the product of the unperturbed dimension $\langle r^2 \rangle_0^{1/2}$ and α_u [109]. Similarly, the maximum extensibility r_m is the product of the number n of skeletal bonds and the factor $1.34 \text{ \AA}$ which gives the axial component of a skeletal bond in the most extended helical form of PDMS, as obtained from the geometric analysis of the PDMS chain [86, 109]. The ratio r/r_m at α_u thus represents the fraction of the maximum extensibility occurring at this point in the deformation. The values obtained indicate that the upturn in modulus generally begins at approximately 60–70% of the maximum chain extensibility [109]. This is approximately twice the value which had been estimated previously [2], in a misinterpretation of stress–strain isotherms of elastomers that did not take into account strain-induced crystallization.

It is also of interest to compare the values of r/r_m at the beginning of the upturn with some theoretical results on distribution functions for PDMS chains of finite length obtained by Flory and Chang [101, 120]. Of relevance here are the calculated values of r/r_m at which the Gaussian distribution function starts to over-estimate the probability of extended configurations, as judged by comparisons with the results of Monte Carlo simulations. The theoretical results [86, 120] suggest, for example, that the network of PDMS chains having $n = 53$ skeletal bonds which was studied experimentally should exhibit an upturn at a value of r/r_m a little less than 0.80. The observed value was 0.77 [109], which is thus in excellent agreement with theory.

A second important characteristic is the value α_r of the elongation at which rupture occurs. The corresponding values of r/r_m show that rupture generally occurred at approximately 80–90% of the maximum chain extensibility [109]. These quantitative results on chain dimensions are very important but need not apply directly to other networks, in which the chains could have very different configurational characteristics and in which the chain-length distribution would presumably be quite different from the very unusual bimodal distribution intentionally produced in the present networks.

The Monte Carlo simulations based on the rotational-isomeric-state (RIS) model for the network chains have been very useful for interpreting these upturns in modulus. Some typical results calculated for (amorphous) polyethylene and PDMS network chains having $n = 20$ skeletal bonds are shown in Fig. 1.28 [45]. The Gaussian distribution function is seen to be a relatively poor approximation to the RIS distribution at this value of n , particularly in the very important region of large r , and was found to become even worse as n decreases. Calculated Mooney–Rivlin isotherms for networks made up of PDMS chains of various lengths are presented in Fig. 1.29 [45]. As expected, the network consisting of relatively long chains ($n = 250$) gives the Gaussian result $[f^*]/(\nu kT) = 1$. The upturns in $[f^*]$ obtained at smaller n are very similar to those found experimentally. Also as expected, the results show that the shorter the network chains, the smaller the elongation at which the upturn occurs.

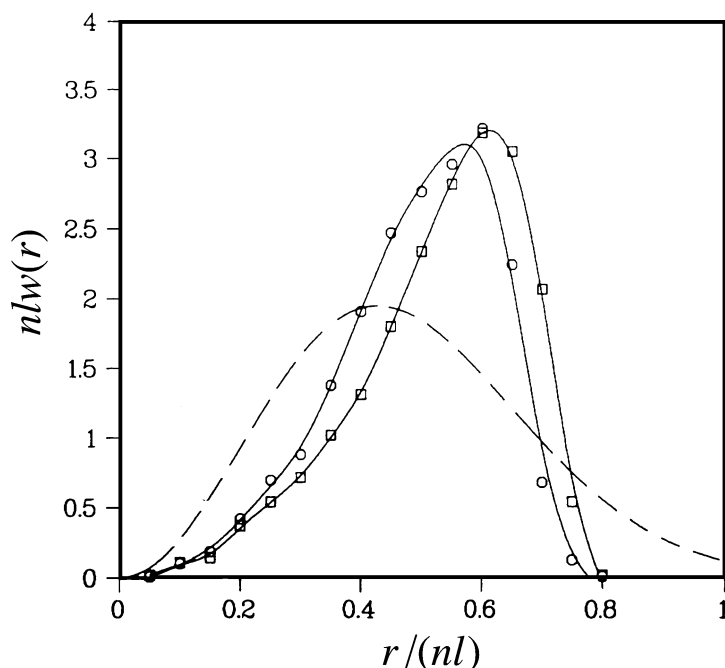


Fig. 1.28. Comparisons among the rotational isomeric (RIS) radial distribution functions at 413 K for polyethylene ($\circ$) and PDMS ($\square$) chains having $n = 20$ skeletal bonds, and the Gaussian approximation (---) to the distribution for PDMS [45]. The RIS curves represent cubic-spline fits to the discrete Monte Carlo data, for 80 000 chains, and each curve is normalized with respect to an area of unity (with l being the skeletal bond length).

It is also possible to interpret the upturns in modulus in these isotherms using analytic expressions, for example the Fixman–Alben modification [121] of the Gaussian distribution function, combined with the constrained-junction theory and reasonable values of the constraint parameter κ [122].

It should be pointed out that there are three requirements for obtaining these improvements. The first is that the ratio M_S/M_L of the molecular weights of the short and long chains be very small (i.e. that their molecular weights be very different). The second is that the short chains be as short as possible; for example, a network having network-chain molecular weights of 200 and 20 000 would be expected to exhibit much greater improvements from the bimodality than would one having molecular weights of 2000 and 200 000. Finally, there should be a large *number* concentration of the short chains, typically around 95 mol%.

There is another advantage to such bimodality when the network can undergo strain-induced crystallization, the occurrence of which can provide an additional toughening effect. This is illustrated by the results for some poly(ethylene oxide)

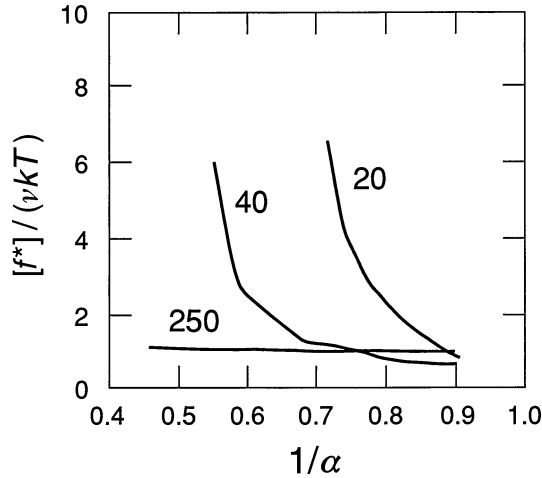


Fig. 1.29. Moduli of PDMS networks having chain lengths of $n = 20, 40$, and 250 skeletal bonds [45]. The values of $[f^*]$ are normalized by the Gaussian prediction for the modulus, νkT , where ν is the number of network chains and kT has the usual significance.

networks shown in Fig. 1.30 [123]. A decrease in temperature is seen to increase the extent to which the values of the ultimate strengths of the bimodal networks exceed those of the corresponding unimodal ones. This suggests that bimodality facilitates strain-induced crystallization.

Because of the improvements in properties exhibited by elastomers having bimodal distributions [22], there have been attempts to prepare and characterize “trimodal” networks [124]. Although experiments have been carried out in order to evaluate the mechanical properties of trimodal elastomers, this has not been done in any organized manner. The basic problem is the large number of variables involved, specifically three molecular weights and two independent composition variables (mole fractions); this makes it practically impossible to do an exhaustive series of relevant experiments. For this reason, the only mechanical-property experiments that have been carried out have involved arbitrarily chosen molecular weights and compositions [125–127]. Perhaps not surprisingly, only modest improvements over the bimodal materials have been obtained.

Results from some recent computational studies [128], however, indicate that it is possible to do simulations to identify those molecular weights and compositions which should maximize further improvements in mechanical properties. Such simulations are being extended to search for optimum properties of trimodal networks, specifically (i) the elastic modulus, (ii) the maximum extensibility, (iii) tensile strength, and (iv) segmental orientability. Results to date [124] suggest that a trimodal network prepared by incorporating small numbers of very long

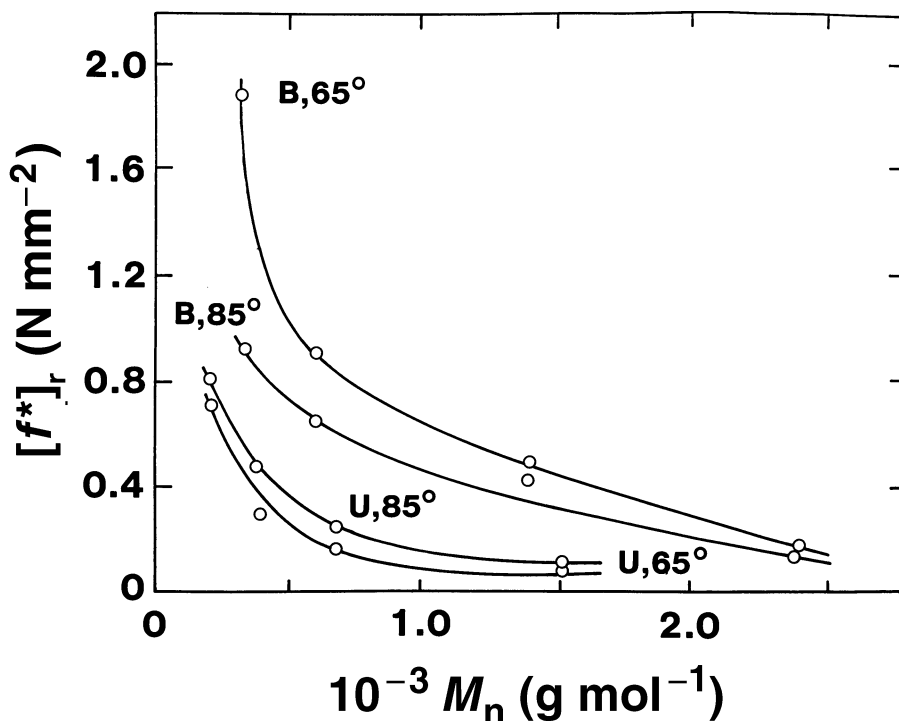


Fig. 1.30. The ultimate strength shown as a function of the molecular weight $M_n = M_c$ between cross-links for unimodal (U) and bimodal (B) networks of crystallizable poly(ethylene oxide) [123].

chains into a bimodal network of long and short chains could have significantly improved ultimate properties.

In practical terms, the above results demonstrate that short chains of limited extensibility may be bonded into a long-chain network to improve its toughness. It is also possible to achieve the converse effect. Thus, bonding a small number of relatively long elastomeric chains into a short-chain PDMS thermoset greatly improves its impact resistance, as is illustrated in Fig. 1.31 [129].

The effects of bimodality for other types of deformation are discussed further in Section 1.7.

1.6.3 Dangling-chain elastomers

Since dangling chains constitute imperfections in a network structure, one would expect their presence to have a detrimental effect on the ultimate properties $(f/A^*)_r$ and α_r of an elastomer. This expectation is confirmed by an extensive series of results obtained on PDMS networks that had been tetrafunctionally cross-linked using a variety of techniques [130]. The largest values of the ultimate strength

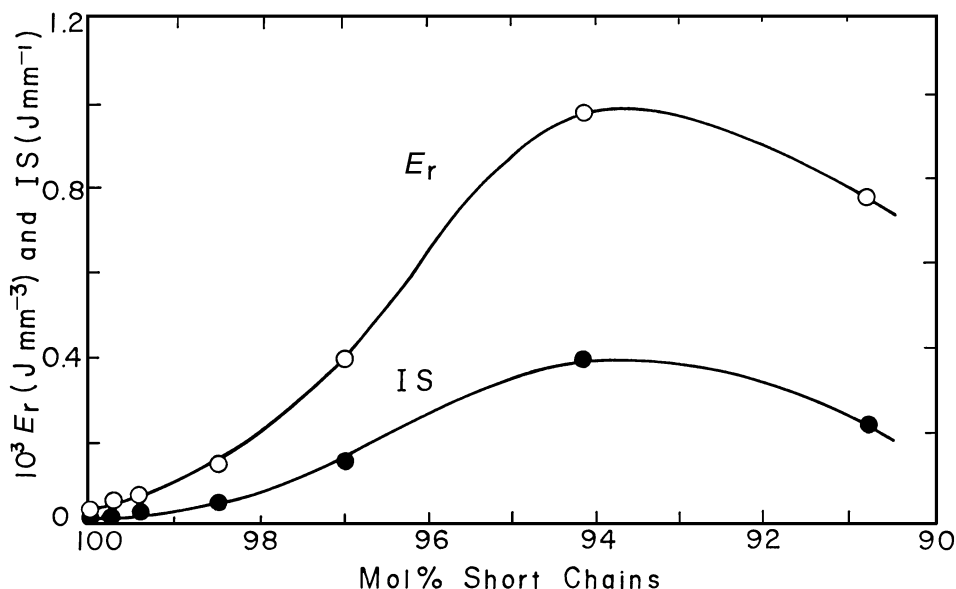


Fig. 1.31. The energy required for rupture and the impact strength (as measured by the falling-dart test) shown as functions of composition for bimodal PDMS networks in the vicinity of room temperature [129].

$(f/A^*)_r$ are obtained for the networks prepared by selectively joining functional groups occurring either as chain ends or as side groups along the chains. This is to be expected, because of the relatively low incidence of dangling ends in such networks. (As has already been described, the effects are particularly pronounced when such model networks are prepared from mixtures of relatively long and very short chains.) Also as expected, the lowest values of the ultimate properties generally occur for the networks cured by radiation (UV light, high-energy electrons, and γ radiation) [130]. The peroxide-cured networks are generally intermediate between these two extremes, with the ultimate properties presumably depending on whether the free radicals generated by the peroxide are sufficiently reactive to cause some chain scission. Similar results were obtained for the maximum extensibility α_r [130]. These observations are at least semiquantitative and certainly interesting, but are somewhat deficient in that information on the number of dangling ends in these networks is generally not available.

More definitive results have been obtained by investigation of a series of model networks prepared by end linking vinyl-terminated PDMS chains [130]. The tetrafunctional end-linking agent was used in varying amounts smaller than that corresponding to a stoichiometric balance between its active hydrogen atoms and the chains' terminal vinyl groups. The ultimate properties of these networks, with known numbers of dangling ends, were then compared with those obtained for

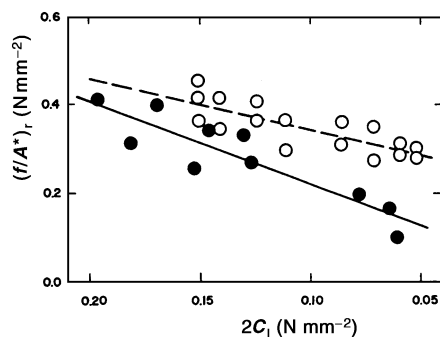


Fig. 1.32. The ultimate strength shown as a function of the high-deformation modulus for tetrafunctional PDMS networks containing a negligible number of dangling ends (○) and dangling ends introduced by using less than the stoichiometrically required amount of end-linking agent (●) [130]. In the latter case, a decrease in $2C_1$ corresponds to an increase in the number of dangling ends [130]. (Reproduced with permission; copyright 1981, John Wiley & Sons, Inc.)

networks that had previously been prepared in such a way as to have negligible numbers of these irregularities [130]. Values of the ultimate strengths of the networks are shown as a function of the high-deformation modulus $2C_1$ in Fig. 1.32 [130]. The networks containing the dangling ends have lower values of $(f/A^*)_r$, with the largest differences occurring for high proportions of dangling ends (small high-deformation moduli $2C_1$), as expected. These results thus confirm the less-definitive results mentioned already, which had been obtained using different cross-linking methods. The values of the maximum extensibility exhibit a dependence similar to that shown in Fig. 1.32.

1.7 Other types of deformation

1.7.1 Biaxial extension

There are numerous other deformations of interest, including compression, biaxial extension, shear, and torsion. The equation of state for compression ($\alpha < 1$) is the same as that for elongation ($\alpha > 1$), and the equations for the other deformations may all be derived from Eq. (1.10) by proper specification of the deformation ratios [1, 2]. Some of these deformations are considerably more difficult to study than simple elongation and, unfortunately, have therefore not been investigated as extensively.

Some measurements regarding biaxial extension have involved the direct stretching of a sheet of sample in two perpendicular directions within its plane, by two independently variable amounts. In the equi-biaxial case, the deformation is equivalent to compression. A good account of such experimental results [131] has been

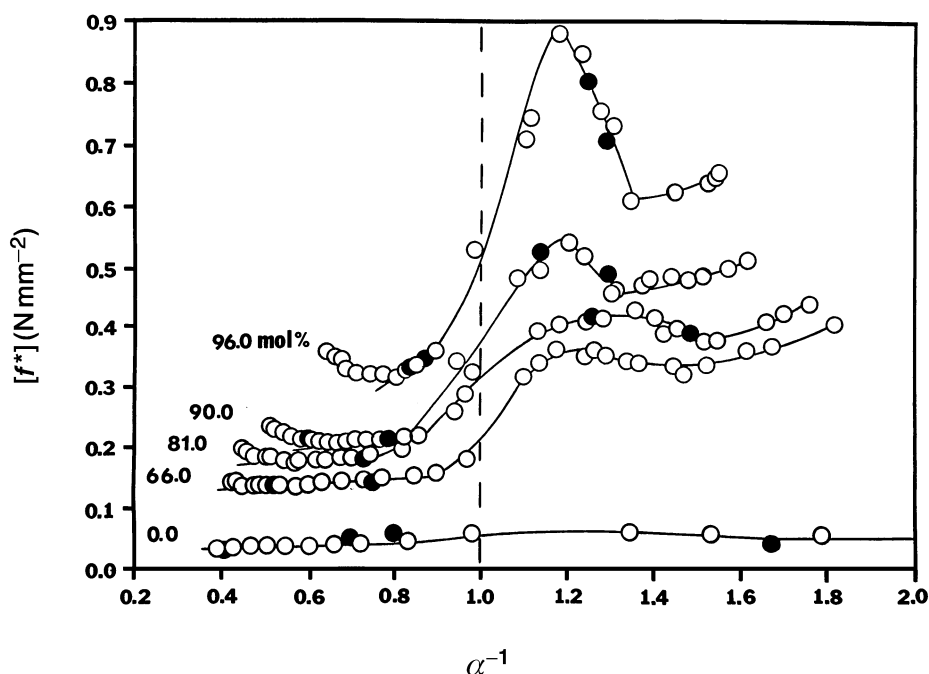


Fig. 1.33. Representative stress–strain isotherms for unimodal and bimodal PDMS networks in uniaxial extension (left-hand side), and biaxial extension (right-hand side) [132]. Each curve is labeled with the mole percentage of the short chains present in the network. The open circles represent data measured using increasing deformations, whereas filled circles represent data obtained out of sequence in order to test for reversibility.

given by the simple molecular theory, with improvements at lower extensions upon use of the constrained-junction theory [9].

Biaxial-extension studies can also be carried out by the inflation of sheets of the elastomer [2]. Such equi-biaxial results for some unimodal and bimodal networks of PDMS are illustrated in Fig. 1.33 [132, 133]. Upturns in the modulus are seen to occur at high biaxial extensions, as expected. Also of interest, however, are the pronounced maxima preceding the upturns. This phenomenon is a challenging feature to explain using molecular theories addressed to bimodal elastomeric networks in general.

1.7.2 Shear and torsion

Experimental results on networks of natural rubber in shear deformation [134] are not well accounted for by the simple molecular theory of rubber-like elasticity. The constrained-junction theory, however, was found to give excellent agreement with experiment. Shear measurements have also been reported for some unimodal and

bimodal networks of PDMS [135]. The upturns in modulus were found to be very similar to those obtained in elongation and biaxial extension.

Very little work has been done on elastomers subjected to torsion. There are, however, some results on stress–strain behavior and network thermoelasticity [2]. More results are presumably forthcoming, particularly on the unusual bimodal networks and on networks containing some of the unusual fillers described in Section 1.11.

1.7.3 Tearing deformations

Tear tests have been carried out on bimodal PDMS elastomers [136–138], using the standard “trouser-leg” method. Tear energies were found to be considerably increased by the use of a bimodal distribution, with documentation of the effects of compositional changes and changes in the ratio of molecular weights of the short and long chains. The increase in tear energy did not seem to depend on the rate of tearing [136], an important observation that seems to suggest that viscoelastic effects are not of great importance in explaining the observed improvements. A subsequent series of shear tests [137] established the dependences of the tearing properties on the compositions of the bimodal networks and the lengths of the chains used to prepare them. The observed increases in strength with decreasing molecular weight of the short chains must eventually become *decreases* when the chains become too short to have any elastic effectiveness at all.

1.7.4 Cyclic deformations

Some Rheovibron viscoelasticity results have been reported for bimodal PDMS [139]. Also, measurements on permanent set for PDMS networks in compressive cyclic deformations have been made [140]. There appeared to be less permanent set or “creep” in the case of the bimodal elastomers. This is consistent in a general way with some early results for polyurethane elastomers [141]. Specifically, cyclic-elongation measurements on unimodal and bimodal networks indicated that the bimodal ones survived many more cycles before the occurrence of fatigue failure. The number of cycles to failure was found to be approximately an order of magnitude higher for the bimodal networks, at the same modulus at 10% deformation [22]!

1.7.5 Swelling

Most studies of networks in swelling equilibrium give values for the cross-link density or related quantities that are in satisfactory agreement with those obtained from measurements of mechanical properties [1, 2].

1.8 Gel collapse

A final phenomenon relevant here is gel collapse [142–144]. It involves the relatively abrupt deswelling of a swollen elastomer (a “gel”) brought about by small changes in some variable, for example (i) temperature, (ii) composition, (iii) pH, or (iv) ionic strength, or caused by (v) application of an electric field, or (vi) irradiation with light. An example is shown schematically in the upper portion of Fig. 1.34. Here, v_2 is the volume fraction of polymer present in the gel, and the discontinuous shrinkage (increase in v_2) occurs upon a decrease in temperature. The deswelling (“syneresis”) is not complete in that the network still contains substantial amounts of diluent, but the amount expelled is enough to give very substantial changes in the dimensions of the gel. Also, the process is reversible, in that the deswollen gel can be reswollen by restoring the changed variable to its earlier value.

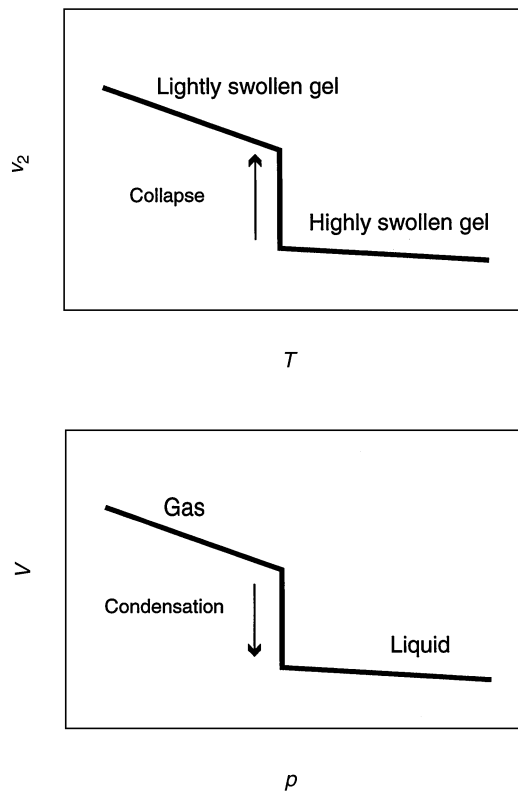


Fig. 1.34. The upper sketch portrays gel collapse, as evidenced by the abrupt increase in volume fraction of polymer in the gel as it shrinks when the temperature drops to a critical value [4]. This syneresis and reswelling can be exploited by harnessing the mechanical motion in a variety of devices. The lower sketch shows the corresponding situation as the pressure of a gas is increased to a critical value that causes condensation to the liquid state.

If all dimensions of the gel are sizable, a considerable amount of time may be required for this deswelling to occur, since outward diffusion of the small molecules is required. The process is, of course, much more rapid in the case of a film or fiber, because of the much larger ratios of surface area to volume when one or more dimensions of the sample are very small. Surface areas can also be increased, of course, by utilizing foamed objects. The possibility of having these changes occur relatively quickly has encouraged attempts to harness the accompanying mechanical motions in a variety of devices. Examples of potential applications include actuators, switches, drug-delivery systems, and artificial muscles.

There are parallels and differences in the case of the condensation of gases, as is illustrated by the p - V isotherm shown in the lower part of Fig. 1.34. Here, an increase in pressure causes a discontinuous decrease in volume to that of the liquid. Again, there are large changes in dimensions upon condensation of a gas to the much denser liquid phase, but the isotropic nature of the phases makes this much more limited with regard to possible mechanical applications.

1.9 Energy storage and hysteresis

The swinging pendulum serves to illustrate the simplest energy-storage concepts, as shown schematically in Fig. 1.35. Point a corresponds to the maximum potential (stored) energy, b is the point at which potential energy is converted into kinetic energy, and c is the point at which kinetic energy is converted back into potential energy. In this case, the molecular origins of losses in stored energy arise from air resistance and friction at the pivot.

The analogous case of a rubber ball bouncing off a surface is shown schematically in Fig. 1.36 [145]. Again, point a corresponds to the maximum potential (stored) energy, and at point b potential energy is converted into kinetic energy. Now, however, kinetic energy is converted into elastic-deformation energy upon impact with the

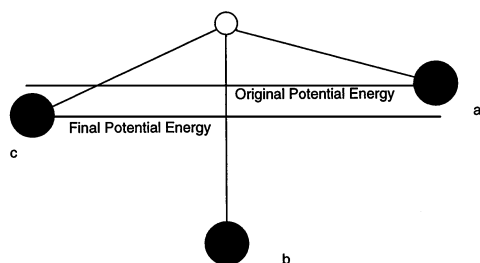


Fig. 1.35. The change in potential energy of a pendulum as it swings from its original position on the right, to a lower level corresponding to decreased potential energy on the left [4].

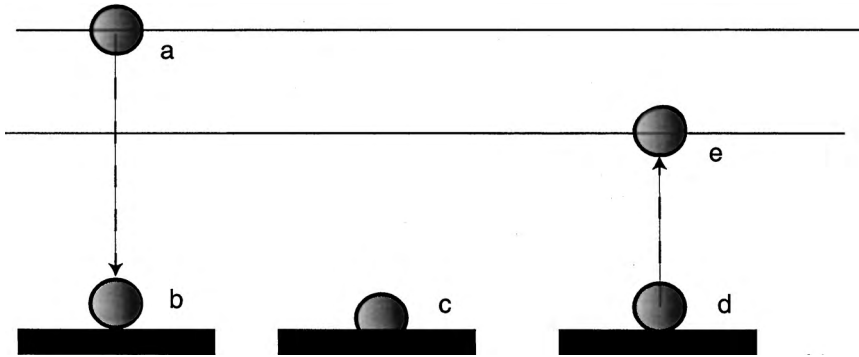


Fig. 1.36. The change in potential energy of a rubber ball as it drops from its original position on the left, via the impact point converting kinetic energy to elastically stored energy, to bouncing up to a level corresponding to a decreased potential energy [4].

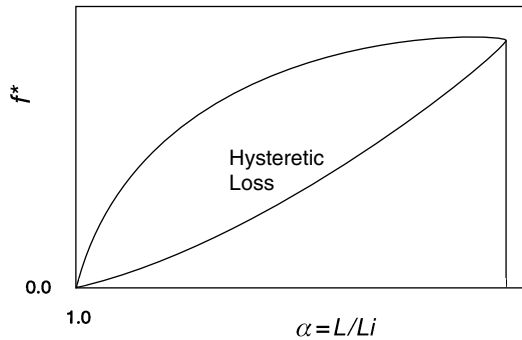


Fig. 1.37. The stress–strain cycle of an elastomer at constant temperature, illustrating the occurrence of hysteresis [4].

surface, at point c. At point d, elastic energy is released and converted into kinetic energy. Finally, at point e kinetic energy is converted back into potential energy. The fraction of the original height recovered is a measure of the efficiency of the storage of energy. In this case, in addition to minor effects from air resistance, the losses in stored energy arise from viscosity effects as chains change their spatial configurations from random to compressed and then back to random.

These energy losses or “hysteretic” effects have parallels in small-molecule systems, for example in magnetization–demagnetization loops [146, 147]. They are particularly important in elastomers since they correspond to wastage of energy, and overheating (“heat build up”, with accompanying increases in thermal degradation). The amount of hysteresis can also be gauged from stress–strain isotherms, as shown schematically in Fig. 1.37. The area below the upper elongation curve corresponds to the energy used in the deformation, and the area below the lower retraction curve

corresponds to the energy recovered. The area between the two curves thus represents the energy wasted in hysteresis. This subject is very important with regard to bioelastomers, as is described below.

It is also of interest to replace the usual Carnot cycle based on a gas undergoing (i) isothermal expansion at an upper temperature T_1 , (ii) adiabatic expansion decreasing the temperature to a lower temperature T_2 , (iii) isothermal compression at T_2 , and (iv) adiabatic compression increasing the temperature back to T_1 . The efficiency ε is found to be $1 - T_2/T_1$, and is stated as being independent of the working substance. This generality can be illustrated by using an elastomer as working substance, and replacing the expansions by retractions and the compressions by extensions [148–150].

The conversion of thermal or chemical energy into mechanical work has been of considerable interest [151, 152]. There are a number of advantages in using an elastomer as a working substance in these applications [74, 153–157]. They include (i) a small adiabatic ΔT that is useful for small differences $T_1 - T_2$, (ii) a broad range of temperatures (hence there is no need for condensation or vaporization transitions), and the facts that (iii) advantageous contractile transitions may be introduced using oriented fibers, (iv) no containment of gas or liquid is required, (v) stalling and starting torques are high, and, finally, (vi) construction is simple, with less material being required.

1.10 Bioelastomers

Some protein bioelastomers are of considerable interest and importance, particularly the elastin occurring in mammals, and investigation of their properties may be used to obtain insights into cross-linking and elastic behavior in general. For example, elastin [9, 158–161] illustrates the relevance of several molecular characteristics to the achievement of rubber-like properties. First, a high degree of chain flexibility is achieved in elastin by virtue of its chemically irregular structure, and by choices of side groups that are almost invariably very small. Since strong intermolecular interactions are generally not conducive to good elastomeric properties, the choices of side chains are also almost always restricted to nonpolar groups. Finally, elastin has a glass-transition temperature of approximately 200 °C in the dry state, which means that it would be elastomeric only above this temperature. Nature, however, apparently also knows about “plasticizers.” Elastin, as used in the body, is invariably swollen with sufficient aqueous solutions to bring its glass-transition temperature below the operating temperature of the body.

The cross-linking in these bioelastomers is carefully controlled by nature, using techniques very unlike those usually used to cure commercial elastomers [9, 162]. The number and spacing of the cross-links are fixed by the ribosome-controlled

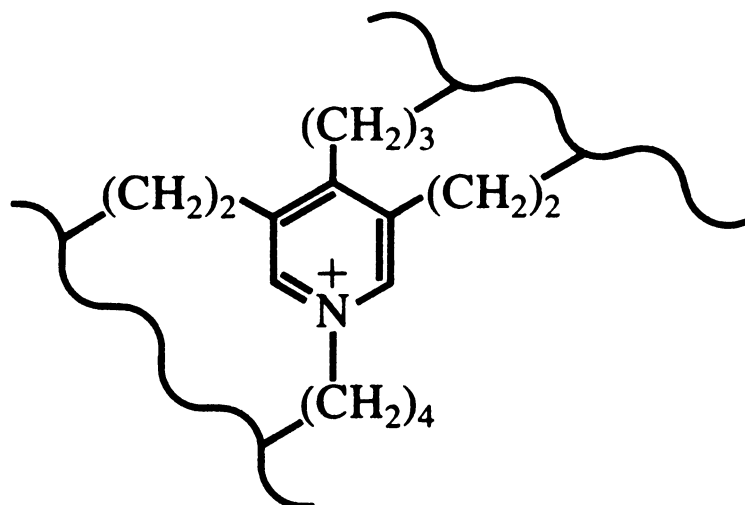


Fig. 1.38. A sketch of one of the types of cross-link appearing in the protein elastin [9].

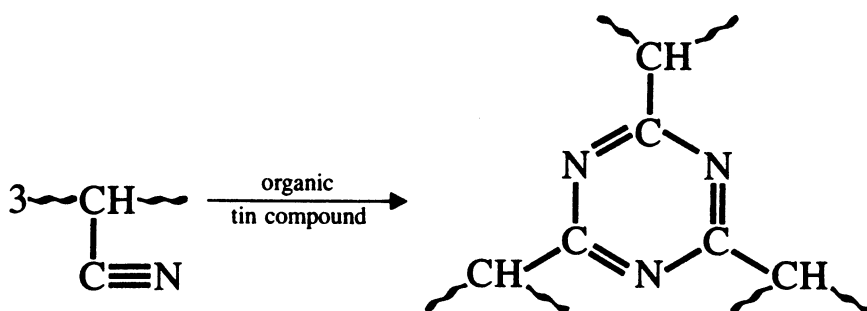


Fig. 1.39. A sketch of a type of cross-link that appears in some perfluoroelastomers [9].

α -amino-acid sequence, since the cross-linking occurs only through the lysines (using a copper-activated enzyme called lysyl oxidase) [22]. Particularly intriguing is the fact that the lysine sites are preceded and succeeded by alanines (which may be in α -helical conformations). Placing these potential cross-linking sites at the ends of two stiff sequences may help control their spatial environment, for example their entangling with other protein repeat units. One type of resulting cross-link is shown in Fig. 1.38 [9]. An analogous reaction has been carried out commercially on perfluoroelastomers, which are usually very difficult to cross-link because of their inertness. Nitrile side groups placed along the chains are trimerized to triazine, thus giving similarly stable, aromatic cross-links, as illustrated in Fig. 1.39 [9].

Minimizing hysteresis is particularly important in the case of the bioelastomers used in jumping by insects, such as grasshoppers, and fleas. In these cases, the elastomer is called resilin [163], and the energy is stored by their compressing a

plug of this material [22]. It is released when the insect wishes to jump, for example away from a predator, and the larger the fraction of the stored energy available the better. The release time is obviously also critically important, and is approximately 1 ms. Insects with more sluggish bioelastomers were presumably phased out by the process of natural selection.

Resilin also is important in flying insects, such as dragonflies, where a plug under the wings smoothes out the flapping by alternating between being compressed and expanding. Large hysteretic effects would be bad not only because of the inefficiencies involved, but also because of possible overheating of the dragonfly. Resilin is an unusual material because it is thought to have a relatively high efficiency in storing elastic energy (i.e. very small losses due to viscosity effects). (Such viscoelastic properties are discussed in Chapter 3 by W. W. Graessley.) A molecular understanding of this very attractive property could obviously have considerable practical as well as fundamental importance.

Trying to parallel the control nature exerts in cross-linking bioelastomers, for example by end-linking reactions, is an example of “biomimicry” or “bio-inspired design”. Other relevant examples are the already-mentioned use of (i) irregular copolymer sequences to suppress crystallinity, (ii) small side groups to enhance flexibility and mobility, (iii) nonpolar side groups to reduce the magnitude of intermolecular interactions, and (iv) plasticizers to reduce brittleness [22]. It is useful to give one illustration, however, of how such “bio-inspiration” can lead one astray. All of the early work on trying to mimic the flight of birds by designing aircraft with flapping wings turned out to be disastrous! The successful approaches involving propellers or jets were probably not inspired at all by analogies with biological systems. Circular motions and jets of fluids for locomotion are relatively rare in biology, and are used in aqueous fluids, rather than in air. Similar arguments can be made with regard to using jets of fluids as a means of propulsion.

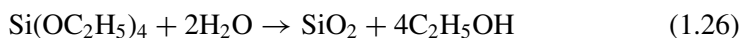
1.11 Filled networks

1.11.1 In situ-generated fillers

Elastomers, particularly those which cannot undergo strain-induced crystallization, are generally compounded with a reinforcing filler [9]. The two most important examples are the addition of carbon black to natural rubber and to some synthetic elastomers [164, 165] and silica to polysiloxane rubbers [166, 167]. The advantages obtained include improvements in abrasion resistance, tear strength, and tensile strength. Disadvantages include increases in hysteresis (and thus heat build up) and compression set (permanent deformation).

The mechanism of the reinforcement is only poorly understood. Some elucidation might be obtained by precipitating reinforcing fillers into network structures rather

than blending badly agglomerated fillers into polymers prior to their cross-linking. This has, in fact, been done for a variety of fillers, for example silica by hydrolysis of organosilicates, titania from titanates, alumina from aluminates, etc. [9, 168, 169]. A typical, and important, reaction is the acid- or base-catalyzed hydrolysis of tetraethylorthosilicate:



Reactions of this type are much used by the ceramists in the new sol–gel chemical route to high-performance ceramics [170, 171]. In the ceramics area, the advantages are the possibility of using low temperatures, the purity of the products, the control of ultrastructure (at the nanometer level), and the relative ease of forming ceramic alloys. In the elastomer-reinforcement area, the advantages include the avoidance of the difficult, time-consuming, and energy-intensive process of blending agglomerated filler into high molecular weight (high-viscosity) polymer, and the ease of obtaining extremely good dispersions.

In the simplest approach to obtaining elastomer reinforcement, some of the organometallic material is absorbed into the cross-linked network, and the swollen sample placed into water containing the catalyst, typically a volatile base such as ammonia or ethylamine. Hydrolysis to form the desired silica-like particles proceeds rapidly at room temperature to yield of the order of 50 wt% filler in less than an hour [9, 22, 168, 169].

A typical transmission electron micrograph, of PDMS elastomer filled with approximately 30 wt% silica, is shown in Fig. 1.40 [172]. The particles formed are seen to be approximately spherical, and are well dispersed and essentially unagglomerated, which suggests that the reaction may involve simple homogeneous nucleation. This is consistent with the fact that particles growing independently of one another and separated by cross-linked polymer would not agglomerate unless very high concentrations were reached. The particles appear to have a relatively narrow size distribution, with almost all of them having diameters in the range 200–300 Å.

Figure 1.41 illustrates the reinforcing ability of such *in situ*-generated particles [173]. The modulus [f^*] is seen to increase by more than an order of magnitude, and the isotherms show the upturns at high elongation that are the signature of good reinforcement. As generally occurs in filled elastomers, there is considerable irreversibility in the isotherms, which is thought to be due to irrecoverable sliding of the chains over the surfaces of the filler particles.

If the hydrolyses in organosilicate-polymer systems are carried out with increased amounts of the silicate, bicontinuous phases can be obtained (with the silica and polymer phases interpenetrating one another) [61]. At still-higher concentrations of the silicate, the silica generated becomes the continuous phase, with the polymer

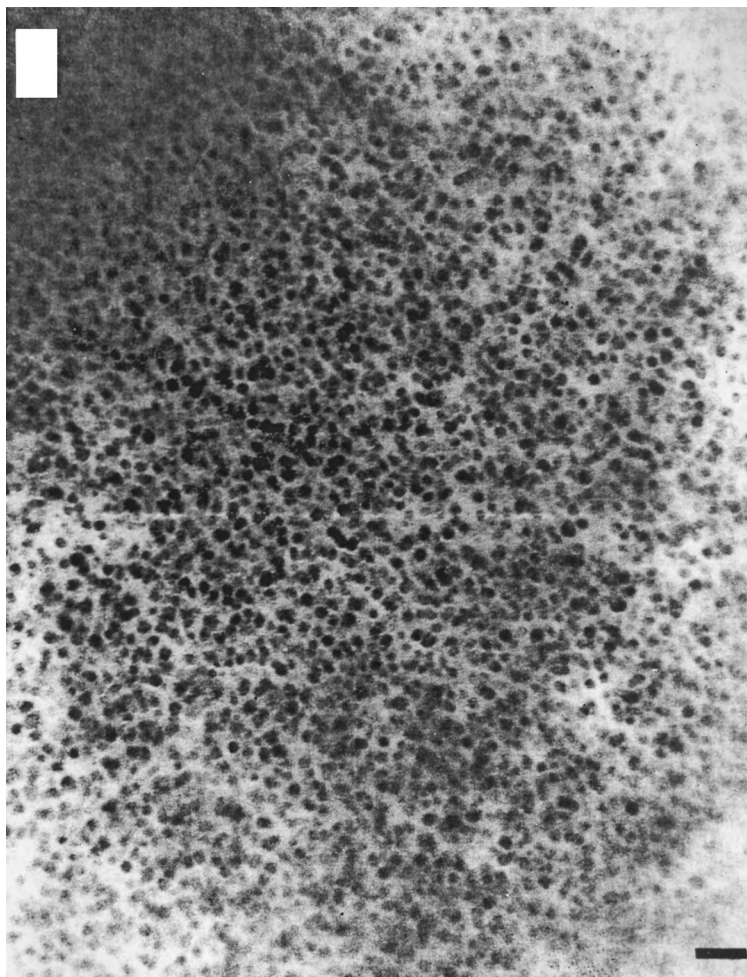


Fig. 1.40. An electron micrograph of a PDMS elastomer containing *in situ*-precipitated silica particles [172].

dispersed in it [174–188]. The result is a polymer-modified ceramic, variously called an “ORMOCER” [174–176], “CERAMER” [177–179], or “POLYCERAM” [183–185]. It is obviously of considerable importance to determine how the polymeric phase, which is often elastomeric, modifies the ceramic in which it is dispersed.

Some typical results on such hybrid organic–inorganic composites are shown in Fig. 1.42, which pertains to PDMS–SiO₂ systems [186]. It can be seen that the hardness of the material can be varied greatly by changing the ratio of organic-to-inorganic character, as measured in terms of the molar ratio of organic R groups (here CH₃ side groups) to Si atoms. Low values of the R/Si ratio yield a brittle ceramic, whereas high values yield a reinforced elastomer. The most interesting

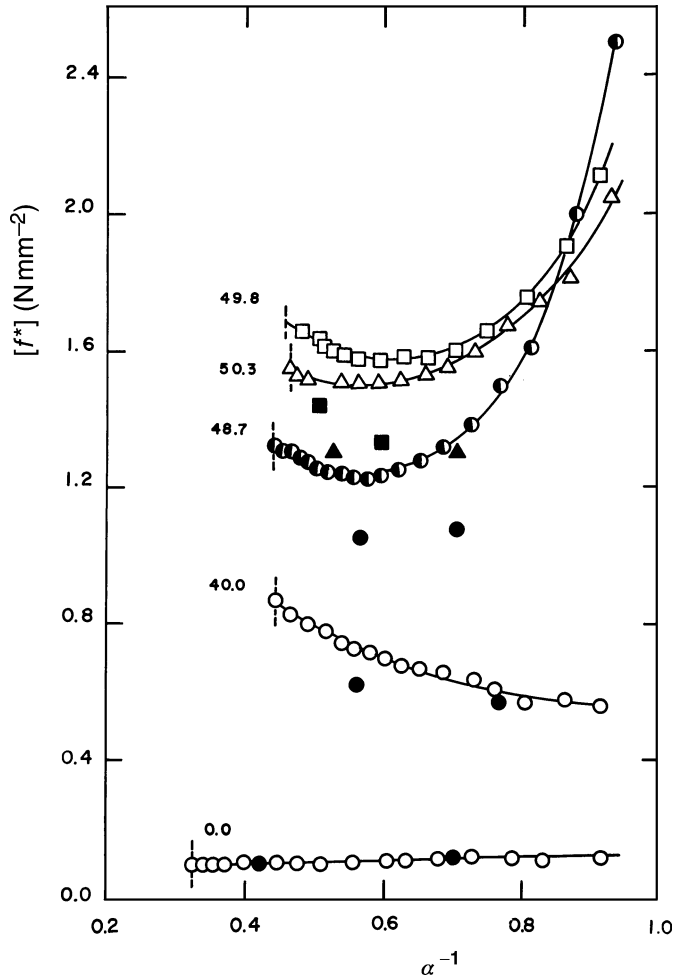


Fig. 1.41. Mooney–Rivlin isotherms for PDMS elastomers filled with *in situ*-generated silica, with each curve labeled with the amount of filler precipitated into it [173]. Filled symbols are for results obtained out of sequence in order to establish the amount of elastic irreversibility, a common occurrence with reinforcing fillers. The vertical lines locate the rupture points.

range of values, $R/Si \sim 1$, can give a hybrid material that can be viewed as a ceramic of reduced brittleness or an elastomer of increased hardness, depending on one's point of view.

1.11.2 Ellipsoidal fillers

Reinforcing fillers can be deformed from their usual approximately spherical shapes in a number of ways. For example, if the particles are made of a glassy polymer

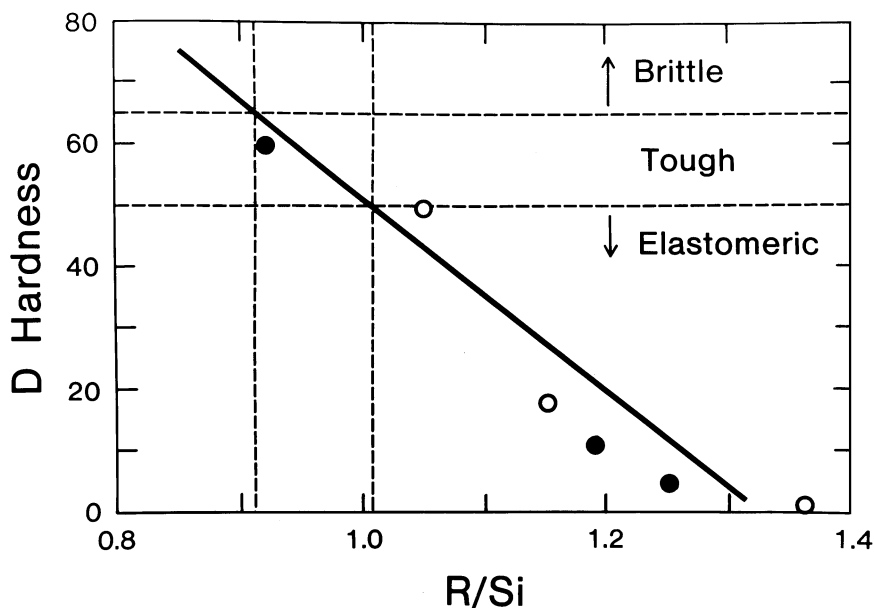


Fig. 1.42. The dependence of the D-scale hardness of PDMS composites on the ratio of alkyl groups to silicon atoms [186]. The open circles correspond to bimodal PDMS, and the filled circles to unimodal PDMS.

such as polystyrene (PS), then deforming the matrix in which they reside above the glass-transition temperature for PS will convert them into ellipsoids. Uniaxial deformations give prolate (needle-shaped) ellipsoids, whereas biaxial deformations give oblate ellipsoids [189, 190]. Prolate particles can be thought of as a conceptual bridge between the roughly spherical particles used to reinforce elastomers and the long fibers frequently used for this purpose in thermoplastics and thermosets. Similarly, oblate (disk-shaped) particles can be considered as analogs of the much-studied clay platelets used to reinforce a variety of materials [191–194]. In the case of nonspherical particles, their orientations are also of considerable importance. One area of interest here is the anisotropic reinforcements such particles provide, and simulations have been performed in order to increase understanding of the mechanical properties of such composites, as mentioned below [11, 195].

1.11.3 Clay-like fillers

Exfoliating layered particles such as the clays, mica, and graphite is being used to provide very effective reinforcement of polymers at loading levels much smaller than those used in the case of solid particles such as carbon black and silica [196–200]. Other properties can also be improved substantially; for example,

resistance to solvents can be increased, and permeability and flammability can be reduced.

1.11.4 Polyhedral oligomeric silsesquioxane (POSS) particles

These fillers are cage-like structures, and have been called the smallest possible silica particles. They typically contain between zero and eight organic functional groups per cage. The particles with no functional groups at all can be blended into polymers using the usual mixing or compounding processing, while those with one functional group can be attached to a polymer as side chains. Those with two functional groups can be incorporated into polymer backbones by copolymerization, and those with more than two can be used for forming cross-linked networks [201–205]. Nanotubes are also of considerable interest in this regard [206–208].

1.11.5 Porous fillers

Some fillers, such as zeolites, are sufficiently porous to accommodate monomers, which can then be polymerized. This threads the chains through the cavities, with unusually intimate interactions between the reinforcing phase and the host elastomeric matrix [207]. Because of the constraints imposed by the cavity walls, these confined materials generally have no glass-transition temperatures [11].

1.11.6 Composites with controlled interfaces

By choosing the appropriate chemical structures, chains that span filler particles in a polymer-based composite can be designed so that they are durable, irreversibly breakable, or reversibly breakable [209–211].

1.11.7 Simulations on filler reinforcement

Monte Carlo computer simulations were also carried out on filled networks [212–215], in an attempt to obtain a better molecular interpretation of how such dispersed fillers reinforce elastomeric materials. The approach taken allowed estimation of the effect of the excluded volume of the filler particles on the network chains and on the elastic properties of the networks. In the first step, distribution functions for the end-to-end vectors of the chains were obtained by applying Monte Carlo methods to rotational-isomeric-state representations of the chains [45]. Conformations of chains that overlapped with any filler particle during the simulation were rejected. The resulting perturbed distributions were then used in the three-chain elasticity model [2] to obtain the desired stress–strain isotherms in elongation.

In one application, a filled PDMS network was modeled as a composite of cross-linked polymer chains and spherical filler particles arranged in a regular array on a cubic lattice [216]. The filler particles were found to increase the non-Gaussian nature of the behavior of the chains and to increase the moduli, as expected. It is interesting to note that composites with such structural regularity have actually been produced [217], and some of their mechanical properties have been reported [218]. In a subsequent study, the reinforcing particles were randomly distributed within the PDMS matrix [215]. One effect of the filler was to increase the end-to-end separations of the chains. These results on the chain-length distributions are in agreement with data from some subsequent neutron-scattering experiments on silicate-filled PDMS [219]. The corresponding stress-strain isotherms in elongation exhibited substantial increases in stress and modulus with increasing filler content and elongation that are in at least qualitative agreement with experiment.

In the case of nonspherical filler particles, it has been possible to simulate the anisotropic reinforcement obtained, for various types of particle orientation [215, 220]. Various types and degrees of agglomeration can also be investigated.

1.12 New developments in processing

Important topics in this area are the use of chaotic mixing to improve compounding [221], and modeling that includes flow-induced crystallization during molding processes.

1.13 Societal aspects

Of interest here are the possible synthesis of elastomers in environmentally friendly solvents, and the understanding and exploitation of biosynthetic techniques [222]. Another environmental goal is recyclability [223, 224]. Other topics much in the news currently are the improvement of safety aspects of tires (with an emphasis on more reliable bonding to tire cords), and better barrier properties in anti-terrorism protective clothing. Educational topics include curriculum development, and mobile laboratories for elastomer experiments and demonstrations [11].

1.14 Current problems and new directions

Some aspects of rubber-like elasticity that are clearly in need of additional research are listed below.

- Understanding the dependences of T_g and T_m on polymer structure.
 - Preparation and characterization of “high-performance” elastomers.
 - Development of new cross-linking techniques.
 - Understanding network topology.
-

- Generalization of phenomenological theory.
- Additional experimental results for deformations other than elongation and swelling.
- Characterization of segmental orientation.
- Detailed understanding of critical phenomena and gel collapse.
- Additional molecular characterization using NMR spectroscopy and various scattering techniques.
- Study of possibly unique properties of bioelastomers.
- Understanding of reinforcing effects of filler particles in a network.
- Quantitative interpretation of the toughening effects of elastomers in blends and in composites, particularly the polymer-modified ceramics.

There is a real need for more high-performance elastomers, which are materials that remain elastomeric on going to very low temperatures and are relatively stable at very high temperatures. Some phosphazene polymers, $[-P(OR)(OR')-N-]$ [225–227], are in this category. These polymers have rather low glass-transition temperatures in spite of the fact that the skeletal bonds of the chains are thought to have some double-bond character. There are thus some interesting problems related to the elastomeric behavior of these unusual semi-inorganic polymers. There is also increasing interest in the study [22] of elastomers that also exhibit the type of mesomorphic behavior described by E. T. Samulski in Chapter 5.

An example of a cross-linking technique currently under development is the preparation of triblock copolymers such as those of styrene–butadiene–styrene. This system undergoes phase separation in such a way that relatively hard polystyrene domains act as temporary, physical cross-links, as is shown in Fig. 1.43 [228]. The resulting elastomer is thermoplastic, and it is possible to reprocess it by simply heating it to above the glass-transition temperature of polystyrene. It is thus a *reprocessible* elastomer. There is a need to develop thermoplastic elastomers that are less expensive than the Kraton[®] styrene–butadiene–styrene triblock copolymers. The leading candidates are stereochemical copolymers of polypropylene, and chemical copolymers of ethylene and comonomers such as hexene-1 [229–231].

As has already been mentioned, more novel approaches could probably be learned by studying the cross-linking techniques used by nature in preparing bioelastomers.

A particularly challenging problem is the development of a more quantitative molecular understanding of the effects of filler particles [232–234], in particular

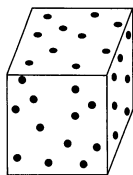


Fig. 1.43. A sketch of a multiphase, thermoplastic elastomer.

carbon black in natural rubber and silica in siloxane polymers. Such fillers provide tremendous reinforcement in elastomers in general, and how they do this is still only poorly comprehended. A related but even more complex problem involves much the same components, namely one that is organic and one that is inorganic. When one or both components are generated *in situ*, however, there is an almost unlimited variety of structures and morphologies that can be generated [22]. How physical properties such as elastomeric behavior depend on these variables is obviously a challenging but very important problem.

An example of an important future trend is the study of single polymer chains, particularly with regard to their stress–strain isotherms [235, 236]. Although such studies are obviously not relevant to the many unresolved issues that involve the interactions among chains in an elastomeric network, they are certainly of interest in their own right.

1.15 Numerical problems

1.15.1 Some typical elongation or compression data

Suppose that a network having tetrafunctional cross-links ($\phi = 4$, $A_\phi = \frac{1}{2}$) and a density of 0.900 g cm^{-3} has $[f^*]$ ($\alpha = \infty$) = 0.100 N mm^{-2} (10^5 N m^{-2} (Pa) = $10^{-1} \text{ MN m}^{-2}$ (MPa) = 1.02 kg cm^{-2}) at 298.2 K. Calculate the network-chain density, the cross-link density, and the average molecular weight between cross-links [9].

1.15.2 Some typical swelling data

A typical network studied in this regard might have been tetrafunctionally cross-linked in the undiluted state ($v_{2S} = 1.00$), and exhibit an equilibrium degree of swelling characterized by $v_{2m} = 0.100$ in a solvent having a molar volume $V_1 = 80 \text{ cm}^3 \text{ mol}^{-1}$ ($8.00 \times 10^4 \text{ mm}^3 \text{ mol}^{-1}$) and an interaction parameter with the polymer corresponding to $\chi_1 = 0.30$. Calculate the network-chain density [9].

1.16 Solutions to numerical problems

1.16.1 Elongation or compression

Use of the above data in Eq. (1.17) with k in units of $1.381 \times 10^{-20} \text{ N mm K}^{-1} \text{ chain}^{-1}$ compatible with $[f^*]$ ($\alpha = \infty$) in N mm^{-2} gives

$$\nu/V = 4.86 \times 10^{16} \text{ chains mm}^{-3}$$

Use of Avogadro's number $N_{\text{avo}} = 6.02 \times 10^{23} \text{ mol}^{-1}$ then gives

$$\nu/V = 8.06 \times 10^{-8} \text{ moles of chains mm}^{-3}$$

As specified by the relationship $\mu = (2/\phi)v$, the density of cross-links would be half $(2/\phi)$ of this value,

$$v/V = 4.03 \times 10^{-8} \text{ moles of cross-links mm}^{-3}$$

Since the polymer has a density $\rho = 0.900 \text{ g cm}^{-3}$ ($9.00 \times 10^{-4} \text{ g mm}^{-3}$), the relationship $M_c = \rho/(v/V)$ indicates that

$$M_c = 1.12 \times 10^4 \text{ g mol}^{-1}$$

1.16.2 Swelling

The standard relationship (Eq. (1.19)) for swelling with $A'_\phi = 1$ would give

$$v/V = 7.13 \times 10^{-8} \text{ moles of chains mm}^{-3}$$

Use of the improved relationship (Eq. (1.20)) with the reasonable estimates [51] $\kappa = 20$ and $p = 2$ gives $K = 0.42$ [51] and thus

$$v/V = 8.95 \times 10^{-8} \text{ moles of chains mm}^{-3}$$

This result is seen to be not very different from the value calculated using the simpler relationship given in Eq. (1.19).

Acknowledgments

It is a pleasure to acknowledge the financial support provided by the National Science Foundation through grants DMR-0075198 and DMR-0314760 (Polymers Program, Division of Materials Research), and by the Dow Corning Corporation.

References

- [1] P. J. Flory, *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, New York, 1953).
- [2] L. R. G. Treloar, *The Physics of Rubber Elasticity*, 3rd edition (Clarendon Press, Oxford, 1975).
- [3] J. E. Mark, *J. Chem. Educ.*, **58** (1981), 898.
- [4] J. E. Mark, *J. Chem. Educ.*, **79** (2002), 1437.
- [5] J. E. Mark, *J. Phys. Chem. B*, **107** (2003), 903.
- [6] P. J. Flory, *Statistical Mechanics of Chain Molecules* (Interscience, New York, 1969; reissued by Hanser Publishers, Munich, 1989).
- [7] W. L. Mattice and U. W. Suter, *Conformational Theory of Large Molecules. The Rotational Isomeric State Model in Macromolecular Systems* (Wiley, New York, 1994).
- [8] M. Rehahn, W. L. Mattice, and U. W. Suter, *Adv. Polym. Sci.*, **131/132** (1997), 1.
- [9] J. E. Mark and B. Erman, *Rubberlike Elasticity. A Molecular Primer* (Wiley-Interscience, New York, 1988).

- [10] P. Mason, *Cauchu, The Weeping Wood* (Australian Broadcasting Commission, Sydney, 1979).
- [11] J. E. Mark, *Macromol. Symp.* **201** (2003), 77.
- [12] W. J. Bobear, in *Rubber Technology*, edited by M. Morton (Van Nostrand Reinhold, New York, 1973), p. 368.
- [13] H. Kobayashi and M. J. Owen, *Macromolecules*, **23** (1990), 4929.
- [14] D. V. Patwardhan, H. Zimmer, and J. E. Mark, *J. Inorg. Organomet. Polym.*, **7** (1998), 93.
- [15] C. Wrana, K. Reinartz, and H. R. Winkelbach, *Macromol. Mater. Eng.*, **286** (2001), 657.
- [16] M. H. Acar, J. A. Gonzales, and A. M. Mayes, *Preprints, American Chemical Society Division of Polymer Chemistry, Inc.*, **43**(2) (2002), 55.
- [17] B. Erman and J. E. Mark, *Ann. Rev. Phys. Chem.*, **40** (1989), 351.
- [18] S. S. Labana and R. A. Dickie (eds.), *Characterization of Highly Cross-Linked Polymers* (American Chemical Society, Washington, 1984).
- [19] K. Dusek, *Adv. Polym. Sci.*, **78** (1986), 1.
- [20] B. E. Eichinger and O. Akgiray, in *Computer Simulation of Polymers*, edited by E. A. Colbourne (Longman, White Plains, New York, 1994), p. 263.
- [21] R. F. T. Stepto, D. J. R. Taylor, T. Partchuk, and M. Gottlieb, in *Silicones and Silicone-Modified Materials*, edited by S. J. Clarson, J. J. Fitzgerald, M. J. Owen, and S. D. Smith (American Chemical Society, Washington, 2000), p. 194.
- [22] B. Erman and J. E. Mark, *Structures and Properties of Rubberlike Networks* (Oxford University Press, New York, 1997).
- [23] J. L. Braun, J. E. Mark, and B. E. Eichinger, *Macromolecules*, **35** (2002), 5273.
- [24] J. E. Mark, *Makromol. Symp.*, **171** (2001), 1.
- [25] J. E. Mark, *Rubber Chem. Technol.*, **55** (1982), 762.
- [26] R. W. Ogden, *Rubber Chem. Technol.*, **59** (1986), 361.
- [27] R. W. Ogden, *Polymer*, **28** (1987), 379.
- [28] H. M. James and E. Guth, *J. Chem. Phys.*, **15** (1947), 669.
- [29] H. M. James and E. Guth, *J. Chem. Phys.*, **21** (1953), 1039.
- [30] M. Rubinstein and S. Panyukov, *Macromolecules*, **35** (2002), 6670.
- [31] G. Ronca and G. Allegra, *J. Chem. Phys.*, **63** (1975), 4990.
- [32] P. J. Flory, *Proc. R. Soc. London, A*, **351** (1976), 351.
- [33] P. J. Flory, *Polymer*, **20** (1979), 1317.
- [34] P. J. Flory and B. Erman, *Macromolecules*, **15** (1982), 800.
- [35] R. Oeser, B. Ewen, D. Richter, and B. Farago, *Phys. Rev. Lett.*, **60** (1988), 1041.
- [36] B. Ewen and D. Richter, in *Elastomeric Polymer Networks*, edited by J. E. Mark and B. Erman (Prentice Hall, Englewood Cliffs, NJ, 1992), p. 220.
- [37] B. Erman and L. Monnerie, *Macromolecules*, **22** (1989), 3342.
- [38] A. Kloczkowski, J. E. Mark, and B. Erman, *Macromolecules*, **28** (1995), 5089.
- [39] A. Kloczkowski, J. E. Mark, and B. Erman, *Comput. Polym. Sci.*, **5** (1995), 37.
- [40] T. A. Vilgis, *Prog. Coll. Polym. Sci.*, **75** (1987), 4.
- [41] T. A. Vilgis, *Prog. Coll. Polym. Sci.*, **75** (1987), 243.
- [42] R. C. Ball, M. Doi, and S. F. Edwards, *Polymer*, **22** (1981), 1010.
- [43] R. J. Gaylord, *Polym. Bull.*, **8** (1982), 325.
- [44] H.-G. Kilian, H. F. Enderle, and K. Unseld, *Coll. Polym. Sci.*, **264** (1986), 866.
- [45] J. E. Mark and J. G. Curro, *J. Chem. Phys.*, **79** (1983), 5705.
- [46] J. E. Mark and J. G. Curro, *J. Chem. Phys.*, **80** (1984), 4521.
- [47] J. E. Mark and J. G. Curro, *J. Chem. Phys.*, **80** (1984), 5262.
- [48] J. E. Mark and J. G. Curro, *J. Polym. Sci.: Polym. Phys. Ed.*, **23** (1985), 2629.

- [49] H. Finkelmann, in *Liquid Crystallinity in Polymers*, edited by A. Ciferri (VCH Publishers, New York, 1991), p. 315.
- [50] R. Zentel and M. Brehmer, *CHEMTECH*, **25**(5) (1995), 41.
- [51] P. J. Flory, *Macromolecules*, **12** (1979), 119.
- [52] L. Bokobza, F. Clément, L. Monnerie, and P. Lapersonne, in *The Wiley Polymer Networks Group Review Series*, Vol. 1 (John Wiley & Sons Ltd, New York, 1998), p. 321.
- [53] L. Bokobza and N. Nugay, *J. Appl. Polym. Sci.*, **81** (2001), 215.
- [54] I. Noda, A. E. Dowrey, and C. Marcott, in *Fourier Transform Infrared Characterization of Polymers*, edited by H. Ishida (Plenum Press, New York, 1987), p. 33.
- [55] M. Sinha, Ph.D. Thesis in Physics, The University of Cincinnati, Cincinnati (2000).
- [56] M. Sinha, J. E. Mark, H. E. Jackson, and D. Walton, *J. Chem. Phys.*, **117** (2002), 2968.
- [57] M. Sinha, B. Erman, J. E. Mark, T. H. Ridgway, and H. E. Jackson, *Macromolecules* **36** (2003), 6127.
- [58] J. S. Higgins and H. Benoit, *Neutron Scattering from Polymers* (Clarendon Press, Oxford, 1994).
- [59] G. D. Wignall, in *Physical Properties of Polymers Handbook*, edited by J. E. Mark (Springer-Verlag, New York, Inc., New York, 1996), p. 299.
- [60] R.-J. Roe, *Methods of X-Ray and Neutron Scattering in Polymer Science* (Oxford University Press, Oxford, 2000).
- [61] D. W. Schaefer, J. E. Mark, D. W. McCarthy, L. Jian, C.-C. Sun, and B. Farago, in *Polymer-Based Molecular Composites*, edited by D. W. Schaefer and J. E. Mark (Materials Research Society, Pittsburgh, 1990), p. 57.
- [62] A. N. Gent and P. Marteny, *J. Appl. Phys.*, **53** (1982), 6069.
- [63] G. D. Patterson, *J. Polym. Sci.: Polym. Phys. Ed.*, **35** (1977), 455.
- [64] M. Sinha, J. E. Mark, H. E. Jackson, and D. J. Walton, unpublished results.
- [65] J. E. Mark and G. Odian, *Polymer Chemistry Course Manual* (American Chemical Society, Washington, 1984).
- [66] J. E. Mark, *Rubber Chem. Technol.*, **48** (1975), 495.
- [67] J. E. Mark, *Acc. Chem. Res.*, **12** (1979), 49.
- [68] P. J. Flory, A. Ciferri, and C. A. J. Hoeve, *J. Polym. Sci.*, **45** (1960), 235.
- [69] A. Ciferri, C. A. J. Hoeve, and P. J. Flory, *J. Am. Chem. Soc.*, **83** (1961), 1015.
- [70] D. Goritz and F. H. Muller, *Kolloid Z. Z. Polym.*, **251** (1973), 679.
- [71] J. E. Mark, *Rubber Chem. Technol.*, **46** (1973), 593.
- [72] J. E. Mark, *Macromol. Rev.*, **11** (1976), 135.
- [73] Y. K. Godovsky, *Adv. Polym. Sci.*, **76** (1986), 31.
- [74] R. J. Farris and R. E. Lyon, *Polymer*, **28** (1987), 1127.
- [75] J. E. Mark, *Makromol. Chem., Suppl.*, **2** (1979), 87.
- [76] P. Rempp and J. E. Herz, *Angew. Makromol. Chem.*, **76/77** (1979), 373.
- [77] J. E. Mark, R. R. Rahalkar, and J. L. Sullivan, *J. Chem. Phys.*, **70** (1979), 1794.
- [78] M. A. Llorente and J. E. Mark, *Macromolecules*, **13** (1980), 681.
- [79] M. Gottlieb, C. W. Macosko, G. S. Benjamin, K. O. Meyers, and E. W. Merrill, *Macromolecules*, **14** (1981), 1039.
- [80] R. Stadler, M. M. Jacobi, and W. Gronski, *Makromol. Chem., Rapid Commun.*, **4** (1983), 129.
- [81] D. R. Miller and C. W. Macosko, *J. Polym. Sci.: Polym. Phys. Ed.*, **25** (1987), 2441.
- [82] J. A. Kornfield, H. W. Spiess, H. Nefzger, H. Hayen, and C. D. Eisenbach, *Macromolecules*, **24** (1991), 4787.

- [83] J. E. Mark, in *Silicon-Based Polymer Science. A Comprehensive Resource*, edited by J. M. Zeigler and F. W. G. Fearon (American Chemical Society, Washington, 1990), p. 47.
- [84] N. R. Langley, R. A. Dickie, C. Wong, J. D. Ferry, R. Chasset, and P. Thirion, *J. Polym. Sci. Pt A-2*, **6** (1968), 1371.
- [85] R. M. Johnson and J. E. Mark, *Macromolecules*, **5** (1972), 41.
- [86] J. E. Mark, A. Eisenberg, W. W. Graessley, L. Mandelkern, and J. L. Koenig, *Physical Properties of Polymers*, 1st edition (American Chemical Society, Washington, 1984).
- [87] S. Kohjiya, K. Urayama, and Y. Ikeda, *Kautschuk Gummi Kunststoffe*, **50** (1997), 868.
- [88] K. Urayama and S. Kohjiya, *Eur. Phys. J. B*, **2** (1997), 75.
- [89] J. Premachandra and J. E. Mark, *J. Macromol. Sci., Pure Appl. Chem.*, **39** (2002), 287.
- [90] J. Premachandra, C. Kumudinie, and J. E. Mark, *J. Macromol. Sci., Pure Appl. Chem.*, **39** (2002), 301.
- [91] C. U. Yu and J. E. Mark, *Macromolecules*, **7** (1974), 229.
- [92] P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, New York, 1979).
- [93] J. E. Mark and Z.-M. Zhang, *J. Polym. Sci.: Polym. Phys. Ed.*, **21** (1983), 1971.
- [94] L. C. DeBolt and J. E. Mark, *Macromolecules*, **20** (1987), 2369.
- [95] S. J. Clarson, J. E. Mark, and J. A. Semlyen, *Polym. Commun.*, **27** (1986), 244.
- [96] L. Garrido, J. E. Mark, S. J. Clarson, and J. A. Semlyen, *Polym. Commun.*, **26** (1985), 53.
- [97] W. W. Graessley and D. S. Pearson, *J. Chem. Phys.*, **66** (1977), 3363.
- [98] J. E. Mark and A. L. Andrady, *Rubber Chem. Technol.*, **54** (1981), 366.
- [99] M. A. Llorente, A. L. Andrady, and J. E. Mark, *Coll. Polym. Sci.*, **259** (1981), 1056.
- [100] Z.-M. Zhang and J. E. Mark, *J. Polym. Sci.: Polym. Phys. Ed.*, **20** (1982), 473.
- [101] J. E. Mark in *Elastomers and Rubber Elasticity*, edited by J. E. Mark and J. Lal (American Chemical Society, Washington, 1982), p. 349.
- [102] J. E. Mark, *Macromol. Symp.*, **191** (2003), 121.
- [103] L. Mullins, *J. Appl. Polym. Sci.*, **2** (1959), 257.
- [104] J. E. Mark, M. Kato, and J. H. Ko, *J. Polym. Sci., Part C*, **54** (1976), 217.
- [105] K. J. Smith, Jr, A. Greene, and A. Ciferri, *Kolloid Z. Z. Polym.*, **194** (1964), 49.
- [106] M. C. Morris, *J. Appl. Polym. Sci.*, **8** (1964), 545.
- [107] L. R. G. Treloar, *Rep. Prog. Phys.*, **36** (1973), 755.
- [108] B. L. Chan, D. J. Elliott, M. Holley, and J. F. Smith, *J. Polym. Sci., Pt C*, **48** (1974), 61.
- [109] A. L. Andrady, M. A. Llorente, and J. E. Mark, *J. Chem. Phys.*, **72** (1980), 2282.
- [110] W. O. S. Doherty, K. L. Lee, and L. R. G. Treloar, *Br. Polym. J.*, **15** (1980), 19.
- [111] J. Furukawa, Y. Onouchi, S. Inagaki, and H. Okamoto, *Polym. Bull.*, **6** (1981), 381.
- [112] T.-K. Su and J. E. Mark, *Macromolecules*, **10** (1977), 120.
- [113] D. S. Chiu, T.-K. Su, and J. E. Mark, *Macromolecules*, **10** (1977), 1110.
- [114] J. E. Mark, *Polym. Eng. Sci.*, **19** (1979), 409.
- [115] S. Hanna and A. H. Windle, *Polymer*, **29** (1988), 207.
- [116] T. M. Madkour and J. E. Mark, *Polymer*, **39** (1998), 6085.
- [117] J. E. Mark, *Makromol. Symp.*, **171** (2001), 1.
- [118] D. S. Chiu and J. E. Mark, *Coll. Polym. Sci.*, **225** (1977), 644.
- [119] M. A. Llorente, A. L. Andrady, and J. E. Mark, *J. Polym. Sci.: Polym. Phys. Ed.*, **19** (1981), 621.

- [120] P. J. Flory and W. C. Chang, *Macromolecules*, **9** (1976), 33.
- [121] M. Fixman and R. Alben, *J. Chem. Phys.*, **58** (1973), 1553.
- [122] B. Erman and J. E. Mark, *J. Chem. Phys.*, **89** (1988), 3314.
- [123] C.-C. Sun and J. E. Mark, *J. Polym. Sci.: Polym. Phys. Ed.*, **25** (1987), 2073.
- [124] B. Erman and J. E. Mark, *Macromolecules*, **31** (1998), 3099.
- [125] T. Madkour and J. E. Mark, *Polym. Bull.*, **31** (1993), 615.
- [126] T. Madkour and J. E. Mark, *J. Macromol. Sci., Macromol. Rep.*, **A31** (1994), 153.
- [127] G. T. Burns, unpublished results, Dow Corning Corporation (1995).
- [128] G. Sakrak, I. Bahar, and B. Erman, *Macromol. Theory Simul.*, **3** (1994), 151.
- [129] M.-Y. Tang, A. Letton, and J. E. Mark, *Coll. Polym. Sci.*, **262** (1984), 990.
- [130] A. L. Andraday, M. A. Llorente, M. A. Sharaf, R. R. Rahalkar, J. E. Mark, J. L. Sullivan, C. U. Yu, and J. R. Falender, *J. Appl. Polym. Sci.*, **26** (1981), 1829.
- [131] Y. Obata, S. Kawabata, and H. Kawai, *J. Polym. Sci.: pt A-2* **8** (1970), 903.
- [132] P. Xu and J. E. Mark, *J. Polym. Sci.: Polym. Phys. Ed.*, **29** (1991), 355.
- [133] P. Xu and J. E. Mark, *Polymer*, **33** (1992), 1843.
- [134] R. S. Rivlin and D. W. Saunders, *Phil. Trans. R. Soc. London, A*, **243** (1951), 251.
- [135] S. Wang and J. E. Mark, *J. Polym. Sci.: Polym. Phys. Ed.*, **30** (1992), 801.
- [136] L. C. Yanyo and F. N. Kelley, *Rubber Chem. Technol.*, **60** (1987), 78.
- [137] T. L. Smith, B. Haidar, and J. L. Hedrick, *Rubber Chem. Technol.*, **63** (1990), 256.
- [138] G. B. Shah, *Macromol. Chem. Phys.*, **197** (1996), 2201.
- [139] A. L. Andraday, M. A. Llorente, and J. E. Mark, *Polym. Bull.*, **26** (1991), 357.
- [140] J. Wen, J. E. Mark, and J. J. Fitzgerald, *J. Macromol. Sci., Macromol. Rep.*, **A31** (1994), 429.
- [141] Y. Kaneko, Y. Watanabe, T. Okamoto, Y. Iseda, and T. Matsunaga, *J. Appl. Polym. Sci.*, **25** (1980), 2467.
- [142] T. Tanaka, in *Polyelectrolyte Gels*, edited by R. S. Harland and R. K. Prud'homme (American Chemical Society, Washington, 1992), p. 1.
- [143] Y. Li and T. Tanaka, *Annu. Rev. Mater. Sci.*, **22** (1992), 243.
- [144] V. Y. Grinberg, A. S. Dubovik, D. V. Kuznetsov, N. V. Grinberg, A. Y. Grosberg, and T. Tanaka, *Macromolecules*, **33** (2000), 8685.
- [145] G. B. Kauffman, S. W. Mason, and R. B. Seymour, *J. Chem. Educ.*, **67** (1990), 198.
- [146] W. J. Moore, *Basic Physical Chemistry* (Prentice Hall, Englewood Cliffs, NJ, 1983).
- [147] P. W. Atkins, *Physical Chemistry*, 4th edition (Oxford University Press, Oxford, 1990).
- [148] F. T. Wall, *Chemical Thermodynamics*, 3rd edition (Freeman, San Francisco, 1974).
- [149] H. B. Callen, *Thermodynamics and an Introduction to Thermostatistics* (Wiley, New York, 2000).
- [150] N. W. Tschoegl, *Fundamentals of Equilibrium and Steady-State Thermodynamics* (Elsevier, Amsterdam, 2000).
- [151] L. Mandelkern, *Crystallization of Polymers* (McGraw-Hill, New York, 1964).
- [152] L. Mandelkern, *An Introduction to Macromolecules*, 2nd edition (Springer-Verlag, New York, 1983).
- [153] C. L. Strong, *Sci. Am.*, **224**(4) (1971), 118.
- [154] R. J. Farris, *Polym. Eng. Sci.*, **17** (1977), 737.
- [155] L. Mandelkern, *J. Chem. Educ.*, **55** (1978), 177.
- [156] R. J. Farris and R. E. Lyon, *J. Mater. Soc.*, **8** (1984), 239.
- [157] R. J. Farris, R. E. Lyon, D. X. Wang, and W. J. MacKnight, *J. Appl. Polym. Sci.*, **29** (1984), 2857.
- [158] R. Ross and P. Bornstein, *Sci. Am.*, **224** (1971), 44.
- [159] C. A. J. Hoeve and P. J. Flory, *Biopolymers*, **13** (1974), 677.

- [160] L. B. Sandberg, W. R. Gray, and C. Franzblau (eds.), *Elastin and Elastic Tissue* (Plenum, New York, 1977).
- [161] A. L. Andrady and J. E. Mark, *Biopolymers*, **19** (1980), 849.
- [162] J. M. Gosline, in *The Mechanical Properties of Biological Materials*, edited by J. F. V. Vincent and J. D. Currey (Cambridge University Press, Cambridge, 1980), p. 331.
- [163] M. Jensen and T. Weis-Fogh, *Phil. Trans. R. Soc. London, B*, **245** (1962), 137.
- [164] B. B. Boonstra, *Polymer*, **20** (1979), 691.
- [165] Z. Rigbi, *Adv. Polym. Sci.*, **36** (1980), 21.
- [166] E. L. Warrick, O. R. Pierce, K. E. Polmanteer, and J. C. Saam, *Rubber Chem. Technol.*, **52** (1979), 437.
- [167] S. Wolff and J.-B. Donnet, *Rubber Chem. Technol.*, **63** (1990), 32.
- [168] J. E. Mark, *CHEMTECH*, **19** (1989), 230.
- [169] J. E. Mark and D. W. Schaefer, in *Polymer-Based Molecular Composites*, edited by D. W. Schaefer and J. E. Mark (Materials Research Society, Pittsburgh, 1990), p. 51.
- [170] B. K. Coltrain, C. Sanchez, D. W. Schaefer, and G. L. Wilkes (eds.), *Better Ceramics Through Chemistry VII: Organic/Inorganic Hybrid Materials* (Materials Research Society, Pittsburgh, 1996).
- [171] C. J. Brinker, E. P. Giannelis, R. M. Laine, and C. Sanchez (eds.), *Better Ceramics Through Chemistry VIII: Hybrid Materials* (Materials Research Society, Warrendale, PA, 1998).
- [172] J. E. Mark, Y.-P. Ning, C.-Y. Jiang, M.-Y. Tang, and W. C. Roth, *Polymer*, **26** (1985), 2069.
- [173] J. E. Mark and Y.-P. Ning, *Polym. Bull.*, **12** (1984), 413.
- [174] H. Schmidt, in *Inorganic and Organometallic Polymers. Macromolecules Containing Silicon, Phosphorous, and Other Inorganic Elements*, edited by M. Zeldin, K. J. Wynne, and H. R. Allcock (American Chemical Society, Washington, 1988), p. 333.
- [175] H. Schmidt and H. Wolter, *J. Non-Cryst. Solids*, **121** (1990), 428.
- [176] R. Nass, E. Arpac, W. Glaubitt, and H. Schmidt, *J. Non-Cryst. Solids*, **121** (1990), 370.
- [177] B. Wang and G. L. Wilkes, *J. Polym. Sci.: Polym. Chem. Ed.*, **29** (1991), 905.
- [178] G. L. Wilkes, H.-H. Huang, and R. H. Glaser, in *Silicon-Based Polymer Science*, edited by J. M. Zeigler and F. W. G. Fearon (American Chemical Society, Washington, 1990), p. 207.
- [179] A. B. Brennan, B. Wang, D. E. Rodrigues, and G. L. Wilkes, *J. Inorg. Organomet. Polym.*, **1** (1991), 167.
- [180] C. A. Sobon, H. K. Bowen, A. Broad, and P. D. Calvert, *J. Mater. Sci. Lett.*, **6** (1987), 901.
- [181] P. Calvert and S. Mann, *J. Mater. Sci.*, **23** (1988), 3801.
- [182] A. Azoz, P. D. Calvert, M. Kadim, A. J. McCaffery, and K. R. Seddon, *Nature*, **344** (1990), 49.
- [183] W. F. Doyle and D. R. Uhlmann, in *Ultrastructure Processing of Advanced Ceramics*, edited by J. D. Mackenzie and D. R. Ulrich (Wiley-Interscience, New York, 1988), p. 795.
- [184] W. F. Doyle, B. D. Fabes, J. C. Root, K. D. Simmons, Y. M. Chiang, and D. R. Uhlmann, in *Ultrastructure Processing of Advanced Ceramics*, edited by J. D. Mackenzie and D. R. Ulrich (Wiley-Interscience, New York, 1988), p. 953.
- [185] J. M. Boulton, H. H. Fox, G. F. Neilson, and D. R. Uhlmann, in *Better Ceramics Through Chemistry IV*, edited by B. J. J. Zelinski, C. J. Brinker, D. E. Clark, and D. R. Ulrich (Materials Research Society, Pittsburgh, 1990), p. 773.

- [186] J. E. Mark and C.-C. Sun, *Polym. Bull.*, **18** (1987), 259.
- [187] Y. P. Ning, M. X. Zhao, and J. E. Mark, in *Frontiers of Polymer Research*, edited by P. N. Prasad and J. K. Nigam (Plenum, New York, 1991), p. 479.
- [188] Y. P. Ning, M. X. Zhao, and J. E. Mark, in *Chemical Processing of Advanced Materials*, edited by L. L. Hench and J. K. West (Wiley, New York, 1992), p. 745.
- [189] S. Wang and J. E. Mark, *Macromolecules*, **23** (1990), 4288.
- [190] S. Wang, P. Xu, and J. E. Mark, *Macromolecules*, **24** (1991), 6037.
- [191] A. Okada, M. Kawasumi, A. Usuki, Y. Kojima, T. Kurauchi, and O. Kamigaito, in *Polymer-Based Molecular Composites*, edited by D. W. Schaefer and J. E. Mark (Materials Research Society, Pittsburgh, 1990), p. 45.
- [192] T. J. Pinnavaia, T. Lan, Z. Wang, H. Shi, and P. D. Kaviratna, in *Nanotechnology. Molecularly Designed Materials*, edited by G.-M. Chow and K. E. Gonsalves (American Chemical Society, Washington, 1996), p. 250.
- [193] E. P. Giannelis, in *Biomimetic Materials Chemistry*, edited by S. Mann (VCH Publishers, New York, 1996), p. 337.
- [194] R. A. Vaia and E. P. Giannelis, *Polymer*, **42** (2001), 1281.
- [195] M. A. Sharaf, A. Kloczkowski, and J. E. Mark, *Polymer*, **12** (2002), 643.
- [196] E. P. Giannelis, R. Krishnamoorti, and E. Manias, *Adv. Polym. Sci.*, **138** (1999), 107.
- [197] R. A. Vaia and E. P. Giannelis, *Mater. Res. Soc. Bull.*, **26** (2001), 394.
- [198] T. J. Pinnavaia and G. Beall (eds.), *Polymer-Clay Nanocomposites* (Wiley, New York, 2001).
- [199] V. T. Vu, J. E. Mark, L. H. Pham, and M. Engelhardt, *J. Appl. Polym. Sci.*, **82** (2001), 1391.
- [200] W. Zhou, J. E. Mark, M. R. Unroe, and F. E. Arnold, *J. Macromol. Sci. Pure Appl. Chem.*, **A38** (2001), 1.
- [201] J. D. Lichtenhan, J. Schwab, and W. A. Reinert Sr, *Chem. Innov.*, **31** (2001), 3.
- [202] R. M. Laine, J. Choi, and I. Lee, *Adv. Mater.*, **13** (2001), 800.
- [203] D. A. Loy, C. R. Baugher, D. A. Schnieder, A. Sanchez, and F. Gonzalez, *Polym. Preprints*, **42**(1) (2001), 180.
- [204] K. J. Shea and D. A. Loy, *Mater. Res. Soc. Bull.*, **26** (2001), 368.
- [205] T. S. Haddad, A. Lee, and S. H. Phillips, *Polym. Preprints*, **42** (2001), 88.
- [206] H. Nakamura and Y. Matsui, *J. Am. Chem. Soc.*, **117** (1995), 2651.
- [207] H. L. Frisch and J. E. Mark, *Chem. Mater.*, **8** (1996), 1735.
- [208] S. J. Tans, M. H. Devoret, H. Dai, A. Thess, R. E. Smalley, L. J. Geerligs, and C. Dekker, *Nature*, **386** (1997), 474.
- [209] B. T. N. Vu, J. E. Mark, and D. W. Schaefer, *Preprints, American Chemical Society Division of Polymeric Materials: Science and Engineering*, **83** (2000), 411.
- [210] B. T. N. Vu, M.S. degree in Chemistry, The University of Cincinnati (Cincinnati, 2001).
- [211] D. W. Schaefer, B. T. N. Vu, and J. E. Mark, *Rubber Chem. Technol.*, **75** (2002), 795.
- [212] J. E. Mark, *J. Comput.-Aided Mater. Design*, **3** (1996), 311.
- [213] Q. W. Yuan, A. Kloczkowski, J. E. Mark, and M. A. Sharaf, *J. Polym. Sci.: Polym. Phys. Ed.*, **34** (1996), 1647.
- [214] J. E. Mark, in *2001 International Conference on Computational Nanoscience*, edited by M. Laudon and B. Romanowicz (Computational Publications, Boston, Hilton Head Island, South Carolina, 2001), p. 53.
- [215] J. E. Mark, *Molec. Cryst. Liq. Cryst.*, **374** (2001), 29.
- [216] M. A. Sharaf, A. Kloczkowski, and J. E. Mark, *Comput. Polym. Sci.*, **4** (1994), 29.
- [217] H. B. Sunkara, J. M. Jethmalani, and W. T. Ford, in *Hybrid Organic-Inorganic Composites*, edited by J. E. Mark, C. Y.-C. Lee, and P. A. Bianconi (American Chemical Society, Washington, 1995), p. 181.

- [218] Z. Pu, J. E. Mark, J. M. Jethmalani, and W. T. Ford, *Chem. Mater.*, **9** (1997), 2442.
- [219] A. I. Nakatani, W. Chen, R. G. Schmidt, G. V. Gordon, and C. C. Han, *Polymer*, **42** (2001), 3713.
- [220] M. A. Sharaf, A. Kloczkowski, and J. E. Mark, *Comput. Theor. Polym. Sci.*, **11** (2001), 251.
- [221] J. M. Ottino, F. J. Muzzio, M. Tjahjadi, J. Franjione, S. C. Jana, and H. A. Kusch, *Science*, **257** (1992), 754.
- [222] T. Koyama and A. Steinbuchel (eds.), *Biopolymers, Volume 2: Polyisoprenoids* (Wiley-VCH, New York, 2001).
- [223] A. I. Isayev, S. H. Kim, and V. Y. Levin, *Rubber Chem. Technol.*, **70** (1997), 194.
- [224] S. E. Shim and A. I. Isayev, *Rubber Chem. Technol.*, **74** (2001), 303.
- [225] J. E. Mark and C. U. Yu, *J. Polym. Sci.: Polym. Phys. Ed.*, **15** (1977), 371.
- [226] A. L. Andrady and J. E. Mark, *Eur. Polym. J.*, **17** (1981), 323.
- [227] J. E. Mark, H. R. Allcock, and R. West, *Inorganic Polymers* (Prentice Hall, Englewood Cliffs, New Jersey, 1992).
- [228] S. L. Aggarwal, *Polymer*, **17** (1976), 938.
- [229] H. H. Brintzinger, D. Fischer, R. Mulhaupt, B. Reiger, and R. M. Waymouth, *Angew. Chem. Ed. Engl.*, **34** (1995), 1143.
- [230] S. Mansel, E. Perez, R. Benavente, J. M. Perena, A. Bello, W. Roll, R. Kirsten, S. Beck, and H.-H. Brintzinger, *Macromol. Chem. Phys.*, **200** (1999), 1292.
- [231] S. Lieber and H.-H. Brintzinger, *Macromolecules*, **33** (2000), 9192.
- [232] G. Heinrich and T. A. Vilgis, *Macromolecules*, **26** (1993), 1109.
- [233] T. A. Witten, M. Rubinstein, and R. H. Colby, *J. Physique II*, **3** (1993), 367.
- [234] M. Kluppel, R. H. Schuster, and G. Heinrich, *Rubber Chem. Technol.*, **70** (1997), 243.
- [235] A. Janshoff, M. Neitzert, Y. Oberdorfer, and H. Fuchs, *Angew. Chem. Int. Ed.*, **39** (2000), 3213.
- [236] T. Hugel and M. Seitz, *Makromol. Rapid Commun.*, **22** (2001), 989.

Further reading

- P. J. Flory, *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, New York, 1953).
- F. T. Wall, *Chemical Thermodynamics*, 3rd edition (Freeman, San Francisco, 1974).
- L. R. G. Treloar, *The Physics of Rubber Elasticity*, 3rd edition (Clarendon Press, Oxford, 1975).
- J. A. Brydson, *Rubber Chemistry* (Applied Science Publishers, London, 1978).
- L. K. Nash, *J. Chem. Educ.*, **56** (1979), 363.
- J. E. Mark, *J. Chem. Educ.*, **58** (1981), 898.
- B. E. Eichinger, *Ann. Rev. Phys. Chem.*, **34** (1983), 359.
- S. S. Labana and R. A. Dickie (eds.), *Characterization of Highly Cross-Linked Polymers* (American Chemical Society, Washington, 1984).
- J. Lal and J. E. Mark (eds.), *Advances in Elastomers and Rubber Elasticity* (Plenum Press, New York, 1986).
- M. Morton (ed.), *Rubber Technology*, 3rd ed. (Van Nostrand Reinhold, New York, 1987).
- S. F. Edwards and T. A. Vilgis, *Rep. Prog. Phys.*, **51** (1988), 243.
- J. E. Mark and B. Erman, *Rubberlike Elasticity. A Molecular Primer* (Wiley-Interscience, New York, 1988).
- G. Heinrich, E. Straube, and G. Helmis, *Adv. Polym. Sci.*, **85** (1988), 33.

- B. Erman and J. E. Mark, *Ann. Rev. Phys. Chem.*, **40** (1989), 351.
- A. Baumgartner and C. E. Picot (eds.), *Molecular Basis of Polymer Networks* (Springer, Berlin, 1989).
- W. Burchard and S. B. Ross-Murphy (eds.), *Physical Networks. Polymers and Gels* (Elsevier, London, 1990).
- J. E. Mark and B. Erman (eds.), *Elastomeric Polymer Networks* (Prentice Hall, Englewood Cliffs, New Jersey, 1992).
- J. E. Mark, *Comput. Polym. Sci.*, **2** (1992), 135.
- A. N. Gent (ed.), *Engineering with Rubber. How to Design Rubber Components* (Hanser Publishers, New York, 1992).
- S. M. Aharoni (ed.), *Synthesis, Characterization, and Theory of Polymeric Networks and Gels* (Plenum Press, New York, 1992).
- J. E. Mark, A. Eisenberg, W. W. Graessley, L. Mandelkern, E. T. Samulski, J. L. Koenig, and G. D. Wignall, *Physical Properties of Polymers*, 2nd edition (American Chemical Society, Washington, 1993).
- R. H. Boyd and P. J. Phillips, *The Science of Polymer Molecules* (Cambridge University Press, Cambridge, 1993).
- J. E. Mark, B. Erman, and F. R. Eirich (eds.), *Science and Technology of Rubber*, 2nd edition (Academic, New York, 1994).
- J. E. Mark (ed.), *Physical Properties of Polymers Handbook* (Springer-Verlag, New York, 1996).
- B. Erman and J. E. Mark, *Structures and Properties of Rubberlike Networks* (Oxford University Press, New York, 1997).
- J. E. Mark and B. Erman, in *Polymer Networks*, edited by R. F. T. Stepto (Blackie Academic, Glasgow, 1998).
- J. E. Mark (ed.), *Polymer Data Handbook* (Oxford University Press, New York, 1999).
- J. E. Mark, in *Molecular Catenanes, Rotaxanes and Knots*, edited by J.-P. Sauvage and C. Dietrich-Buchecker (Wiley-VCH, Weinheim, 1999), p. 223.
- J. E. Mark, *Rubber Chem. Technol.*, **72** (1999), 465.
- J. E. Mark, in *Silicones and Silicone-Modified Materials*, edited by S. J. Clarson, J. J. Fitzgerald, M. J. Owen, and S. D. Smith (American Chemical Society, Washington, 2000), p. 1.
- H. B. Callen, *Thermodynamics and an Introduction to Thermostatistics* (Wiley, New York, 2000).
- J. E. Mark, in *Applied Polymer Science – 21st Century*, edited by C. D. Craver and C. E. Carraher Jr (American Chemical Society, Washington, 2000), p. 209.
- J. E. Mark and B. Erman, in *Performance of Plastics*, edited by W. Brostow (Hanser, Cincinnati, 2001), p. 401.
- J. P. Queslel and J. E. Mark, in *Encyclopedia of Polymer Science and Technology* (Wiley-Interscience, New York, 2001), p. 365.
- J. E. Mark, *Makromol. Symp.*, **171** (2001), 1.
- J. P. Queslel and J. E. Mark, in *Encyclopedia of Physical Science and Technology*, 3rd edition, edited by R. A. Meyers (Academic Press, New York, 2002), p. 813.
- J. E. Mark, *J. Chem. Educ.*, **79** (2002), 1437.
- J. E. Mark, *J. Phys. Chem. B*, **107** (2003), 903.
- J. E. Mark, *Macromol. Symp.*, **191** (2003), 121.
- J. E. Mark, *Macromol. Symp.* **201** (2003), 77.

2

The glass transition and the glassy state

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2.1 Introduction

The glass transition in noncrystalline polymers under ordinary experimental conditions occurs on cooling when the characteristic time of molecular motions responsible for structural rearrangements becomes longer than the timescale of the experiment. As a result, structural relaxation toward equilibrium is arrested below some temperature, T_g , and the polymer is in the glassy state. The molecular motions responsible for structural relaxation in polymers involve only a small number of repeat units of each chain, and it is appropriate to refer to them henceforth as local segmental motions. In polymers, molecular motions involving more repeat units of each chain are possible and they contribute to viscoelastic properties over broad ranges. The molecular motions of longer range have characteristic times longer than the local segmental motions, and therefore a necessary condition for the former to contribute to observable viscoelastic properties of the polymer is mobility of the latter, which means that the temperature has to be higher than the glass-transition temperature, T_g . Thus, the glass transition is perhaps the most important factor that determines at any temperature and pressure the viscoelastic properties and applications of noncrystalline polymers. For example, if T_g is much higher than the temperature of application, the polymer is a hard glass and may be suitable for applications as engineering plastics. If T_g is sufficiently lower, the polymer is rubbery and may be used in the rubber industry. Many polymers have no crystalline solid state because there are stereochemical variations along their molecular chain-like backbones. This lack of long-range regularity in the molecular structure precludes an assembly with the long-range order which is the essence of the crystalline state. In other words, irregular molecules cannot crystallize and they become glassy on cooling. On the other hand, even some polymers with stereoregular chains such as polycarbonate do not crystallize readily due to exceedingly low rates of nucleation.

Glass-transition phenomena are found also in the disordered regions of partially crystalline polymers.

In addition to T_g , the temperature dependence of the characteristic time of local segmental motions at temperatures above T_g is important in the consideration of the other viscoelastic mechanisms of longer length-scales (see Chapter 3, by W. W. Graessley). The basic importance of the glass transition in determining the mobility of various viscoelastic mechanisms is generally recognized. Except for this recognition, authors of most treatises on viscoelasticity of polymers [1–4] have considered the glass transition and the dynamics of local segmental motions as a subject of special interest that does not need much further consideration. Sometimes effort is made to rationalize the physical origin of the glass transition and the temperature dependence of the structural (local segmental) relaxation time [1, 3, 4]. The crucial assumption that is often made is that the temperature dependences of the characteristic times of all other viscoelastic mechanisms are the same as that of the local segmental motions at all temperatures. From this point onward, local segmental motions drop out from further discussions. In a treatise on viscoelasticity [5], the glass transition is not mentioned at all. On the other hand, most reviews on the glass transition in polymers [6–9] are focused on the subject itself without making serious connection with the viscoelastic properties at longer times. These treatises neither dispelled nor endorsed the common belief that the temperature dependence of the local segmental relaxation time at all temperatures is shared by all viscoelastic mechanisms of longer length-scales. Is this common belief true? If it were true, the chapter on the glass transition and the glassy state would be written in the same fashion as others. The subject would be treated as an area of special interest, having no important impact on the other viscoelastic properties of the polymer originating from motions of longer length-scales, except for the location of T_g . However, this is not true. At any temperature, the viscoelastic response of a polymer from the glassy state to the terminal flow extends over an enormous time or frequency range and cannot be measured by any experimental technique that has a limited time/frequency measurement range. In practice, one makes measurements by the same technique at a number of temperatures in order to capture the viscoelastic response from all the viscoelastic mechanisms. The complete viscoelastic response at some reference temperature is then acquired by shifting the isothermal response curves horizontally along the time/frequency axis to superpose them and form a master curve. Sometimes minor vertical shifts are applied to the data. Successful superposition of data is often used as justification of the assumption that all viscoelastic mechanisms are governed by the same friction coefficient, and the shifts required to superpose data taken at various temperatures give the temperature dependence of the common friction coefficient shared by all viscoelastic mechanisms [1, 2]. This highly touted procedure of time–temperature superposition is the most

effective way to show the complete isothermal viscoelastic dispersion of a polymer and to obtain the supposedly common temperature dependence over an extensive temperature range. If in fact polymers were such, then we can understand why most scientists and engineers, who are interested mainly in the viscoelastic response from motions of longer length-scales, consider glass-transition phenomena as a subject of peripheral interest, because the only thing they need to know about the glass transition is the value of T_g . However, experimental data obtained by techniques that can directly measure different viscoelastic mechanisms at the same temperature range show that there is a failure of time-temperature superposition. These breakdowns of thermorheological simplicity are caused by the shift factors of various viscoelastic mechanisms having different temperature dependences. Their differences increase with decreasing temperature, especially on approaching T_g , giving rise to anomalous viscoelastic properties in high and low molecular weight polymers [10, 11]. All these deviations from the conventional wisdom are difficult to understand, and this difficulty explains why they were not discussed upfront or not even mentioned in most textbooks and monographs on viscoelastic properties of polymers. This chapter addresses the breakdown of thermorheological simplicity and the anomalous viscoelastic properties, taking them seriously. The subject is appropriate in a chapter on the glass transition because the cause of the effects originates from the local segmental relaxation. Such an impact of the glass transition on viscoelasticity of polymers is not mentioned in treatises on the glass transition or viscoelasticity of polymers, except in a few cases [1, 12].

Although the focus of this chapter is on synthetic polymeric materials, the glass transition occurs in many other types of materials. Examples include (1) natural polymers such as selenium, (2) networks such as SiO_2 , GeO_2 , B_2O_3 , and P_2O_3 , and networks modified by introduction of alkali oxides or alkali earth oxides into these networks, (3) the chalcogenides such as As_2S_3 and multicomponent systems containing S, Se, Te, As, and Ge, (4) hydrogen-bonded materials such as the primary alcohols, ethanol, glycerol, sorbitol, and maltitol, and secondary alcohols, (5) salts such as $0.4\text{Ca}(\text{NO}_3)_2 \cdot 0.6\text{KNO}_3$, ZnCl_2 , and BeF_2 , (6) amorphous metals such as $\text{Pd}_{80}\text{Si}_{20}$ and $\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$, and (7) the vast number of small-molecular or low molecular weight organic materials having carbon or modified carbon rings in the structure, such as 1,2-diphenylbenzene, or without, such as 3-bromopentane. Naturally, these chemically widely different glass-forming materials have T_g varying over a huge range of temperatures. Some properties of these materials in the glassy state, such as the mechanical modulus, can differ greatly. Nevertheless, the glass-transition phenomena in synthetic polymeric materials, as we shall discuss, are very similar to those in these other materials. The indication from the phenomena observed is that the physics of the glass transition is to a large extent common to all materials. Those who are interested in a more fundamental understanding of

the glass transition of polymers should not lose sight of the wealth of experimental data, phenomenology, conceptual understanding, models, and theories developed in the study of the other types of glass-formers. This chapter utilizes these resources to enhance our understanding of the glass-transition properties of polymers. On the other hand, polymeric glass-formers are unique in having additional properties contributed by viscoelastic mechanisms of longer length-scales, the properties of which can be used to check whether any proposed theory of the glass-transition is consistent.

New techniques, including neutron scattering [13], nuclear magnetic resonance [14], dynamic light scattering [15], and computer experiments including Monte Carlo and molecular-dynamics simulations [16–22], have been introduced in recent years in order to study glass transitions of polymeric and nonpolymeric materials. These techniques widen the frequency range that can be accessed in the study of the structural relaxation from the low frequencies of conventional mechanical and dielectric measurements to molecular-vibration frequencies. The advantage of these new techniques goes beyond the extension of the spectral range. Neutron-scattering measurements and computer simulations can probe dynamics over length-scales ranging from within the size of a repeat unit to the sizes of entire polymer chains. In neutron scattering, the dynamics at specific sites is accessed by designed substitution of some hydrogen atoms in the repeat units by deuterium in synthesis. Various new techniques in nuclear magnetic resonance to probe the dynamics of molecular motion that have been developed in the last two decades increase the spectral range, but also yield site-specific information, again by the replacement of hydrogen by deuterium. The microscopic information available from experimental data obtained using these techniques enriches our understanding of the molecular dynamics in the glass transition and will be discussed in this chapter.

This chapter is intended as a short introduction to the glass transition and the glassy state of polymers. It tells the reader what problems are reasonably well understood as well as outlining many challenging problems that remain to be solved. Though studies of the glass transition have a long history, it is still a vibrant area of basic research. In keeping the length of the chapter within a reasonable limit, some topics have had to be omitted and many relevant works in the literature could not be cited. My apologies to many colleagues whose works I am not able to cite.

2.2 The phenomenology of the glass transition

2.2.1 Structural relaxation and the glass-transition temperature

The equilibrium liquid state is specified not only by the temperature, T , pressure, P , etc., but also by its average “structure.” We have a fairly accurate picture of

the average structure of liquids, including polymers, from the works using various scattering techniques (see Chapter 7, by G. D. Wignall) and spectroscopic methods (see Chapter 6, by J. L. Koenig). Associated with the average local structure of an equilibrium liquid are experimentally measurable properties such as enthalpy H , volume V , and refractive index. Although the average structure of an equilibrium liquid does not change with time, molecules are mobile and the local structure is continually rearranging in time. This continual structural rearrangement gives rise to the linear response to small mechanical and electrical perturbations, and the concomitant fluctuations cause the scattering of light and neutrons as well as spin relaxation in nuclear magnetic resonance. Experimental methods based on these effects allow us to gain information on the molecular motion. The molecular motions of an equilibrium liquid at any given T and P are difficult to describe, because of the crowding of, and mutual interactions between, the molecules.

Following a change in T or P , structural relaxation effects the change in the average local structure necessary to maintain equilibrium. The rate of structural relaxation decreases with decreasing temperature or increasing pressure. At a sufficiently low temperature/high pressure this rate becomes so small that the structure cannot attain equilibrium on the timescale of the experiment. At and below this temperature, generally referred to as the glass-transition temperature T_g , the local structure is frozen and the material has the mechanical and thermodynamic properties of an amorphous solid, which is referred to as the glassy state.

2.2.2 The dependence of T_g on the cooling rate q

The transition of the structure from the equilibrium liquid to the glassy state with a change in temperature is observed experimentally from the changes in enthalpy H and volume V . For example, at a fixed rate of cooling a liquid, the liquid's H and V become increasingly greater than their equilibrium values at each lower temperature. The departure of H , V , etc. from equilibrium liquid values during cooling signals the onset of the glass-transition region. Below some temperature, the structural relaxation is completely arrested on the experimental timescale, and the glassy state is reached. This transition is shown in Fig. 2.1 by the dilatometric measurements by Greiner and Schwarzl [23] of the specific volume, v , of high molecular weight polystyrene (PS) on cooling from the equilibrium liquid down to the glassy state at various rates of cooling. For any cooling rate, the glassy state is characterized by the glass line, i.e. the linear dependence of v on T found at lower temperatures. The transition region clearly depends on the rate of cooling, q , over the range of $3\frac{1}{2}$ decades. A glass-transition temperature, T_g , determined from the intersection of the equilibrium line with the glass line extrapolated to higher temperatures, varies from 96 °C at the highest q of 2.0 °C min⁻¹ down to 86 °C at

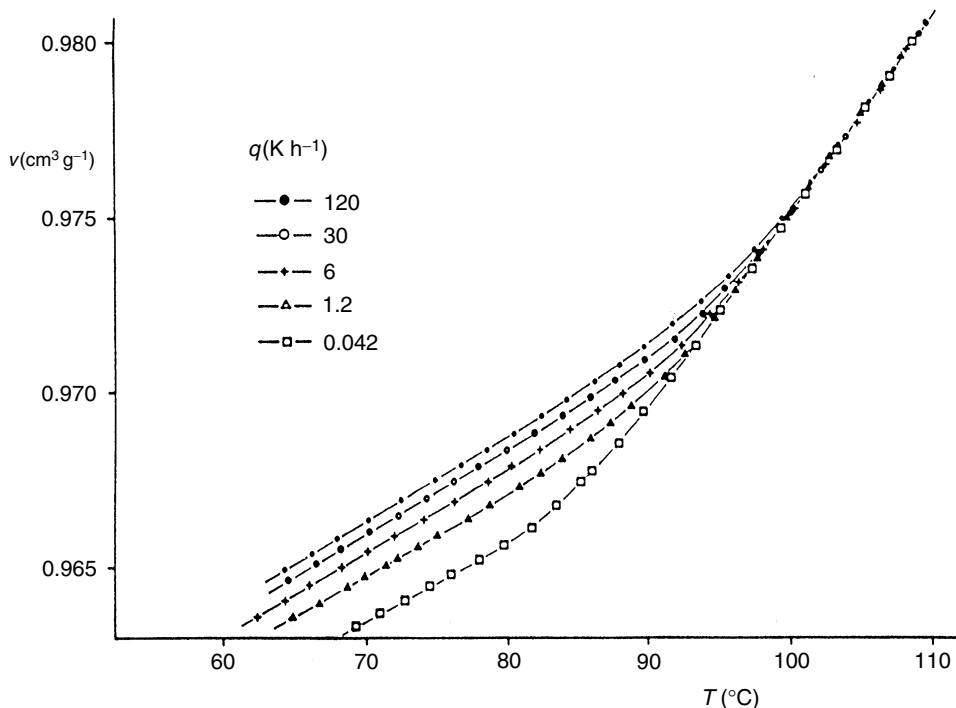


Fig. 2.1. Volume–temperature curves of PS extending through T_g under various rates of cooling as indicated. From Greiner and Schwarzl by permission [23].

the lowest q of $7 \times 10^{-4} \text{ }^\circ\text{C min}^{-1}$. This procedure of obtaining T_g s is explicitly demonstrated in Fig. 2.2 with specific volume–temperature cooling curves for a fully cured epoxy resin [24], which is a molecular network that precludes flow and hence a viscoelastic solid. This is in contrast to the polystyrene in Fig. 2.1, which is a viscoelastic liquid. The rate dependence of T_g on q shown in Fig. 2.2 is similar to those for polystyrene and other polymers.

Illustrative curves of the thermal expansion coefficient, $\alpha = v^{-1}(\partial v / \partial T)_P$, calculated from the curves of Fig. 2.1, are shown in Fig. 2.3. A slightly lower glassy α is found with decreasing q . The transition region, defined here by the temperature span between the limiting equilibrium and glassy lines, is found to diminish significantly with decreasing q . This observation is in accord with those reported for several inorganic glasses [25].

The definition and determination of T_g given above in terms of cooling from an equilibrium state at any given q is only one among several other alternative methods to be described below. For workers on viscoelastic liquids who are not interested in the glassy solid state, the value of T_g obtained in this way for a standardized cooling rate is the most appropriate parameter for considering the temperature dependences

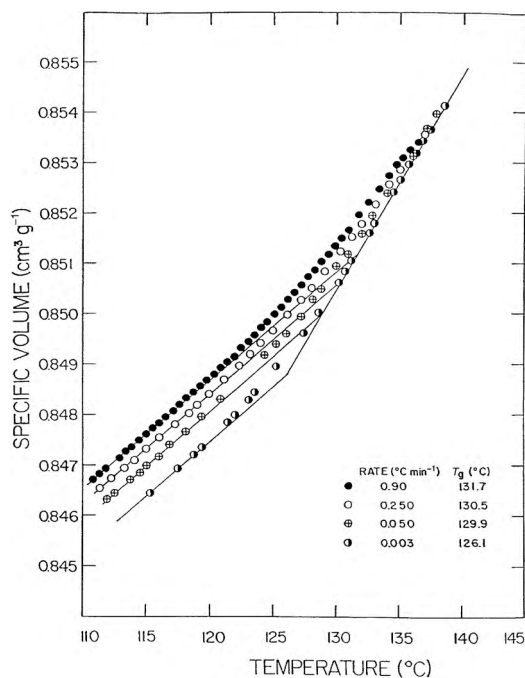


Fig. 2.2. The specific-volume-temperature cooling curves for the epoxy resin EPON 1001F/DDS fully cured at four different rates of cooling as indicated. The corresponding T_g s identified by the intersection point of the equilibrium and glass lines are listed.

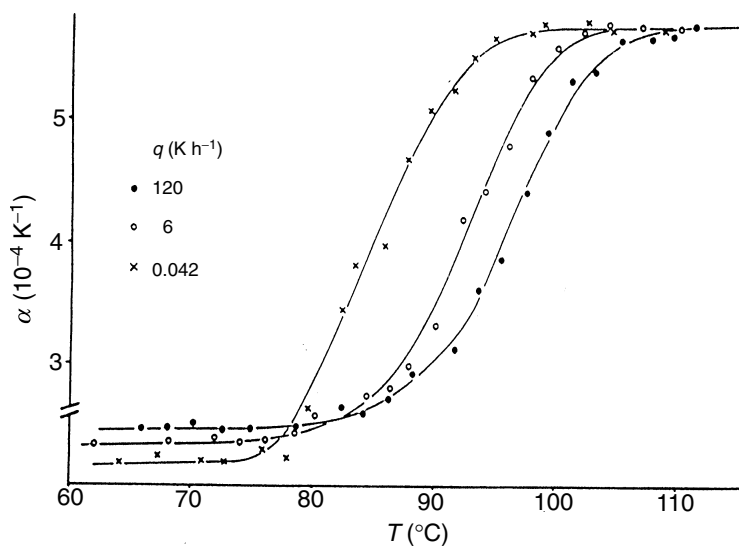


Fig. 2.3. Values of the coefficient of thermal expansion α calculated from the data of Fig. 2.1 for PS under various rates of cooling. From Greiner and Schwarzl by permission [23].

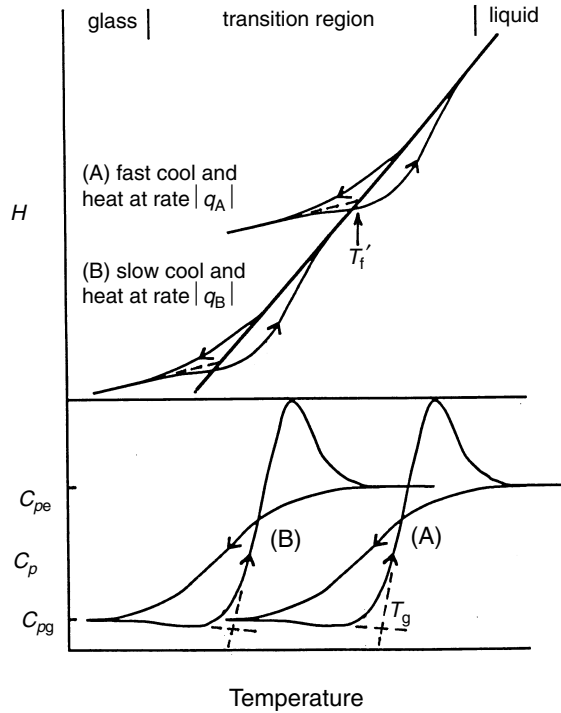


Fig. 2.4. Schematic plots of enthalpy H and heat capacity C_p versus temperature during cooling and reheating through the glass-transition region at two different rates. From Moynihan *et al.* [26] by permission.

of viscoelastic properties. Such determination of T_g is not restricted to specific-volume-temperature cooling measurements and T_g can be similarly obtained from enthalpy-temperature cooling curves. This is shown schematically in the upper part of Fig. 2.4 for fast cooling at rate q_A and slow cooling at rate q_B [26]. During cooling from the liquid, the slope of the H - T curve decreases monotonically in the transition region before the glassy line is reached. The two dashed lines are extrapolations of the two glassy lines to higher temperatures, and their intersections with the equilibrium line determine the T_g s. The T_g so determined at cooling rate q_A is denoted by T_f' in Fig. 2.4. The latter is also the fictive temperature of the glass state according to the definition of Tool [27]. Hence, along the glassy line in Fig. 2.4, the fictive temperature remains as T_f . Along the equilibrium line, the fictive temperature is the same as the temperature.

The specific heat, C_p , is related to H by the definition $C_p = (\partial H / \partial T)_p$. This is the quantity monitored by differential scanning calorimetry (DSC) or differential thermal analysis (DTA). The sigmoidal variation of C_p with temperature on cooling is shown in the lower part of Fig. 2.4 for the two cooling rates by the lines with

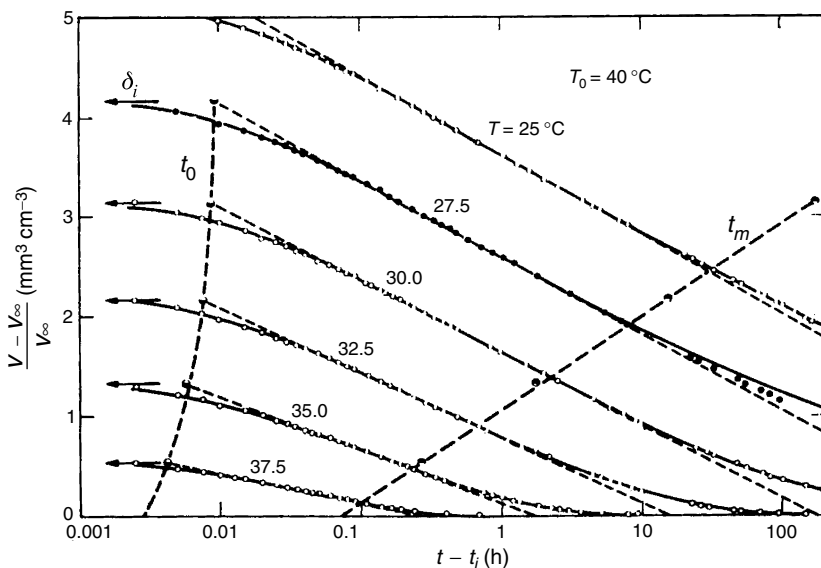


Fig. 2.5. Isothermal contraction of poly(vinyl acetate) glass after down-quenching from $T_0 = 40^\circ\text{C}$ to various temperatures as indicated. From Kovacs by permission [28].

arrows pointing downward, and is analogous to α in Fig. 2.3. We shall return to discuss the temperature dependences of H and C_p on reheating after cooling later.

2.2.3 Structural relaxation toward equilibrium (structural recovery)

Before describing the temperature dependences of H and C_p on reheating after cooling, which are also shown in Fig. 2.4, it is important to appreciate the inherently metastable or non-equilibrium nature of the glassy state, and its tendency to undergo structural relaxation toward equilibrium. This tendency is illustrated in Fig. 2.5 by the time evolution of the glassy structure of poly(vinyl acetate) after the temperature is changed from $T_0 = 40^\circ\text{C}$, near and above T_g , to various temperatures T below it by rapid cooling (a down-quench or down-jump). In Fig. 2.5, taken from the classic data of Kovacs [28], the evolution of the glassy structure toward equilibrium (structural recovery) is monitored in terms of the normalized departure of the specific volume from equilibrium, $\delta = (v - v_\infty)/v_\infty$, where v_∞ is the specific volume in equilibrium at temperature T attainable only at long times. As can be seen in Fig. 2.5, the time taken to reach equilibrium increases rapidly as T is decreased. Similar results are obtained if one measures the enthalpy H instead of v . After a down-quench, the enthalpy H decreases monotonically with time toward the equilibrium enthalpy H_e .

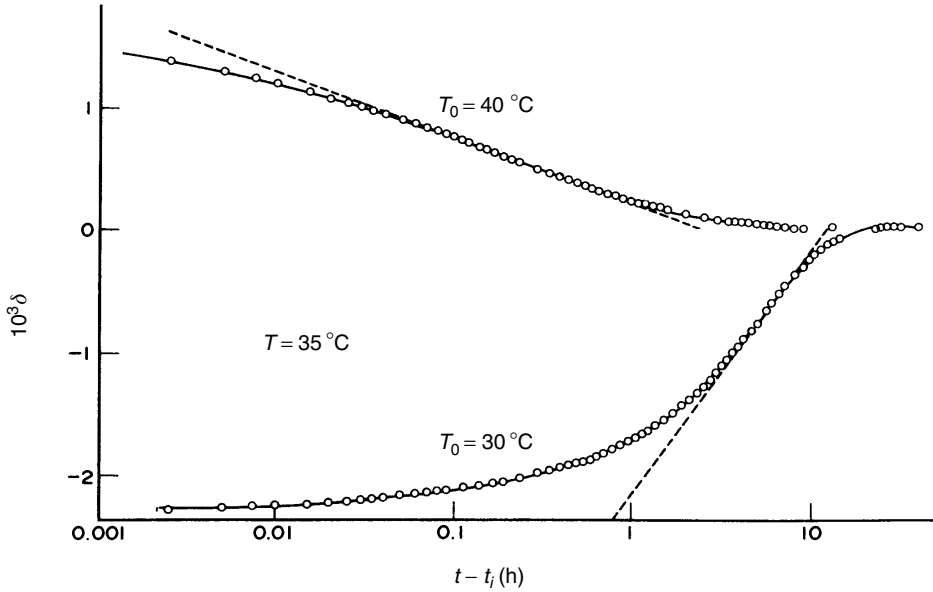


Fig. 2.6. Contraction and expansion isotherms of poly(vinyl acetate) at a final temperature of $T = 35^\circ\text{C}$ for initial temperatures of $T_0 = 30$ and 40°C , showing the asymmetry of the approach to equilibrium for contraction and expansion. From Kovacs by permission [28].

The tendency of structural relaxation toward equilibrium is found also in an up-quench. Figure 2.6 shows another set of Kovacs' data on poly(vinyl acetate) [28]. The upper curve is the structural recovery for a down-quench from the equilibrium liquid at $T_0 = 40^\circ\text{C}$ to 35°C , and has been seen before in Fig. 2.5. In the lower curve the glass was given enough time to equilibrate at 30°C (so that its initial specific volume is the equilibrium volume), and then up-quenched to 35°C and allowed to relax at that temperature. At long times, the polymer structurally recovers to equilibrium and has the same specific volume both in the up-quench and in the down-quench experiments. Therefore, in general, the glassy state always tends to relax structurally toward equilibrium, and this tendency is often referred to as structural recovery.

2.2.4 Asymmetry of structural recovery (nonlinearity)

However, one finds in Fig. 2.6 that the progress of structural recovery with time for a down-quench is significantly different from that for an up-quench, even though both specimens are relaxing at the same temperature of 35°C . Besides that, the time developments in the two cases are asymmetric, the recovery for the down-quench being faster. In this example, the magnitude of the change in temperature

is the same for the up-quench and down-quench, although the initial magnitude of departure of the specific volume from equilibrium is not the same. One can arrange up-quench and down-quench experiments to a common temperature with the same magnitude of the initial departure of the specific volume from equilibrium (but different magnitudes of the temperature jumps) and yet the results are the same as those in Fig. 2.6. In particular, structural recovery is faster for a down-quench than it is for an up-quench. An example of this can be found from experimental data on an inorganic glass-former [29].

This *asymmetry* in the recovery means that the structural-relaxation time depends not only on the temperature but also on the instantaneous structure. In particular, when the approach toward equilibrium is from above, the initial structure of the material will have a higher molecular mobility than that of the equilibrium structure, although the difference decreases as the departure from equilibrium decreases. On the other hand, the opposite is true when the approach toward equilibrium is from below. This feature of isothermal structural relaxation is sometimes referred to in the literature as the *nonlinearity* of the process, in the sense that the structural relaxation cannot be described by the linear differential equation

$$d(v - v_{\infty})/dt = -(v - v_{\infty})/\tau \quad (2.1)$$

with a rate, $1/\tau$, that is independent of the relaxing structure itself [30–32].

2.2.5 The non-exponential character of structural relaxation

The isothermal time dependence of relaxation and fluctuation due to molecular motions in liquids at equilibrium usually cannot be described by the simple linear exponential function $\exp(-t/\tau)$, where τ is the relaxation time. This fact is well known, especially for polymers, from measurements of the time or frequency dependence of the response of the equilibrium liquid to external stimuli such as in mechanical [6], dielectric [7, 33], and light-scattering [15, 34] measurements, and nuclear-magnetic-resonance spectroscopy [14]. The correlation or relaxation function measured usually decays slower than the exponential function and this feature is often referred to as non-exponential decay or “non-exponentiality.” Since the same molecular motions are responsible for structural recovery, certainly we can expect that the time dependence of the structural-relaxation function under non-equilibrium conditions is also non-exponential. An experiment by Kovacs on structural relaxation involving a more complicated thermal history showed that the structural-relaxation function even far from equilibrium is non-exponential. For example (Fig. 2.7), poly(vinyl acetate) is first subjected to a down-quench from $T_0 = 40^\circ\text{C}$ to 10°C , and then, holding the temperature constant, the sample

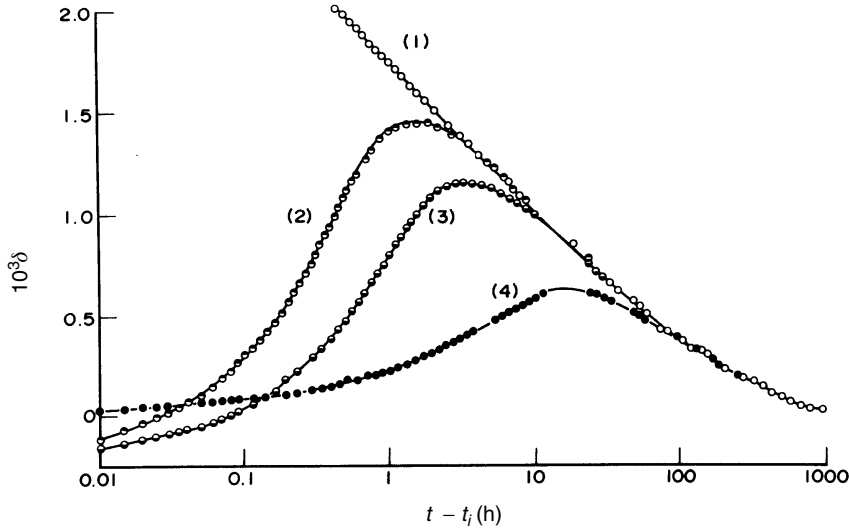


Fig. 2.7. The evolution of $\delta = [v - v_{\infty}(30^{\circ}\text{C})]/v_{\infty}(30^{\circ}\text{C})$ at $T = 30^{\circ}\text{C}$ of poly(vinyl acetate) showing the memory effect. (1) quench from 40°C to 30°C ; (2) quench from 40°C to 10°C , wait for 160 h followed by up-quench to 30°C ; (3) quench from 40°C to 15°C , wait for 140 h followed by up-quench to 30°C ; (4) quench from 40°C to 25°C , wait for 90 h followed by up-quench to 30°C . Note that the initial departure from equilibrium is nearly zero. From Kovacs by permission [28].

is allowed to undergo structural recovery partially for 160 h, whereafter the volume extrapolated along the glassy (thermal-expansion) line from 10°C to 30°C is the same as the equilibrium volume at 30°C . The sample is then up-quenched from 10°C to 30°C and the volume is measured as a function of time after the up-quench, $t - t_i$. According to the thermal history and condition described, after this up-quench to 30°C , the volume of the sample should be nearly the same as $v_{\infty}(30^{\circ}\text{C})$, the equilibrium volume at 30°C . Therefore, if structural relaxation proceeds according to the simple rate equation (2.1), no significant change in volume should be seen after the up-quench because the glass is already near equilibrium. In other words, the departure from equilibrium, $\delta = [v - v_{\infty}(30^{\circ}\text{C})]/v_{\infty}(30^{\circ}\text{C})$, immediately after the up-quench is nearly zero and should remain nearly zero. However, as can be seen in a plot of δ versus $t - t_i$ in Fig. 2.7, δ instead goes through a maximum before returning to zero. The results indicate that the structural-relaxation function is not $\exp(-t/\tau)$ that would follow from Eq. (2.1), and naturally it has to be non-exponential. Interestingly, the decrease of δ with time after the maximum follows the path of the down-quench directly from 40°C to 30°C shown previously in Fig. 2.5, as if the glass “remembers” it started from equilibrium at 40°C .

2.2.6 Hysteresis effects

We are now ready to discuss fully the structural relaxation during cooling and reheating. For elucidating the relaxation processes in the simplest case of cooling followed immediately by reheating at the same rate, we borrow the illuminating scheme constructed by Moynihan *et al.* [26]. Cooling and heating at a rate q can be approximated by a series of small temperature steps ΔT followed by isothermal holds of duration $\Delta t = \Delta T/q$. In Fig. 2.8(a) is shown the change of H of a hypothetical glass-forming liquid during stepwise cooling followed by stepwise reheating over the same temperature range. The dashed line represents both T and the equilibrium enthalpy H_e . The solid line represents the experimentally measured H . Initially, at time t_0 and temperature T_0 , the material is in the equilibrium liquid state. After the first downward step in temperature the structural-relaxation time at temperature $T_0 - \Delta T$ is supposed to be sufficiently short compared with the time

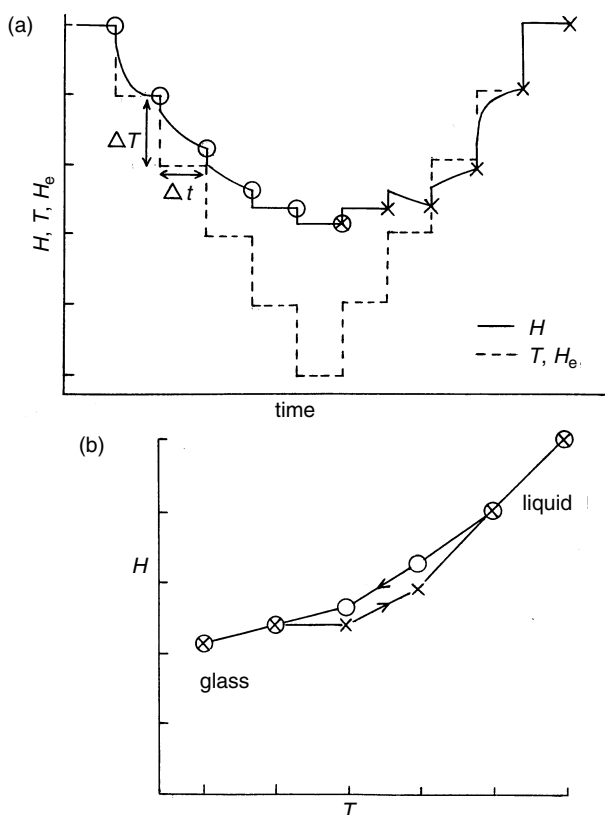


Fig. 2.8. Schematic plots of (a) variations of temperature T , equilibrium enthalpy H_e , and experimental enthalpy H with time, and (b) H versus T during stepwise cooling and reheating in the glass-transition region. From Moynihan *et al.* by permission [26].

interval Δt that the material reaches equilibrium during the hold, and $H = H_e$ at $t = t_0 + \Delta t$. Following the second downward step, however, at the lower temperature $T_0 - 2 \Delta T$ the structural-relaxation time is now supposed to be longer than the next hold, and the material is unable to equilibrate completely. As a result, H is larger than H_e at $t = t_0 + 2 \Delta t$, as illustrated in Fig. 2.8(a). After the third downward temperature step the temperature, $T_0 - 3 \Delta T$, is lower, the extent of equilibration in time Δt is less, and the difference, $(H - H_e)$, at $t = t_0 + 3 \Delta t$ is larger. Following the fourth and fifth downward temperature steps, the temperature becomes even lower. The structural-relaxation time is so long that virtually no structural relaxation occurs in the time interval $t_0 + 3 \Delta t \leq t \leq t_0 + 5 \Delta t$, and the difference $H - H_e$ increases to the maximum after the fifth downward temperature step. Although structural relaxation is nonexistent in the last two downward temperature steps, there is still a “fast” change in H associated with the vibrational degrees of freedom. These smaller “fast” decreases, immediately following the fourth and fifth downward temperature steps, are illustrated in Fig. 2.8(a), and come from the glass-like change in H . The sixth temperature step is the first upward step in temperature during reheating. After that, the relaxation time is still too long to allow structural relaxation within the time interval Δt . Hence the enthalpy has only a fast glass-like increase. Following the second upward temperature step, there is immediately a fast glass-like increase, and the temperature is sufficiently higher that the material exhibits partial relaxation. Now we come to the point at which the tendency of the non-equilibrium state to undergo structural relaxation toward equilibrium discussed in Section 2.2.3 gives rise to an interesting effect. Since, however, H is above the equilibrium value H_e at this point (see Fig. 2.8(a)), the tendency makes the partial relaxation *downward*. In other words, the change in H is a *decrease*, even though the material is now being heated. Following the third and subsequent upward temperature steps, H is below the equilibrium value H_e . Hence, the tendency now makes H relax upward. H is still below H_e before the fourth upward temperature step, but eventually it attains the equilibrium value H_e in time Δt after the fourth upward temperature step. The material has returned to the equilibrium liquid state at the highest temperatures. The enthalpies H at the beginning and end of each time/temperature step in Fig. 2.8(a) are plotted versus temperature in Fig. 2.8(b). The important result one can learn from this illustrative example is that the H – T cooling curve is different from the H – T heating curve, so there is hysteresis when a liquid is cooled to form a glass and subsequently reheated through the transition region, returning it to a liquid. It is important to point out that, at least for the scenario in Fig. 2.8(a) and (b), the occurrence of the hysteresis is *not* due to a nonlinearity (Section 2.2.4) or non-exponentiality (Section 2.2.5) of structural relaxation. Of course, nonlinearity and non-exponentiality can play their parts in determining the

hysteresis in other cases with more complicated thermal histories than that shown in Fig. 2.8(a).

With the origin of hysteresis explained, we can now understand the change of H with temperature on reheating after cooling through the transition region at the same rate as that shown in the upper part of Fig. 2.4 for two different rates, q_A and q_B . Because of the hysteresis, the curve of the heat capacity C_p , which is $(\partial H/\partial T)_P$, versus T does not have the same sigmoidal shape as the C_p - T cooling curve. Instead it rapidly increases and passes through a maximum near the upper end of the glass-transition region. A value of T_g is taken as the extrapolated onset of the rapid increase of the C_p - T heating curve determined by the procedure shown at the bottom in the lower part of Fig. 2.4. Other characteristic points in the C_p - T heating curve, such as the midpoint of the rapid rise and the maximum, are often taken as T_g . Since the DSC output is proportional to C_p , these various ways to obtain T_g from experimental traces obtained on reheating are often used and reported. However, these values may differ from the T_g (T_f in Fig. 2.4) determined from cooling (Figs. 2.1, 2.2, and 2.4). In particular, T_g given by the maximum of C_p can be significantly higher, as shown in Fig. 2.4. This T_g should not be taken seriously because it is an artifact originating from the kinetics of structural relaxation due to interplay of the departure from equilibrium and changing temperature during reheating.

Hysteresis of the enthalpy H and specific volume v occurs also when the cooling rate q_c and the heating rate q_h differ in magnitude. Consider first the case if the sample is cooled very rapidly and subsequently reheated much more slowly than the rate at which it was cooled. Figure 2.8(a) can still be used to help one to understand the change of H with time if the first up-quench is delayed to a longer time and the duration of the isothermal holds $\Delta t = \Delta T/q_h$ following each up-quench is much longer than that shown in Fig. 2.8(a). This modification is a realization of the condition that $q_h \ll |q_c|$. Given much longer time before the first up-quench and between two consecutive up-quenches, the aforementioned downward relaxation becomes more prominent and occurs earlier than shown in Fig. 2.8(a). The result in a plot of H versus T is that, on reheating, H falls below the glassy line obtained by cooling and hysteresis starts at lower temperatures than shown in Fig. 2.8(b) for the case of $q_h = |q_c|$. A different effect is observed when the sample is cooled very slowly and subsequently heated very rapidly. As shown in the upper part of Fig. 2.4, slow cooling results in a lower glass-transition temperature and a glass with lower enthalpy. These factors make the structural-relaxation time much longer. The total duration is also much shorter for rapid reheating to the same final temperature as in Fig. 2.8(b). On rapid reheating to any of the temperatures, the structural relaxation has gone to a significantly lesser extent than that shown in Fig. 2.8(a) at the same temperature, and hence the increase of H is less than that shown in Fig. 2.8(b) at the same temperature. A higher temperature than that shown in Fig. 2.8(b)

has to be reached on rapid reheating before H attains the equilibrium enthalpy H_e . Consequently, the final rise of H to H_e is expected to be more rapid than those shown in Fig. 2.8(b) and in the upper part of Fig. 2.4 by the heating curve obtained at rate $|q_B|$. A more complicated case is allowing the glass to equilibrate (or anneal) isothermally for a long period of time after cooling down from the equilibrium liquid state, before the sample is reheated again. The heating curve and the hysteresis depend on the annealing time.

2.2.7 Models for the description of structural relaxation

The two essential features of structural relaxation and structural recovery have been brought out by experiments (Figs. 2.6 and 2.7). They are (1) the structural-relaxation time depends not only on temperature T , but also on the instantaneous structure (nonlinearity); and (2) the time dependence of the structural-relaxation process is not a simple exponential function (non-exponentiality). Naturally, a viable model must incorporate these two features. There are two such models. The one formulated by Moynihan and co-workers [31] is based on the constructs of Tool [27] and Narayanaswamy [30] and is known as the TNM model. The other is the KAHR model developed by Kovacs and co-workers [32]. Both models account for nonlinearity and non-exponentiality and they are essentially equivalent. We shall describe only one of them, the TNM model and its variations. A review of the KAHR model can be found in [8].

2.2.7.1 The fictive temperature, T_f

In the TNM model, nonlinearity is taken into account by modifying the linear differential equation (2.1) for volume and

$$d(H - H_e)/dt = -(H - H_e)/\tau \quad (2.2)$$

for enthalpy by making τ dependent not only on T but also on v and H , respectively. Actually the model is formulated on the evolution of the fictive temperature T_f , instead of v or H . T_f can be defined as the instantaneous contribution of the structural-relaxation process to either v or H expressed in temperature units. For example, following quenching an equilibrium liquid at temperature T_0 down to T_1 , the enthalpy $H(t)$ relaxes from the initial value H_0 toward the equilibrium enthalpy H_{e1} at temperature T_1 . Correspondingly, $T_f(T)$ varies from T_0 to T_1 in parallel with the changes in $H(t)$. The progress of structural relaxation with time described by the normalized relaxation function, $\phi(t) \equiv [H(t) - H_e]/(H_0 - H_{e1})$, is now replaced by $[T_f(T) - T_1]/(T_0 - T_1)$.

Note that T_f is equal to T for the equilibrium liquid, and remains so during cooling or heating as long as the sample is in equilibrium. Thus, for the equilibrium

liquid, $dT_f/dT = 1$, $dH/dT = C_{pe}$, and $dv/dT = v\alpha_{pe}$. Here C_{pe} and α_{pe} are the heat capacity and thermal-expansion coefficient of the equilibrium liquid. For a glass whose structure remains frozen during cooling or heating, T_f is unchanged and hence $dT_f/dT = 0$, but $dH/dT = C_{pg}$ and $dv/dT = v\alpha_{pg}$. Here C_{pg} and α_{pg} are the heat capacity and thermal-expansion coefficient of the glass. T_f can be used as a convenient substitute in modeling the structural relaxation as in the TNM model. However, on converting the results expressed in terms of T_f and dT_f/dT to v or H and their derivatives with respect to temperature, the above differences between them have to be taken into account. For example, after calculating T_f and dT_f/dT during heating (after cooling through the glass-transition region to reach the glassy state) by use of the model, the heat capacity C_p has to be obtained from the expression

$$C_p = C_{pg} + (C_{pe} - C_{pg}) dT_f/dT \quad (2.3)$$

Although the fictive temperature T_f is expedient for model computation and conceptual understanding, it should be emphasized that it is not a quantity of fundamental importance. It will not necessarily be able to specify completely the structural state of even a frozen glass. This deficiency can be seen from the often-found difference between the T_f values calculated from H and v for a glass formed at the same cooling rate.

2.2.7.2 The Tool–Narayanaswamy–Moynihan model

Nonlinearity is accounted for in the Tool–Narayanaswamy–Moynihan (TNM) model by replacing τ in the linear equations (2.1) and (2.2) by τ given by the so-called Tool–Narayanaswamy (TN) equation:

$$\tau = \tau_0 \exp\left(\frac{x \Delta h}{RT} + \frac{(1-x) \Delta h}{RT_f}\right) \quad (2.4)$$

where x ($0 \leq x \leq 1$) is the nonlinearly parameter, τ_0 a pre-exponential factor, Δh an activation enthalpy, and R the ideal-gas constant and all of them except R are taken to be fitting parameters. Another way of introducing nonlinearity is by modifying [35] the Adam–Gibbs equation [36] for the relaxation time of an equilibrium liquid, $\tau = \tau_0 \exp\{C/[TS_c(T)]\}$, where C is a constant and $S_c(T)$ is the configurational entropy. The modification is made by replacing $S_c(T)$ by $S_c(T_f)$:

$$\tau = \tau_0 \exp\left(\frac{C}{TS_c(T_f)}\right) \quad (2.5)$$

As will be discussed further, one of the assumed temperature dependences of $S_c(T)$ is $S_c(T) = \Delta C_p \ln(T/T_K)$, where $\Delta C_p = C_{pe} - C_{pg}$, and T_K is the Kauzmann temperature (to be defined later) [37]. Accordingly, nonlinearity enters into

Eq. (2.5) via

$$S_c(T_f) = \Delta C_p \ln(T_f/T_K) \quad (2.6)$$

In spite of the difference between the two choices for nonlinearity, Eqs. (2.4) and (2.5), the calculated results are similar for moderate departures from equilibrium and over a small temperature range [35]. Most recently a combination of the two has been suggested [38].

The non-exponential character of the structural-relaxation process is accounted for by incorporating a distribution of relaxation times, instead of the single relaxation time in Eq. (2.4), into the normalized relaxation function

$$\phi(t) = \sum_i g_i \exp\left(-\int_0^t \frac{dt'}{\tau_i}\right) \quad (2.7)$$

where the g_i are temperature-independent coefficients weighting the contributions from the various relaxation times τ_i . Each τ_i has the same dependence on T and T_f as τ in Eq. (2.4):

$$\tau_i = \tau_{i0} \exp\left(\frac{x \Delta h}{RT} + \frac{(1-x) \Delta h}{RT_f}\right) \quad (2.8)$$

The distribution of τ_i comes from the distribution of the pre-exponential factor τ_{i0} . The assumed temperature independence of the g_i may hold for a moderate departure from equilibrium but cannot be guaranteed for a large departure. The integral over time in Eq. (2.7) is needed because of the variation of τ_i with time coming from T_f in Eq. (2.8).

In practice, the Kohlrausch–Williams–Watts (KWW) or stretched-exponential relaxation function

$$\phi(t) = \exp\left[-\left(\int_0^t \frac{dt'}{\tau}\right)^\beta\right] \quad (2.9)$$

is used to account for non-exponentiality instead of Eq. (2.7). In this equation, τ is given by Eq. (2.4) or the alternative Eq. (2.5), and β is a temperature-independent fractional exponent ($0 < \beta < 1$). This has the advantage over Eq. (2.7) of reducing the number of adjustable parameters from the many g_i to a single parameter β . Besides, the KWW functions are often found to fit well the time dependence of relaxation in equilibrium liquids [33, 34].

Structural relaxation in response to any thermal history, simple or complicated, can now be calculated by application of the TNM model using the relaxation function given by Eq. (2.9) and τ given by Eq. (2.4) or (2.5). Any thermal history can be described as a sequence of temperature changes, ΔT_j , at time t_j , $j = 1, 2, \dots, m$. The response to any temperature step ΔT_j at time t ($> t_j$) is

given by $\Delta T_j [1 - \phi(t, t_j)]$, where

$$\phi(t, t_j) = \exp \left[- \left(\int_0^{t-t_j} \frac{d(t' - t_j)}{\tau} \right)^\beta \right] \quad (2.10)$$

The total response is then the sum of these responses, upon assuming that the Boltzmann superposition principle applies. If initially (before t_1) the sample is at equilibrium at temperature T_0 , then the fictive temperature $T_f(t)$ at time t ($> t_m$) is given by

$$T_f(t) = T_0 + \sum_{j=1}^m \Delta T_j [1 - \phi(t, t_j)] \quad (2.11)$$

and, during the course of the thermal treatment, $T_f(t)$ at time t ($t_i < t < t_{i+1}$, where $1 < i$, and $(i + 1) \leq m$) is given by

$$T_f(t) = T_0 + \sum_{j=1}^i \Delta T_j [1 - \phi(t, t_j)] \quad (2.12)$$

From the response $T_f(t)$, the heat capacity C_p can be calculated. For example, if the thermal history is cooling at some rate from a temperature T_0 of equilibrium liquid to well below the glass-transition region and then reheating at the same or a different rate to T_0 , then C_p is obtained by using Eq. (2.3), after converting the time dependence of T_f into a temperature dependence. The parameters, x , τ_0 , Δh , and β are not known *a priori*, and they are determined by fitting experimental data. Figure 2.9 shows experimental $C_p(T)$ data on poly(vinyl acetate) normalized with respect to the difference between liquid and glassy heat capacities, C_{pl} and C_{pg} , respectively; i.e. $C_p^N = [C_p(T) - C_{pl}(T)]/[C_{pl}(T) - C_{pg}(T)]$. The temperature dependences of C_{pl} and C_{pg} were obtained by linear extrapolation of the liquid- and glassy-state data. The sample was cooled from well above T_g to well below T_g at several cooling rates, 5, 10, 20 and 40 K min⁻¹, followed immediately by reheating at 10 or 20 K min⁻¹. The data shown in Fig. 2.9 were taken during reheating. For any cooling and heating rates, T_g can be defined as the temperature at which $C_p^N = 0.5$. The lines are best fits to the data with $\ln[\tau_0(\text{s})] = -275.4$, $\Delta h = 8.8 \times 10^4 R$, $x = 0.28$, and $\beta = 0.53$ [39].

2.2.7.3 Remarks on the models of structural recovery

There is no doubt that, by capturing the two important features of structural relaxation, nonlinearity and non-exponentiality, the TNM and the KAHR models can explain qualitatively the structural relaxation even for complicated thermal histories. Quantitatively, good agreement with experimental data can also be reached by

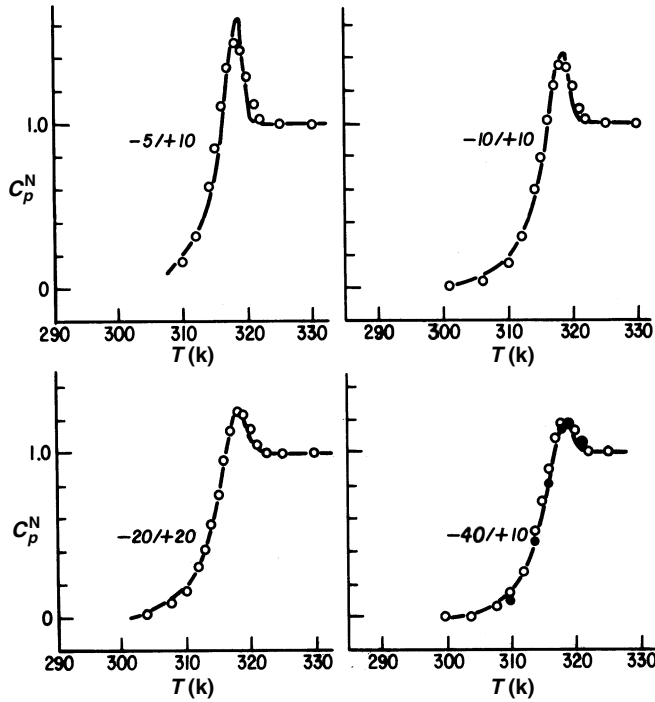


Fig. 2.9. Experimental heat-capacity data of poly(vinyl acetate) normalized with respect to the difference between liquid and glassy heat capacities (circles), and fits obtained by applying the TNM model for various rates of cooling and heating (lines). From Hodge by permission [39].

adjusting the fitting parameters, but this is unsurprising because of the abundance of parameters. Good quantitative agreement of results of calculations using the TNM or the KAHN model with experimental data can never be expected because Eq. (2.4) is quite arbitrary and Eq. (2.6) is not exact in accounting for nonlinearity. Hence a good or “best” quantitative fit to the data does not mean that the parameters used are realistic, particularly when several parameters are allowed to vary at the same time. An example of this is the TNM-model fits to volume- and enthalpy-recovery data for polystyrene [40]. The β value used to fit the data is significantly larger than the value found by light-scattering measurement on polystyrene at equilibrium near T_g [34]. The number of parameters can be reduced by replacing the activation enthalpy h and KWW exponent β in the TNM model by their respective values determined from experimental data on the equilibrium liquid at temperatures near T_g . The pre-exponential factor τ_0 shifts the time or temperature scale but does not change the shape of the calculated C_p . Hence essentially x is the only parameter that remains to fit the data. The fit might not be the best, but at least the h and β used are consistent with equilibrium measurements.

Recent advances in experimental techniques employed to probe the microscopic dynamics of molecules in polymers [41] and in inorganic and organic small-molecule [42] glass-formers have revealed a feature of the non-exponentiality of the equilibrium state. Although the relaxation is a superposition of exponential processes with different relaxation times (i.e. the relaxation is heterogeneous), there are fluctuations within the heterogeneous distribution occurring on the same timescale as the average relaxation time. In other words, the heterogeneous distribution is not static but dynamic. Molecules relaxing at faster and slower rates interchange their roles on the timescale of the average relaxation time such as τ in the KWW function (Eq. (2.9)). This dynamic heterogeneous property is a consequence of the cooperative multimolecular dynamics, which will be elaborated further in later sections. The usage of a distribution of the pre-exponential factor τ_{i0} in the standard TNM model (Eq. (2.8)) to account for non-exponentiality of structural relaxation has little or no connection to dynamic heterogeneity of molecular motions. In a recent attempt [43], this was replaced by a distribution of local “structural” or fictive temperatures T_{si} , and Eq. (2.8) by

$$\tau_i = \tau_{i0} \exp\left(\frac{x \Delta h}{RT} + \frac{(1-x) \Delta h}{RT_{si}}\right) \quad (2.13)$$

T_{si} reflect local fluctuations in free volume or configurational entropy. The mean value of the T_{si} , $\langle T_{si} \rangle$, gives the fictive temperature T_f at any instant. This modification allows the variance of the fluctuations, $\langle \Delta^2 T_s \rangle (= \langle T_{si}^2 \rangle - \langle T_{si} \rangle^2)$, to be calculated for any thermal history. When this approach is applied to the refractive-index measurement, T_{si} is the local refractive-index “structural” temperature. $\langle \Delta^2 T_s \rangle$ corresponds to the variance of the fluctuations of the refractive index, which is proportional to the light-scattering intensity. This modified TNM model has had success [43] in accounting for the temperature dependence of the experimental light-scattering intensity of boron trioxide during heating following cooling and isothermal annealing just below the glass-transition region. The achievement is noteworthy, although the assumed static distribution of local structural temperature is not congruent with the heterogeneous dynamics in the equilibrium liquid.

2.2.8 Physical aging in glasses

From the discussions in previous sections, we know that the glassy state is not in equilibrium and that its structure evolves toward equilibrium even under isothermal conditions. Concomitantly, its properties also will change with time. We have encountered this change in enthalpy and volume before, when, after cooling or quenching from the liquid, the glass is isothermally annealed for a length of time. The change in mechanical properties of a glass with (aging) time, t_e , accompanying the isothermal structural change was studied extensively by Struik and the effects

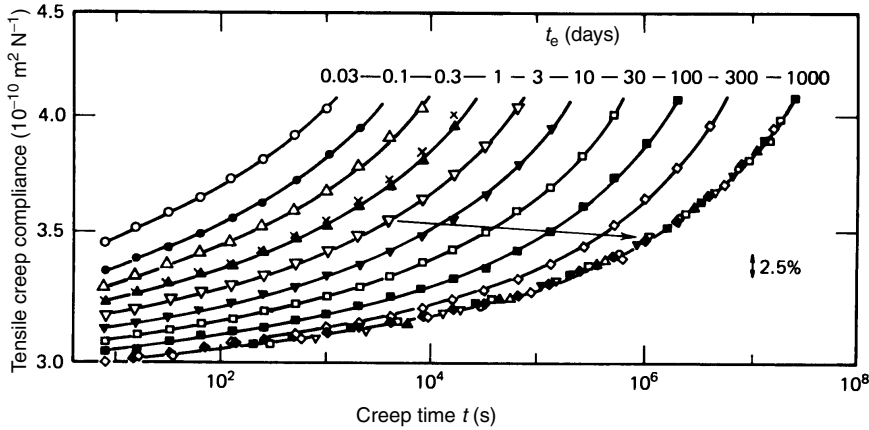


Fig. 2.10. The small-strain tensile-creep compliance versus creep time of poly(vinyl chloride) quenched from 90 °C to 20 °C and aged at 20 ± 0.1 °C for a period of time in days (indicated above the curves), after which each individual creep measurement was performed. The reduced curve on the extreme right was obtained by shifting the individual creep data to the longest-aging-time (1000 days) response as indicated by the arrow. From Struik by permission [44].

observed are called “physical aging” in his treatise [44] on the subject. The change in mechanical properties was monitored by measuring shear compliance (creep) in the linear viscoelastic (small-stress) range at some evenly spaced values of $\log t_e$. The duration of the measurement starting at any of the chosen t_e must be short compared with t_e (i.e. less than $0.1t_e$) in order that the structural changes that occur during the measurement be small and not influence the measurement. Under this condition, the creep data replicate the progressively changing mechanical properties of the glass with aging time. Taking the example from Struik’s work [44] on poly(vinyl chloride) down-quenched from 90 °C ($T_g = 80$ °C) to 20 °C, continued shift of the creep curves toward longer times was observed with increasing t_e from 0.03 to 1000 days (see Fig. 2.10). The maximum shift in timescale is by about a factor of 10^5 . An important feature of the data is that physical aging is observed even at temperatures far below T_g . Another feature is that the creep curves can be superposed by implementing nearly horizontal shifts along the $\log(\text{time})$ axis, indicating that, although the viscoelastic response of the glass is retarded with aging, the shape of the time dependence is unchanged. From the shifts $\log[a(t_e)]$ required to superpose the creep curves at t_e , one obtains the amount of shift per decade of aging time,

$$\mu = \frac{d \log[a(t_e)]}{d \log t_e} \quad (2.14)$$

Struik found that μ is approximately equal to unity for many systems, including polymers.

2.3 Models of the glass transition

As discussed in Section 2.2, when a glass-forming liquid is cooled the experimentally observed glass transition occurs when the molecular mobility becomes so low that the structure cannot attain equilibrium on the timescale of the experiment. Thus a theory of the glass transition has to address at least the mobility of molecular motion of the equilibrium liquid at temperature above T_g . Preferably, the theory should also address other characteristics of the molecular motion in the equilibrium liquid. There are two well-known competing theories of molecular mobility leading to glass transition: the free-volume theory [1, 8, 45] and the thermodynamic theory of Gibbs and DiMarzio based on the configurational entropy of a polymer [46, 47]. More recently, other sophisticated statistical-mechanical treatments have been introduced [48]. Models based on the energy landscapes in configurational space introduced by Goldstein [49] are currently being developed. Nevertheless, a complete theoretical understanding of the glass transition is not yet available. In this chapter we confine our consideration to the standard free-volume and configurational-entropy theories. In some later sections, we shall point out that an essential physical ingredient seems to be missing from these standard theories and other current statistical-mechanical treatments. It will be shown that the inclusion of the missing ingredient allows a fuller explanation of the dynamics of molecular motions of glass-forming liquids, and resolution of a number of anomalous viscoelastic properties of polymers to be described later on.

2.3.1 Free-volume theory

The concept of free volume, v_f , and the idea that the mobility of molecules at any temperature is primarily controlled by the free volume, was brought forth by Doolittle [45] in explaining the non-Arrhenius temperature dependence of the viscosity, η , of liquids of low molecular weight. The free volume is defined as the difference between the total specific volume v and an occupied volume, v_o . The Doolittle equation,

$$\ln \eta = \ln A + B(v - v_f)/v_f \quad (2.15)$$

where A and B are constants, describes well the temperature dependence of viscosity. The physical basis for free volume can be understood from the theory of Cohen and Turnbull [50]. According to them, motion of a molecule can occur only when a void having volume greater than a certain critical value is available for it to move into. The voids are created by fluctuations or the redistribution of free volume originating from the collective or cooperative motion of molecules. On cooling, the glass-transition region commences when the free volume falls below

some value at which the molecular mobility is low enough that the material cannot attain equilibrium.

2.3.1.1 The WLF equation

Viscoelastic response of a polymer from the glassy state to terminal flow occurs over a very extended time/frequency range that cannot all be measured isothermally by any mechanical technique, which usually has a limited time/frequency range [1–4, 6]. At any temperature one can capture only a part of the entire response. Other parts can be seen separately by repeatedly making measurements at a number of temperatures. To obtain an idea of what the entire viscoelastic response of a high polymer at one temperature would look like, one has to construct a composite (master) curve. After choosing one of the measurement temperatures as the reference temperature T_0 , the composite curve is obtained by shifting the data at the next higher temperature along the logarithmic time/frequency axis to superpose them as well as one can with the data at T_0 , and the procedure is repeated for the next higher temperature. A similar procedure is applied to data taken at temperatures lower than T_0 . Sometimes, a vertical shift, b_T , also is applied to the measured mechanical property, compliance or modulus [1, 51]. This procedure is called time–temperature superposition (or reduction). Often viscoelastic data taken at different temperatures, after shifting, superpose well onto each other to form an acceptable master curve, particularly for measurements taken using instruments that have relatively narrow time/frequency windows. The polymer liquid is said to obey the principle of time–temperature superposition or thermorheological simplicity. The success in constructing an acceptable master curve is used to justify the assumption that the relaxation (or retardation) times of all viscoelastic mechanisms with different length-scales have the same temperature dependence, which is given by the shift factor, a_T , used in constructing the master curve. Examples of master curves can be found in the chapter by W. W. Graessley.

Williams, Landel, and Ferry (52) found that the temperature dependences of the empirical values of $\log a_T$ of many polymers are well described by their (WLF) equation,

$$\log a_T = -C_1(T - T_0)/(C_2 + T - T_0) \quad (2.16)$$

where C_1 and C_2 are constants. Initially C_1 and C_2 were thought to be universal constants, but this turned out not to be the case when more polymers were considered. Historically, the establishment of the WLF equation in the study of polymer viscoelasticity was instrumental in making the concept of free volume for molecular mobility of polymers popular because it provided a theoretical basis for the WLF equation. Ferry [1] suggested, on the basis of the Rouse model for an unentangled polymer, that the shift factor for the viscosity is given by $a_T = (\eta_0 T_0 \rho_0)/(\eta T \rho)$,

where η and ρ are the viscosity and density at the temperature T and η_0 and ρ_0 are the corresponding quantities at the reference temperature T_0 . From Doolittle's equation, (2.15), the shift is given by

$$\log a_T = \log(\eta/\eta_0) + \log\left(\frac{T_0\rho_0}{T\rho}\right) = \frac{B}{2.303}\left(\frac{1}{f} - \frac{1}{f_0}\right) + \log\left(\frac{T_0\rho_0}{T\rho}\right) \quad (2.17)$$

where $f \equiv v_f/v$ is the fractional free volume at any temperature T and f_0 is its value at T_0 . Ignoring the $\log[T_0\rho_0/(T\rho)]$ term and assuming that f increases linearly with temperature like

$$f = f_0 + \alpha_f(T - T_0) \quad (2.18)$$

one finds by substituting this into Eq. (2.17) that

$$\log a_T = -\frac{B}{2303f_0}(T - T_0)/(f_0/\alpha_f + T - T_0) \quad (2.19)$$

which is identical in form to the WLF equation. This derivation of the WLF equation by using *only* the viscosity shift factor (Eq. (2.17)) is motivated by the assumption that the relaxation (or retardation) times of *all* viscoelastic mechanisms, including the terminal relaxation that determines the viscosity, have the *same* temperature dependence. The validity of this assumption is a necessary condition for the *entirety* of the viscoelastic responses or spectrum at temperature T_0 being faithfully captured by the master curve obtained by time–temperature superposition of isothermal data. It is precisely this assumption that justified time–temperature reduction of data and led Williams, Landel, and Ferry to their empirical equation.

However, more precise measurements of the creep compliance $J(t)$ of polystyrene [53], poly(vinyl acetate) [54] and atactic polypropylene [55] by Plazek have shown that there is failure of time–temperature superposition of data taken at different temperatures. An example is polystyrene with nearly uniform molecular weight 46 900. Creep-compliance measurements are shown as $J_p(t) \equiv J(t)[T\rho/(T_0\rho_0)]$ in Fig. 2.11. The shift factors, $a_T = \eta_0 T_0 \rho_0 / (\eta T \rho)$ with $T_0 = 100^\circ\text{C}$ according to Eq. (2.17) and rewritten as $\eta_p(100^\circ\text{C})/\eta_p(T)$ in labeling the x axis, were calculated from the actually measured values of the viscosity. These shift factors superpose well the data in the terminal zone, but fail to superpose the data at shorter reduced times in the softening dispersion (glass–rubber transition zone). The shift factors of the viscosity (i.e. the terminal-flow mechanism) do not apply to the viscoelastic mechanisms in the glass–rubber-transition zone. The use of Doolittle's free-volume equation (2.15) to derive the temperature shifts of the entire viscoelastic function from measurements of viscosity is flawed, the achievement of providing a theoretical basis for the acclaimed WLF equation (2.19) notwithstanding. Hence it is a fallacy to state that the WLF equation represents the common

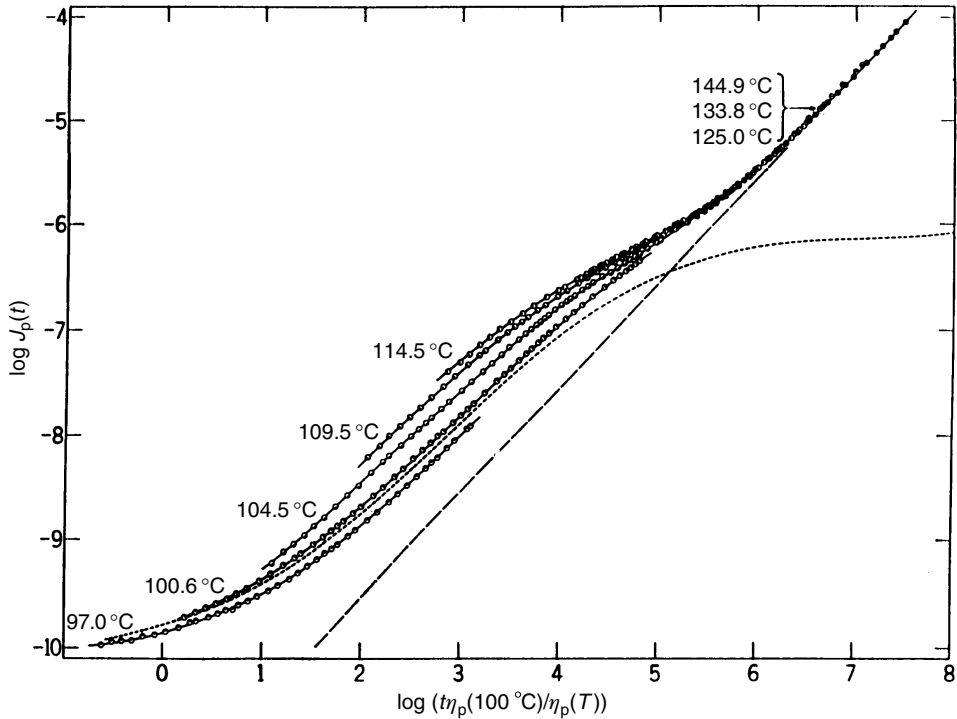


Fig. 2.11. Creep-compliance measurements at several temperatures (indicated in the figure) on a polystyrene sample with molecular weight 46 900, reduced to 100 °C with shift factors calculated from the steady-state viscosity. Subscript p denotes multiplication by $T\rho/(T_0\rho_0)$. From Plazek [53], by permission.

temperature dependence of the relaxation (or retardation) times shared by *all* viscoelastic mechanisms of a polymer liquid. In fact, Plazek as well as others had further shown that the shift factors of data covering the entire viscoelastic range of high molecular weight amorphous polymers cannot be described by a single WLF equation [56]. We shall return in Section 2.6 to discuss in more detail the breakdown of thermorheological simplicity [10, 11] by delineating three distinctly different viscoelastic mechanisms in the softening dispersion and showing that the temperature dependences of their shift factors, as well as that of the viscosity, are all different from each other.

2.3.1.2 Measurement of hole volume

Free volume or hole volume is ostensibly measured experimentally by positronium-annihilation-lifetime spectroscopy (PALS). In organic glasses, including amorphous polymers, the ortho-positronium (*o*-Ps) bound state of a positron has a strong tendency to localize in heterogeneous regions of low electron density. *In vacuo*, an

o-Ps quasiparticle has a well-defined lifetime, τ_3 , of 142 ns. This lifetime is cut short in condensed matter via the “pick-off” mechanism whereby *o*-Ps prematurely annihilates with one of the surrounding bound electrons. The quantum mechanical probability of *o*-Ps “pick-off” annihilation depends on the electron density of the medium, or the size of the heterogeneity. Typically the heterogeneity is assumed to be a spherical hole [57, 58] so that τ_3 can be easily related to an average radius R_h of the hole by $\tau_3 = [1 - R_h/R_0 + (2\pi)^{-1} \sin(2\pi R_h/R_0)]/2$. Here $R_0 = (R_h + \Delta R)$ and ΔR , the depth of penetration of *o*-Ps into the electron cloud surrounding the hole, is a constant ≈ 1.66 Å. The measured PALS relative intensity I_3 is commonly assumed to be proportional to the number density of the holes. Hence the free-volume fraction is given by the relation $f(T) = K_h V_h(T) I_3(T)$, where $V_h = 4\pi R_h^3/3$ is the mean free-volume hole size and K_h is a proportionality constant determined by various methods [59–61]. The microstructures of polymers have been profitably studied by PALS under various conditions, such as monitoring the effect of physical aging [62, 63]. Another application of PALS is the measurement of the hole volume over an extended temperature range from below T_g to high above T_g [60, 64, 65]. The temperature dependence of the hole volume is then compared with that of the dynamic properties of the glass-formers measured with various spectroscopic techniques such as dielectric relaxation [64], light scattering [66] and neutron scattering [66, 67]. The changes of dynamic properties of glass-formers across T_g and in the equilibrium liquid state with temperature correlate well with the thermal variations of the hole-volume parameters, τ_3 and I_3 , or with $f(T) = K_h V_h(T) I_3(T)$. An example of such correlations for poly(methyl methacrylate) is shown in Fig. 2.12, where the free-volume fraction deduced from PALS and the intensity of the fast relaxation measured by quasi-elastic neutron scattering as well as quasi-elastic light scattering (QELS) have similar temperature dependences. This correlation is intriguing because the fast relaxations are measured on the 10^{-12} s timescale, whereas the free-volume concept applies to longer times. We shall return to discuss this and a similar situation in Section 2.5.3.

Several other models based on free volume intended for other uses have been presented [8]. Together they can explain the dependence of the glass-transition temperature on molecular weight, cross-link density, mechanical deformation, plasticizer content, blending with another polymer, etc. However, the applicability of the models to polymers is confined to glass-transition behavior and thermodynamics (pressure–volume–temperature relations) and they do not address the temperature dependence of the viscoelastic response of motion on longer length-scales in polymers. Thus, if one’s main interest is in the viscoelastic properties of polymers, these models offer no serious connection. Since one of the main goals of this chapter is to tie together glass transition and viscoelastic properties, no further discussion of these other free-volume models is given. A review of these models

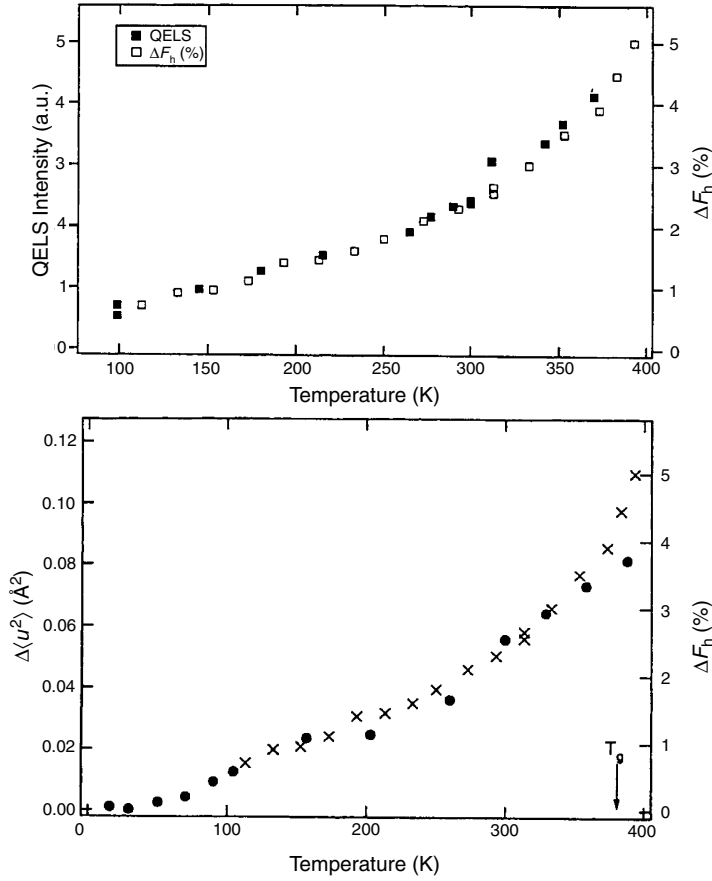


Fig. 2.12. Upper part, a comparison between the QELS intensity (■) and the dynamic hole volume fraction, ΔF_h , (□) as a function of temperature. Lower part, a comparison between the quasi-elastic-neutron-scattering mean-square displacement, $\Delta\langle u^2 \rangle$, (●) and the dynamic hole volume fraction ΔF_h , (+). From Mermet *et al.* [66], by permission.

together with their success and shortcomings for describing the glass-transition phenomena can be found in [8].

2.3.2 Thermodynamic glass-transition theories

The experimentally observed glass transition is observed to be a kinetic phenomenon and the glass-transition temperature T_g is determined by kinetics. Nevertheless, one cannot exclude the possibility of the existence of a true thermodynamic transition responsible for the slowing down of the molecular motions. The thermodynamic transition, if it exists, would occur at some temperature below T_g , had kinetics

not preempted its observation. Belief in this scenario is motivated by Kauzmann's extrapolation [37] to lower temperatures of the entropy of the equilibrium liquid of some nonpolymeric glass-formers and his observation that the extrapolated entropy of the liquid would become less than that of the crystalline solid at temperatures not far below T_g . Of course, the entropy of the liquid cannot be less than that of the crystal, and this paradoxical possibility is hereafter called the Kauzmann paradox. Although Kauzmann himself did not suggest that there is a thermodynamic glass transition, his paradox has become a motivating force behind the constructions of thermodynamic transition theory to explain the glass-transition phenomena. The Gibbs–DiMarzio theory [46, 47] starts with the application of the Flory–Huggins [68] lattice model of a polymeric system to calculate the partition function under some assumptions. The important quantity is the configurational entropy, S_c , which is determined by the number of allowed arrangements of the molecules on the lattice. As the polymer is cooled at constant pressure this number decreases because the number of holes decreases following the decrease in volume, and the increasing preference of the chains for low-energy states. Hence S_c decreases with cooling and a second-order thermodynamic transition occurs at T_2 , where S_c first becomes zero.

Consistently with the Gibbs–DiMarzio theory for a thermodynamic glass transition, Adam and Gibbs [36] constructed a model in which the configuration entropy S_c determines the rate of structural relaxation. The entropy crisis noted by Kauzmann led Adam and Gibbs to propose that the rearrangements over energy barriers of molecular units must be cooperative, involving a number of molecular units z^* that necessarily increases with decreasing temperature. Several assumptions were made in the theory of Adam and Gibbs. The first one is that the transitions of the cooperative regions involve the z^* molecules surmounting simultaneously the individual potential energy barriers, $\Delta\mu$, hindering their cooperative rearrangement, which is a temperature-independent constant. The relaxational correlation function is $\phi(t) = \exp[-t/\tau(T)]$, where $\tau(T) = \tau_\infty \exp[z^* \Delta\mu/(RT)]$ and τ_∞ is the relaxation time at infinite temperature. The temperature dependence of z^* is determined by the molar configurational entropy $S_c(T)$: $z^*(T) = N_A s_c^*/S_c(T)$, where s_c^* is the entropy of the smallest number of rearranging molecular units and N_A is Avogadro's number. These equations combined yield

$$\tau(T) = \tau_\infty \exp\left(\frac{\Delta\mu s_c^*}{kT S_c}\right) = \tau_\infty \exp\left(\frac{C}{T S_c(T)}\right) \quad (2.20)$$

The value of $S_c(T)$ is computed from

$$S_c(T) = \int_{T_2}^T \frac{\Delta C_p(T')}{T'} dT' \quad (2.21)$$

where $\Delta C_p(T)$, the configurational heat capacity, is the difference between the experimental measured heat capacities of the liquid and the crystal. Examples of calculations of $S_c(T)$ from calorimetric data for some nonpolymeric and polymeric glass-forming materials can be found in [69–75]. With $S_c(T)$ determined, one can test Eq. (2.20) by plotting $\log \eta(T)$ versus $(TS_c)^{-1}$ [69] or $\log \tau(T)$ versus $(TS_c)^{-1}$ [71, 76, 77]. The data show the linear dependence of Eq. (2.20) at lower temperatures, but invariably there is deviation above some characteristic temperature, T_B , for organic glass-formers. Evaluation of $S_c(T)$ for some polymers is hampered by the failure of the material to exhibit clear crystallization, and hence a direct test of Eq. (2.20) is not possible.

If $\Delta C_p(T)$ were independent of temperature, the equilibrium configurational entropy $S_c(T)$ from Eq. (2.21) would be given by $\Delta C_p(T) \ln(T/T_2)$. This expression is the origin of Eq. (2.6), which, together with Eq. (2.5), introduces nonlinearity into structural recovery. If the temperature dependence of $\Delta C_p(T)$ is well approximated by the hyperbolic expression, $\Delta C_p(T) = A/T$, which is the case for some glass-formers [75], then $\Delta S(T) = A(T - T_2)/(TT_2)$, which, after substitution into Eq. (2.20), leads to the equation

$$\tau(T) = \tau_\infty \exp[BT_2/(T - T_2)] \quad (2.22)$$

This equation is a special form of the empirical Vogel–Fulcher–Tammann–Hesse (VFTH) equation [78–80],

$$\tau(T) = \tau_\infty \exp[A/(T - T_0)] \quad (2.23)$$

where T_0 is a temperature below T_g , and A , like B in Eq. (2.22), is a constant. For polymers the temperature dependence of $\Delta C_p(T)$ is weaker than the hyperbolic relation and Eq. (2.22) is at best an approximation. It is easy to verify that the VFTH equation and the WLF equation (2.16) are equivalent in the sense that they gave essentially the same temperature dependence.

The Gibbs–DiMarzio theory offers predictions including of the change in heat capacity at T_g , and of the dependence of T_g on various variables including molecular weight, cross-link density, mechanical deformation, plasticizer content, and blending with any polymer. These predictions explain well the data which are discussed next, in conjunction with the alternative explanations from the free-volume models.

2.4 Dependences of T_g on various parameters

The glass-transition temperature of a particular polymer depends on various controllable parameters such as molecular weight, diluent concentration, cross-link density, tacticity, degree of crystallinity, pressure, and mechanical deformation.

The following subsections consider the effects of changes in these various parameters on the glass-transition temperature T_g . A more fundamental understanding of the glass transition requires other properties of the molecular motions of structural relaxation (such as time/frequency dependence), not just T_g , to be specified. The effects of the various controllable parameters on these other properties also are of interest, and will be discussed later in Section 2.5.

2.4.1 Molecular weight

There is a significant dependence of the glass-transition temperature on the molecular weight of the polymer for linear polymers. A linear polymer chain has two chain ends. Intuitively it is obvious that, at any temperature, each chain end has higher mobility than that of the inner repeat units because a chain end is bonded on one side to other repeat units, whereas an inner repeat unit is bonded on both sides. On decreasing the molecular weight, M , the concentration of chain ends increases and the mobility averaged over all repeat units is enhanced, resulting in a decrease in T_g . Experimental data show that the decrease of T_g with increasing concentration of chain ends is well described by the so-called Fox–Flory equation [81, 82]: $T_g(M) = T_g(\infty) - K/M$, where $T_g(\infty)$ is the glass-transition temperature for the polymer with infinite molecular weight and K is a constant. Usually $T_g(M)$ becomes constant at molecular weights larger than the critical molecular weight for entanglement (see Chapter 3, by W. W. Graessley) and thus the Fox–Flory equation is no longer valid beyond some upper bound of M . There is also a lower bound for validity of the equation.

In terms of the free-volume concept, by virtue of its greater mobility, a chain end necessarily has associated with it a greater free volume. If θ is the excess free volume per chain end, N_A Avogadro's number, and ρ the density, then the excess free volume per chain is 2θ , that per mole of chains is $2\theta N_A$, that per unit mass of chains is $2\theta N_A/M$, and, finally, that per unit volume of chains is $(2\theta N_A/M)\rho$. If f_g is the fractional free volume at the glass-transition temperature $T_g(\infty)$ for the polymer with infinite molecular weight, then the presence of the excess fractional free volume in the linear polymer with molecular weight M means that it is still a liquid at $T_g(\infty)$. It has to be cooled down to a lower temperature $T_g(M)$ before the excess free volume is lost and glass transition occurs. This temperature can be deduced from the assumed temperature dependence of the fractional free volume (Eq. (2.18)), now written as $2N_A\rho\theta/M = \alpha_f[T_g(\infty) - T_g(M)]$. After rearranging this equation, $T_g(M)$ is given by

$$T_g(M) = T_g(\infty) - 2N_A\rho\theta/(\alpha_f M) = T_g(\infty) - K/M \quad (2.24)$$

which is the Fox–Flory equation.

The molecular weight dependence of T_g of linear polymers was obtained by application of the Gibbs–DiMarzio theory [8]. The derivation is complicated and will not be reproduced here. The result reveals a decrease with decreasing M and, with one parameter, fits some data well. An interesting prediction on the molecular weight dependence of T_g is the difference between linear chains with open ends and chains with ends closed to form uncatenated rings [83, 84]. The T_g of small rings is predicted to increase with decreasing molecular weight. There is a limited amount of experimental data on the dependence of T_g on the molecular weight of rings. The data concerning T_g of poly(dimethyl siloxane) (PDMS) rings [85] exhibit the predicted increase. Plotted against the logarithm of the number of repeat units in Fig. 2.13 is the reference temperature T_s of the WLF equation, $\log[\tau(T)/\tau(T_s)] = -C_1(T - T_s)/(C_2 + T - T_s)$, which has been used to fit the temperature dependence of the dielectric relaxation time τ of linear and cyclic PDMS [86]. The reference temperature was chosen such that $\tau(T_s) = 1$ s. The T_s of linear PDMS is well described by the M^{-1} dependence of the Fox–Flory equation (2.14). On the other hand, the T_s of cyclic PDMS increases when the average number of repeat units falls below about 14, but at about 7.5 it levels off to the maximum value. Similar behavior of the calorimetric T_g has also been observed for cyclic poly(methylphenyl siloxane) [87]. For cyclic polystyrene, a sample with $M_n = 4.36 \text{ kg mol}^{-1}$ has a calorimetric glass temperature of 373.7 K (at a cooling rate of 10 K min^{-1}) [88], which is significantly lower than the predicted value of 411 K [84]. All indications are that the theory over-estimates the increase of T_g for rings. Although no free-volume model has addressed the increase in T_g for

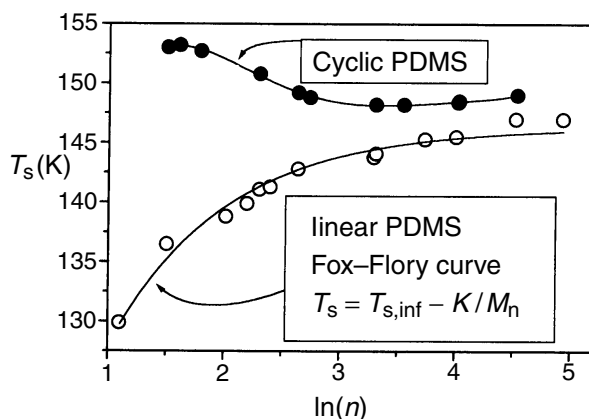


Fig. 2.13. The reference temperature T_s of the WLF equation used to fit the temperature dependence of the dielectric relaxation time τ of linear and cyclic PDMS plotted against the logarithm of the number of repeat units of PDMS. From Kirst *et al.* [86], by permission.

low molecular weights for cyclic polymers, one cannot exclude the simple explanation of there being a decrease in free volume with decreasing ring size as the rings become tighter and tighter. Measurements of free volume in rings by PALS may help to investigate this possibility.

The change of T_g , or equivalently the change of the effective structural-relaxation time τ , with molecular weight is not the only information of interest. The relaxation spectrum gives more insight into the dynamics of the local segmental motion, which is responsible for the glass transition. Hence it is also important to investigate the possibility that the relaxation spectrum changes with molecular weight. Such an undertaking was accomplished by performing measurements of the relaxation spectra of a low molecular weight linear polystyrene ($M_n = 1.1 \text{ kg mol}^{-1}$, $M_w/M_n = 1.03$, $T_g = 40^\circ\text{C}$) as a function of temperature using photon-correlation spectroscopy [89]. These measurements combined with previously obtained creep-compliance measurements [90] showed that the relaxation spectrum of low molecular weight polystyrene is strongly temperature dependent, narrowing with increasing temperature. This behavior, which is not found for high molecular weight polystyrene ($T_g = 100^\circ\text{C}$), is attributed to blending of the more-mobile chain ends with the less-mobile inner repeat units. Fluctuations in concentration of the two components, similar to those found in binary mixtures and miscible polymer blends (see Section 2.4.3), give rise to broadening of the relaxation spectrum which is temperature dependent.

2.4.2 Diluents

Usually diluents or solvents with lower T_g s of their own decrease the T_g of a polymer [91]. This can be seen in Fig. 2.14, where the T_g of polystyrene in a number of solvents decreases monotonically with the weight fraction of the solvent. On the other hand, the T_g s of solutions of a polymer in solvents with higher T_g s of their own will usually be higher than that of the neat polymer [92]. Both the free-volume approach and the Gibbs–DiMarzio theory provide accounts of the change of T_g with diluent content. The free-volume approach starts with Eq. (2.18) for the fractional free volume, $f_i = f_g + \alpha_{fi}(T - T_{gi})$, for the two components, $i = p$ and d , which stand for the polymer and the diluent, respectively. Assuming that f_g is the same for both and that the fractional free volume of the mixture is the sum of the f_i s of the two components weighed by their volume fractions ϕ_i , T_g is given by the Kelly–Bueche equation [93], $T_g = [\phi_p \alpha_{fp} T_{gp} + (1 - \phi_p) \alpha_{fd} T_{gd}] / [\phi_p \alpha_{fp} + (1 - \phi_p) \alpha_{fd}]$.

This equation and the counterpart from Gibbs–DiMarzio entropy theory [8] can fit the data quite well when some of the parameters therein are taken as adjustable. They give a *single* T_g for the mixture. However, for polystyrene dissolved in *m*-tricresyl phosphate (TCP), DTA measurements [94] indicated the existence of double T_g s

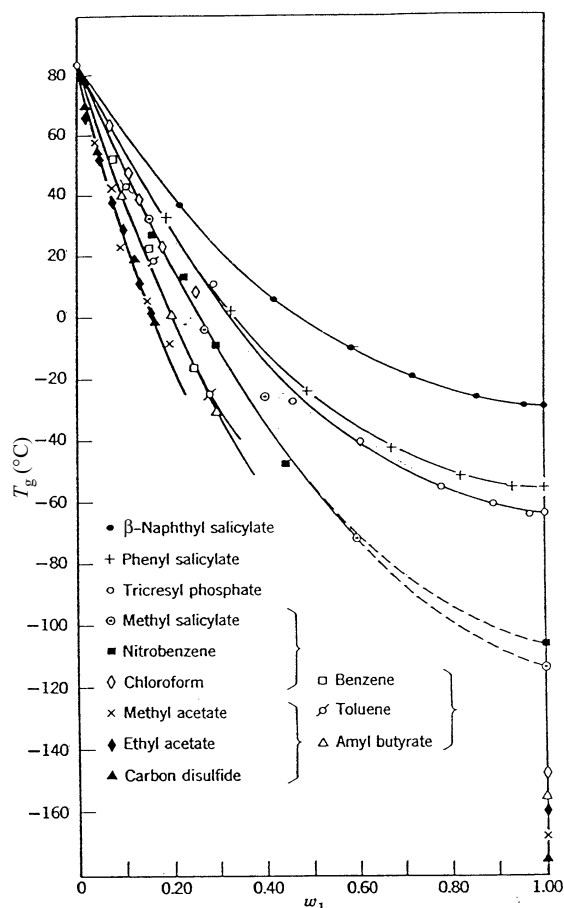


Fig. 2.14. The variation with concentration of T_g of PS in 12 different solvents. w_1 is the weight fraction of solvent. From Jenckel and Heusch by permission [91].

for solutions with lower polymer concentrations, as shown in Fig. 2.15. The higher T_g s reflect those of the local segmental motion of the polymer in an averaged solvent-altered environment and the lower T_g s reflect the motion of the solvent molecules in the presence of the polymer. Thus, there are *intrinsic* differences between the relaxation properties of the two components in polymer solutions, which are neglected in the treatments employing free-volume and entropy theories. For completeness, one should go beyond the two T_g s to include dynamic properties such as mechanical or dielectric dispersions (i.e. frequency or time dependences) of the two components. The effects due to fluctuations in concentration of the two components also have to be taken into account (see the following Section 2.4.3).

The facts that the dynamics of the solvent is modified by the polymer and is distinctly different from that of the polymer in the mixture have been confirmed

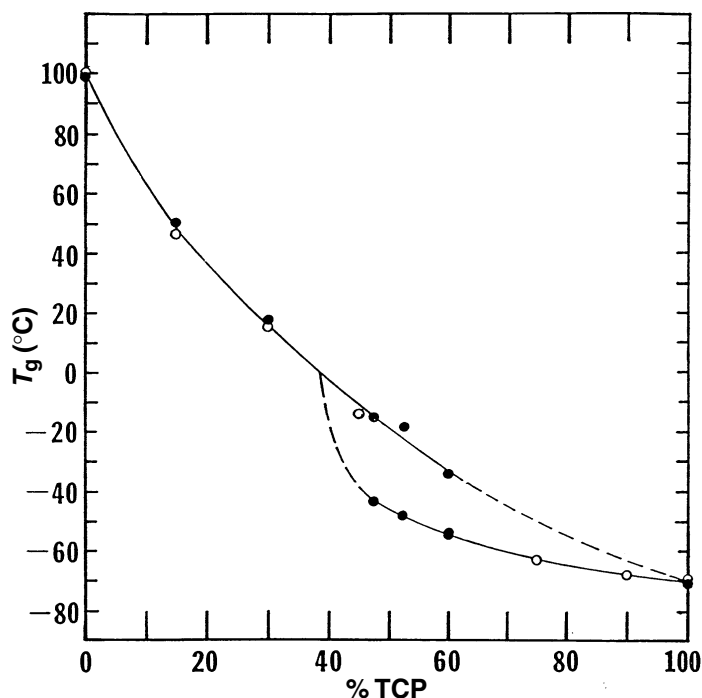


Fig. 2.15. The T_g s of a polystyrene dissolved in *m*-tricresyl phosphate (TCP) as a function of the weight percentage of the solvent. From Plazek *et al.* by permission [94].

by other techniques for other polymer solutions [95–99]. Furthermore, there are solutions in which the solvent's mobility is *increased* by the presence of a polymer whose undiluted T_g is higher than that of the solvent [98, 100]. Free-volume and entropy theories cannot explain these effects and the additional concept of intermolecular coupling has to be introduced [98, 100]. It is worthwhile to point out that some of the effects seen in polymer solutions are found also in binary miscible polymer blends [101], which will be discussed in the next section.

2.4.3 Blending

Equations for T_g based on the free-volume concept have been proposed for miscible polymer blends and they are similar to the Kelly–Bueche equation given above for polymer–diluent systems. Likewise, this description in terms of a single T_g over-simplifies the dynamics of the components in the blend and neglects some important elements. An important element for interpreting the relaxation behavior of blends is fluctuations in concentration or composition [102]. Models have been

proposed in order to address specifically the fluctuations in composition and the effect of local composition on the glass-transition temperature and the dynamics [103, 104]. However, these models have not taken into account another physical element, which is the intrinsic difference between the local segmental mobilities of the components. The first direct evidence that the two components of a miscible polymer blend have different local segmental dynamics came from solid-state ^{13}C NMR spectroscopy on PIP–PVE blends [105]. The solid-state ^{13}C MAS NMR technique allows the components of a blend to be differentiated by their isotropic chemical shifts. Later, results from a two-dimensional NMR study confirmed that the two components have significantly different mobilities [106]. Combined mechanical and dielectric spectroscopies were used to determine the different local segmental dynamics of the two components in this blend [107], yielding results in quantitative agreement [108] with subsequent deuterium NMR measurements [109]. Neutron-scattering measurement [110, 111] on the same blends at temperatures high above the T_g s of both components also found the differences in the local segmental mobility of the components. At such high temperatures, models based solely on fluctuations in concentration [103, 104] would not predict such a difference between the mobilities of the two components and hence they are inadequate for explaining blend dynamics.

Actually, an early model for the dynamics of polymer blends [112, 113] had correctly taken into account both the differences in intrinsic mobility of the components and the local compositional heterogeneity arising from fluctuations in concentration. On top of these two physical aspects, an effect due to intermolecular coupling between the relaxing units was also taken into account in this model. Through the component's own intrinsic mobility, the dynamics of local segmental relaxation depends on which component it originates from. It also depends on the complexion of its local environment because the intermolecular coupling considered depends on the constraint imposed by the molecular units in its environment, and the constraint in turn depends on the complexion. Thus, fluctuations in concentration engender a distribution of intermolecular coupling parameters. In the framework of another model, based on the concept of local concentration biased by chain connectivity, there was proposed a method for calculating the different effective T_g s of the two polymers in the blend [114]. This model is consistent with separate mobilities of the two components because of different local concentrations, but no prediction on dynamics has been given so far.

The component dynamics in polymer–diluent mixtures discussed in the previous section are similar to those of polymer blends, such as the appearance of two different T_g s (Fig. 2.15). Thus, a theory of component dynamics of polymer blends is robust only if it is also applicable to polymer–diluent mixtures and can explain the anomalous component dynamics found therein [98–101]. If it can be extended

to polymer–diluent mixtures, one also should continue to explain the dynamics of a probe molecule in polymers [115–117], i.e. in the limit of a very low concentration of diluent. This limit is interesting because each probe molecule sees the same environment, thus eliminating fluctuations in concentration. Nevertheless, there remain challenging phenomena in the dynamics of the probes to be explained [98–100]. In fact, there is experimental evidence for a dependence of the relaxation dynamics of the probe on the degree of constraint imposed by its local environment, measured in terms of the ratio, τ_c/τ_α , where τ_c is the rotational relaxation time of the probe and τ_α is the local segmental relaxation time of the host polymer [100]. Also, different probes in the same polymer are found to have different mobilities and dynamics, analogously to the distinct intrinsic mobilities of the two components in a blend. These findings in the simpler system indicate the need to incorporate coupling of the local segmental relaxation of each component at any location to its local environment in studies of polymer blends.

Naturally, a theory of polymer-blend dynamics is less desirable if it is constructed just for explaining the local segmental dynamics of polymer blends, but has no utility for the consideration of problems related to local segmental dynamics in homopolymers. Some examples of challenging problems regarding homopolymers will be discussed in Sections 2.5 and 2.6.

2.4.4 Cross-linking

The introduction of cross-links into a polymer strongly affects the local segmental relaxation, and hence the T_g , through the restrictions imposed by the network junctions. These restrictions reduce the configurational degree of freedom or the free volume, and thereby increase the T_g . This effect increases with increasing ρ , the number of cross-links per gram [82]. However, in cross-linking, a specific cross-linker has to be added to the polymer. This modifies the chemical structure of the polymer and influences the T_g . The increase in T_g with cross-linking can be understood by invoking the decrease of the specific volume (and hence possibly the free volume) because of the replacement of van der Waals interactions by the shorter covalent bonds [82]. It has also been explained by the Gibbs–DiMarzio theory [118].

There are other changes in the local segmental dynamics caused by cross-linking, beyond just an increase in the T_g . For example, the dispersion of the local segmental relaxation systematically broadens with increasing cross-link density [119]. These additional features in the dynamics indicate that there is an increase of intermolecular coupling with cross-linking.

Complementary to the study of the effects of cross-linking on the local segmental relaxation is the investigation of the dynamics of the network junctions of a

cross-linked polymer. A specific chemical moiety can link up a fixed number of polymer chains at a junction point. The formation of multiple junction points converts the polymer chain into a network. The dynamics of the junctions has been studied experimentally using NMR techniques [120, 121]. The constraint on the motion of the junctions is expected to be decreased by lowering the density of junctions or addition of a diluent. These expected changes in intermolecular coupling and their effects on the junction relaxation time and dispersion were indeed observed in the NMR measurements of the junction dynamics [120, 121].

2.4.5 Crystallinity

Nearly all crystalline polymers contain chain segments that do not reside in a crystalline lattice. Usually these noncrystalline segments can be considered to constitute an amorphous phase, which can therefore become glassy. The T_g of this amorphous phase depends on the degree of crystallinity. It can increase or decrease with the degree of crystallinity, depending on the relative density of the amorphous and crystalline states. Most often the more orderly crystalline state has the higher density and the molecular chains in the amorphous region are constrained by being anchored to the immobile crystallites [122]. The constraints reduce the mobility of the local segmental motion and the T_g increases. On rare occasions the crystalline state has a lower density than that of the amorphous material [123]. In this case, there is less constraint on the noncrystalline chain segments, which increases the entropy, causing T_g to decrease.

2.4.6 Chain stiffness and internal plasticization

Chain stiffness can be increased by inserting longer rigid units such as *para*-phenyl rings into the chain backbone or by adding more bulky side groups such as in polystyrene, which drastically increases the potential-energy barriers to rotation and causes a substantial increase in T_g . An increase of steric hindrance to rotation occurs in some cases if a second side group is introduced at alternate chain-backbone carbon atoms, also causing an increase in T_g . The pair poly(methyl methacrylate) (PMMA) ($T_g = 115^\circ\text{C}$) and poly(methacrylate) (PMA) ($T_g = 14^\circ\text{C}$) and the pair poly(α -methyl styrene) (P α MS) ($T_g = 168^\circ\text{C}$) and polystyrene ($T_g = 100^\circ\text{C}$) illustrate the effect. On the other hand, introducing additional methylene ($-\text{CH}_2-$) groups or oxygens into the backbone lowers T_g because of the increase in flexibility of the chain.

If the modification of the structure is an increase in length of the side chains brought about by introducing flexible units, it is generally observed that T_g decreases. Examples include attaching the flexible alkyl side chains to polymers to

yield series such as the acrylates, methacrylates, α -olefins, and *p*-alkylstyrenes, and to side-chain liquid-crystalline polymers. The decrease of T_g caused by “internal plasticization” is ostensibly due to either the increase of fractional free volume or the increase in configurational entropy in terms of the Gibbs–DiMarzio theory arising from the presence of the flexible linear side chains. However, there is evidence that a decrease in intermolecular coupling or constraints of the repeat units in the backbone is brought about by the presence of the flexible alkyl side [124, 125], and this effect contributes also to the decrease in T_g .

2.4.7 Tacticity

Stereochemical variations in tacticity in most polymers that possess only one substituent on every second carbon atom (i.e. PMA and polystyrene) have no measurable effect on the T_g . However, they have a substantial effect on the T_g of polymers such as PMMA and P α MS [126]. The explanation appears to lie in the added steric repulsion hindering rotation, which is due to the presence of the asymmetric double side groups on alternate chain-backbone carbon atoms of PMMA and P α MS. There is a significant difference between the T_g of syndiotactic PMMA (115 °C) and that of isotactic PMMA (45 °C). Concomitantly, there is an interesting difference in the relaxation dynamics [6, 127]. Highly syndiotactic samples of PMMA have a dominant secondary β -relaxation loss peak in the dielectric spectrum that is well resolved from the primary α -relaxation peak, whereas in isotactic PMMA the β -relaxation loss peak is weaker and lies closer to the α -relaxation peak. The lesser prominence of the β -relaxation in isotactic PMMA is reflected in a much smaller glassy compliance (higher glassy modulus) [128].

2.4.8 Pressure

The T_g can be determined at various constant pressures by measuring the specific volume as a function of temperature [129, 130]. Typically, the T_g increases with pressure at the rate of approximately 20 °C per 1000 atm (1 atm = 101 323 Pa). One also can observe the glass transition as a function of pressure at constant temperature by measurement of the specific volume. The break in the slope of the curve of specific volume versus pressure gives the glass-transition pressure at various temperatures. In analogy to a temperature jump, a rapid change in pressure will cause structural relaxation and recovery that can be monitored by measuring a time-dependent change in volume. The responses recorded by Goldbach and Rehage are similar to temperature jumps [131].

An increase in pressure on an amorphous material increases the molecular crowding. Concomitantly, the free volume is reduced in the context of the free-volume

model and the entropy is decreased according to the entropy theory. Thus, regardless of which point of view is taken, an increase of T_g is expected when a polymer is subjected to hydrostatic pressure. A qualitative prediction of the effect was given from the free-volume approach [129].

The effect of pressure on the local segmental α -relaxation and the secondary β -relaxations at temperatures above T_g was assessed by dielectric measurements on a number of systems in the early 1960s [7]. It was found that pressure exerts a stronger influence on the α -relaxation than it does on the secondary β -relaxations. However, since then and until only recently, the lack of a versatile experimental set-up put a halt to these studies and made pressure, for a number of years, the “forgotten” variable in the study of dynamics. Recent advances in techniques have rejuvenated the study of dynamics with pressure. The introduction of pressure as a variable in addition to temperature in the study of the local segmental relaxation makes possible a test of whether the specific volume plays a role in determining the relaxation time. This test is performed by making dielectric-relaxation measurements as a function of temperature separately under isochoric (constant-volume) and isobaric (constant-pressure) conditions. Such measurements on poly(vinyl acetate) (PVAc) in the equilibrium liquid state have been analyzed [132]. The results on the temperature dependence of the dielectric-relaxation times for PVAc at atmospheric pressure and at three constant volumes are shown in Fig. 2.16. The slopes at the intersection of the isobaric and isochoric lines yield values for the respective activation energies at constant pressure and constant volume: $E_a = 250$ and 437 kJ mol^{-1} ($\tau = 1 \text{ s}$), $E_a = 293$ and 490 kJ mol^{-1} ($\tau = 10 \text{ s}$), and $E_a = 330$ and 553 kJ mol^{-1} ($\tau = 100 \text{ s}$). The ratio of the isochoric and isobaric activation energies is a measure of the relative contribution of thermal energy and volume; that is, this ratio would be unity if the molecular motion were entirely thermally activated, and zero if it were strictly dominated by density. For PVAc, the ratio is ≈ 0.6 , indicating that both contributions are significant. The same conclusions have been drawn from similar experimental data for a number of small-molecular glass-forming liquids including the diglycidylether of bisphenol A and 1,2-diphenylbenzene [133]. These results from pressure studies support the hypothesis that structural relaxations in glass-formers are at least in part dependent on the specific volume and perhaps also on the free volume.

2.4.9 Polymer thin films

Reductions of the T_g had been found in polymers confined to form a thin film on a substrate [134, 135]. When the substrate is eliminated by making a free-standing thin polystyrene (PS) film, even larger reductions of T_g and the local segmental-relaxation time have been observed as the thickness of the films is decreased [136].

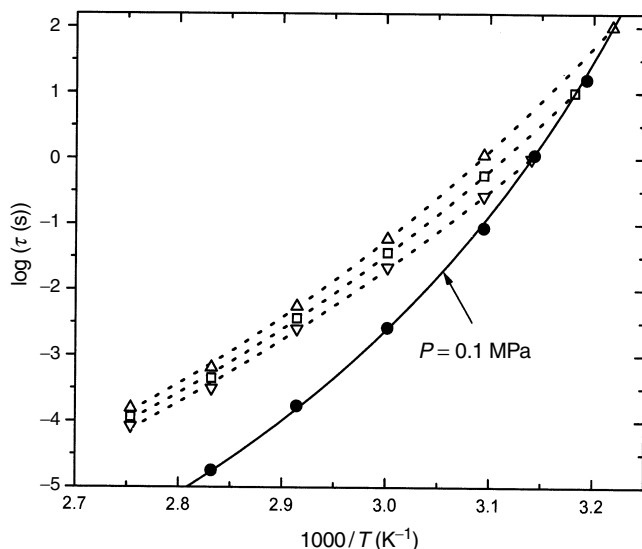


Fig. 2.16. Temperature dependences of the dielectric relaxation times for PVAc at atmospheric pressure (●) and at a constant volume equal to 0.847 ml g^{-1} (Δ), 0.849 ml g^{-1} ($\square$), and 0.852 ml g^{-1} (∇). The slopes at the intersection of the isobaric and isochoric lines yield values for the respective activation energies at constant pressure and constant volume: $E_a = 238$ and 448 kJ mol^{-1} ($\tau = 2.5 \text{ s}$) and $E_a = 166$ and 293 kJ mol^{-1} ($\tau = 0.003 \text{ s}$). The ratio of the isochoric and isobaric activation energies is a measure of the relative contribution of thermal energy and volume; that is, this ratio would be unity if the molecular motion were thermally activated, and zero if it were strictly dominated by density. For PVAc, the ratio is ≈ 0.6 , indicating that both contributions are significant. From Roland and Casalini by permission [132].

Since the density of the free-standing PS thin films has been measured [136] to be comparable to that of the bulk PS and there is the absence of the interfacial interaction, the large reductions of T_g found seem to be nontrivial (Fig. 2.17). It was suggested that the cause of this increase in local segmental mobility is a decrease of intermolecular coupling between the local segmental motions in freely standing thin films [137, 138]. The reduction of intermolecular coupling is possibly due to several causes. First, orientations of the chains parallel to the surface are induced when the thickness of the film, h , is smaller than the end-to-end distance of the polymer in the bulk, $\langle r \rangle$, and motion of parallel chain segments in the chain-backbone direction encounters a smaller occupied volume. Secondly, the presence of free surfaces enhances the mobility of nearby repeat units. Thirdly, the slowing down of local segmental motions with decreasing temperature is caused by the cooperative involvement of more and more molecules, i.e. growth of the cooperative length-scale, as suggested by the entropy model [36]. Hence mobility is enhanced in thin

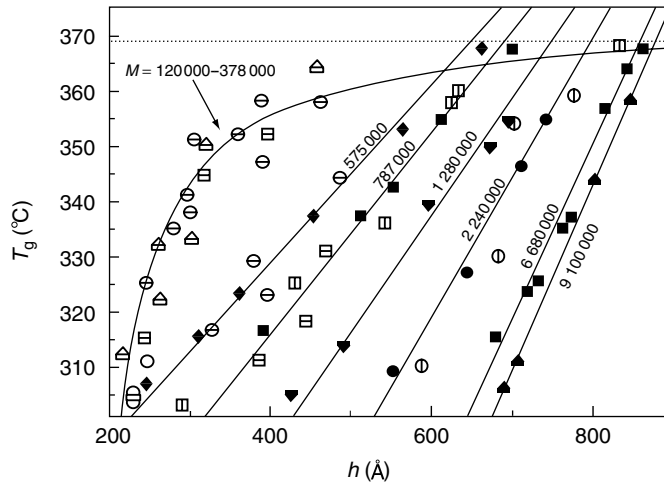


Fig. 2.17. Measured T_g s for free-standing films. The solid symbols were obtained with ellipsometry. The hollow symbols were obtained using Brillouin light scattering. From Forrest and Dalnoki-Veress by permission [136].

films when h becomes not much larger or less than the cooperative length-scale. Confirmation of these suggestions [138] comes from results from recent Monte Carlo simulations [139, 140].

Much-thinner polymer films with thicknesses of the order of 1.5–2.0 nm have been obtained by intercalating the polymer poly(methylphenyl siloxane) (PMPS) within parallel layers of the inorganic layered silicates [141]. The result is well-ordered multilayers of extremely thin polymer films with a repeat distance of the order of 1.5 nm. The root-mean-square end-to-end distance of the chains is estimated to be of the order of 3 nm, which is about twice the thickness of the films, and hence there are significant induced orientations in the chains. The thickness is less than any estimate of the cooperative length-scale of bulk PMPS. These extreme conditions suggest that there has been a large decrease in intermolecular coupling in local segmental motions and a large increase in mobility in the thin films [138], which was observed by dielectric-relaxation measurements [141].

Computer simulations [139, 140] of thin films of low molecular weight polymer provided an interesting finding. The local segmental dynamics becomes faster with decreasing film thickness as usual, whilst the change for the modes of longer length-scale is much weaker [139]. The relaxation time for the Rouse mode was found to *increase* with decreasing film thickness, although the increase from the bulk value is not large [140]. These observed opposite dependences of the Rouse relaxation time and the local segmental relaxation time on film thickness are remarkable. An explanation based on intermolecular cooperativity in

the local segmental relaxation and the lack of it in the Rouse modes has been given [138].

Studies of polymeric thin films formed on substrates are of interest owing to their relevance to nanotechnologies such as lithography in the fabrication of electronic devices. The results on supported thin films are complicated by the possibility of chemical interaction or bonding of the polymer with the substrate. The interaction with, or bonding to, the substrate imposes a constraint on the molecular chains in the thin film and, just like the case in which the chains in the amorphous regions of crystalline polymers are constrained by being anchored to the immobile crystallites, T_g is raised. Hence, combined with the aforementioned effect that lowers T_g , variation of the interaction with the substrate can lead either to decreases or to increases in T_g [142]. This situation of supported polymeric thin film is similar to the case of small-molecule glass-formers confined in nanometer glass pores, where the dynamics of the liquid depends on the interaction with the wall [143].

2.4.10 Confinement in nanometer pores of glasses

A large reduction of T_g when nonpolymeric liquids are confined in nanometer-sized glass pores was observed for OTP and other glass-formers first by calorimetry [144]. The effect becomes more pronounced as the pore size is decreased. This interesting phenomenon has been confirmed by dielectric-relaxation [145] and light-scattering measurements [146], showing that a reduction of the structural-relaxation time at constant temperature can be brought about by confining the liquid in small pores. Care must be exercised to eliminate chemical bonding of the liquid molecules to the glass walls by chemical treatment of the latter. Work on confinement of polymers in glass pores has just started. Results of a recent investigation reported by Schönhals and co-workers on poly(dimethyl siloxane) (PDMS) confined in porous glass with a narrow pore-size distribution revealed similar effects [147]. The internal surfaces of the pores had been silanized in order to eliminate interaction between the polymer and the confining glass surfaces. Shown in Fig. 2.18 are plots of the dielectric-loss maximum frequency, f_p , versus $1000/T$ for bulk PDMS and for PDMS confined in porous glass with various average pore sizes as indicated. At constant temperature, f_p increases with decreasing pore size. The temperature dependence also becomes weaker and approaches nearly an Arrhenius dependence with an activation enthalpy typical of secondary relaxation in polymers.

2.5 Structural relaxation in polymers above T_g

Liquid–glass transition occurs when the molecular rearrangements (structural relaxation) necessary to alter the liquid structure in order to maintain the equilibrium

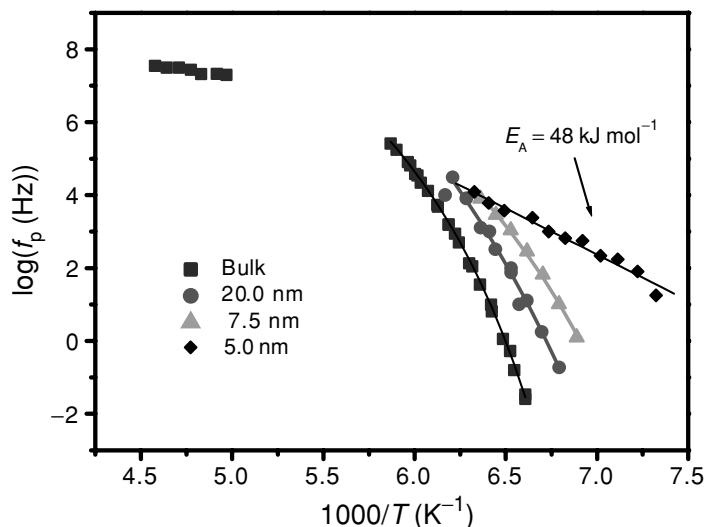


Fig. 2.18. The dielectric-loss peak frequency f_p versus $1000/T$ for bulk PDMS and PDMS confined in controlled porous glass with various average pore sizes as indicated. From Schönhals *et al.* by permission [147].

density and enthalpy become so sluggish that they cannot keep up with the rate of cooling of the liquid. Hence, for a more fundamental understanding of the glass transition on a molecular level, the nature of the molecular motions in the equilibrium liquid must be investigated. The molecular motions can be characterized in terms of the linear response of the liquid to a mechanical or electrical perturbation [1]. Associated with the molecular motions are fluctuations in density, which scatter light or neutrons, and the response function can be obtained from the spectrum of scattering intensity [13]. NMR offers many special methods [14]. These spectroscopic techniques give the time or frequency dependence of the molecular motions through correlation functions or scattering functions. Techniques such as creep compliance, stress relaxation, dielectric relaxation, and light scattering measure macroscopic quantities, whereas neutron scattering and various NMR methods yield more microscopic information. By employing several techniques with different spectral ranges, molecular motions can be probed over an immense range from terahertz (10^{12} Hz) down to 10^{-6} Hz. The wide spectral range also allows an investigator to monitor a particular molecular relaxation process across a broad range of temperature from below T_g to high above it.

There is a vast amount of literature on these investigations of many kinds of glass-forming liquids by use of various experimental techniques. The volume of data accumulated over the greater part of the last century until now would make any review a Herculean effort. Fortunately, general patterns have been found in the

dynamic properties of glass-forming liquids, including polymers, and they are used to our advantage for a concise description here and in more detail elsewhere [148].

2.5.1 Primary relaxation

Of primary interest in the glass transition is the structural relaxation that equilibrates density and enthalpy with a change in temperature. In amorphous polymers this is the local segmental relaxation. Unlike the case of nonpolymeric glass-formers, shear mechanical measurements of polymers have other contributions with longer length-scales and there is no obvious method by which to isolate the contribution of local segmental relaxation from the compliance or modulus data. However, there are other techniques that probe mainly the local segmental relaxation and these include dielectric relaxation, NMR relaxation, and quasi-elastic light scattering and neutron scattering.

The local segmental relaxation or α -relaxation in amorphous polymers is fitted well by the empirical KWW “stretched exponential” function (see also Eq. (2.9)),

$$\phi(t) = \exp[-(t/\tau_\alpha)^{1-n_\alpha}] \quad (2.25)$$

which was first reported by R. Kohlrausch in 1847 and 1854 for time-dependent phenomena [149] and in 1970 by Williams and Watts [33] for frequency-dependent dielectric relaxations. The exponent, $1 - n_\alpha$, in Eq. (2.25) is a fraction of unity often denoted by β . We prefer the way it is written in Eq. (2.25) to avoid confusion with the customary use of β to designate secondary relaxation. For dielectric relaxation, $\phi(t)$ is supposed to approximate the normalized dipole-moment autocorrelation function, $\phi(t) = \langle M(0)M(t) \rangle / \langle M^2(0) \rangle$. The complex permittivity, $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$, is given by

$$\frac{\varepsilon^*(\omega) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \int_0^\infty \exp(-i\omega t') [-d\phi(t')/dt'] dt' \quad (2.26)$$

where ε_0 and ε_∞ are the low- and high-frequency limits of $\varepsilon'(\omega)$. The KWW function has been found by many workers to give an adequate fit to the dielectric data for amorphous polymers and nonpolymeric supercooled liquids [7]. Invariably there is deviation at high frequencies, which is possibly due to the excess contributions from secondary relaxations. Photon-correlation spectroscopy (PCS) utilizes scattering of light by fluctuations in density to obtain directly the autocorrelation functions in the time domain [15, 34]. The local segmental mode is the main contributor to the fluctuation in density. Results of most PCS studies on bulk polymers as well as nonpolymeric glass-forming liquids have shown that the KWW functions are adequate representations of the experimental time-correlation functions for the density fluctuations. NMR-relaxation [14] and neutron-scattering [13] data were

fitted well by the KWW function. From the fits to data, n_α and the local segmental relaxation time τ_α in Eq. (2.25) are determined over some temperature range.

2.5.1.1 The local segmental relaxation time τ_α

The temperature dependence of τ_α is usually described well by the VFTH equation (2.23), or the equivalent WLF equation (2.16), where $a_{T,\alpha} \equiv \tau_\alpha(T)/\tau_\alpha(T_g)$, over a limited temperature range. The local segmental relaxation time τ_α of polystyrene was measured as a function of temperature by two-dimensional exchange NMR up to long times exceeding 100 s [150] together with deuteron spin-lattice-relaxation measurements of τ in the range 10^{-7} – 10^{-6} s. The actual data (not shown) are fitted well by the WLF equation, $\log[\tau_\alpha(T)/\tau_\alpha(T_g)] = -C_1(T - T_g)/(C_2 + T - T_g)$, where $T_g = 373$ K, $\tau_\alpha(T_g) = 100$ s, $C_1 = 16.35$, and $C_2 = 52.5$ K. The lower solid line in Fig. 2.19 is $\tau_\alpha(T)$ from the WLF fit and is drawn to span the same range as the measured $\tau_\alpha(T)$, and thus it truly represents the local segmental relaxation time. We compare the temperature dependence of $\tau_\alpha(T)$ with that of the shift factor, $a_{T,S}$, from time-temperature superposition of curves of the recoverable creep compliance, $J_r(t)$, in the glass-rubber softening region of another high molecular weight polystyrene described earlier (Fig. 2.11). Comparison is also made with the viscosity shift factor in Fig. 2.11, $a_T = \eta_0 T_0 \rho_0 / (\eta T \rho)$, now rewritten as $a_{T,\eta}$ to distinguish it from the others. Again only the WLF fits to $a_{T,S}$ and $a_{T,\eta}$ are shown in Fig. 2.19, and the range of $a_{T,\eta}$ shown by the line drawn corresponds to the actual measurements. We already know from the failure of time-temperature superpositioning in Fig. 2.11 that $a_{T,S}$ and $a_{T,\eta}$ do not have the same temperature dependence. By inspection of Fig. 2.19, we see that the NMR τ_α or $a_{T,\alpha}$ has the same temperature dependence as $a_{T,S}$ in the temperature range below 384 K, and, since NMR probes only local motion, the latter for $T < 384$ K are the shift factors of the local segmental motions. In this lower temperature range, the $a_{T,S}$ are determined principally from measurements of $J_r(t)$ that are less than 10^{-7} Pa $^{-1}$ [90] and we may infer that local segmental motions contribute no more than 10^{-7} Pa $^{-1}$ to the compliance. Later on we shall give a more exact estimate.

Above 384 K, τ_α starts to exhibit a stronger temperature dependence than does $a_{T,S}$. Between approximately 384 and 407 K, $a_{T,S}$ is determined by shifting recoverable compliance curves with $J_r(t)$ larger than 10^{-7} Pa $^{-1}$ and consists of Rouse modes and possibly some shorter-timescale modes in the plateau. Thus the NMR data give another proof that the local segmental relaxation time has a stronger temperature dependence than that of the Rouse modes [10, 11, 152]. Above approximately 407 K, the creep-compliance data are contributed entirely by the terminal viscoelastic mechanism, which has exactly the same temperature dependence as $a_{T,\eta}$. It is interesting to observe that the extrapolation of $a_{T,S}$ to this high-temperature regime reveals a temperature dependence that is different from (weaker than) the

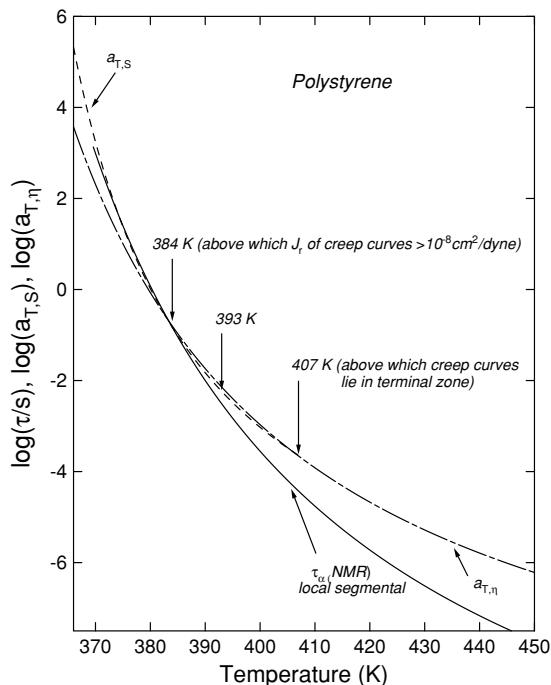


Fig. 2.19. The local-segmental-relaxation correlation time, $\tau_{\alpha}(\text{NMR})$, of high molecular weight polystyrene as a function of temperature obtained by two-dimensional exchange NMR [150] up to long times exceeding 100 s, and compared with the shift factor, $a_{T,S}$, from time-temperature superposition of curves of the recoverable creep compliance, $J_r(t)$, of another high molecular weight polystyrene (PS-A25) in the glass-rubber transition region [90]. Only the fits to the data of $\tau_{\alpha}(\text{NMR})$ (solid line) and $a_{T,S}$ (short dashed line) obtained by applying the WLF equation are given. The viscosity shift factor, $a_{T,\eta}$, is shown also (shot-dashed-long-dashed line). The NMR τ clearly has a stronger temperature dependence than does the viscosity over the *entire* temperature range. There is also good agreement between the temperature dependences of $\tau_{\alpha}(\text{NMR})$ and $a_{T,S}$ at temperatures below 384 K, where after $a_{T,S}$ becomes sequentially the shift factor first of the sub-Rouse modes and secondly of the local segmental modes as the temperature is decreased toward T_g .

actual shift factor for the viscosity. More important is that the NMR local segmental relaxation time τ_{α} or its shift factor $a_{T,\alpha}$ clearly has a stronger temperature dependence than does the viscosity shift factor $a_{T,\eta}$ throughout the *entire* temperature range shown in Fig. 2.19. The same conclusion was drawn for atactic polypropylene [152–154] by using PCS instead of NMR to measure $\tau_{\alpha}(T)$ and compare its shift factor $a_{T,\alpha}$ with $a_{T,S}$ and $a_{T,\eta}$ obtained from shear-creep and stress relaxation measurement [55]. The results are shown in Fig. 2.20, and they need no further explanation. The disparity between $a_{T,\alpha}$ and $a_{T,\eta}$ becomes larger as T_g is approached

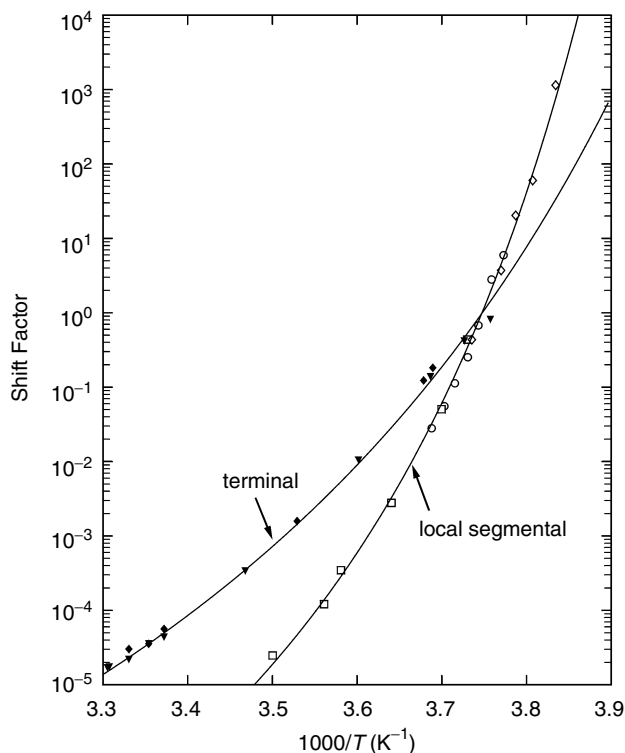


Fig. 2.20. Temperature dependences of the shift factors of the viscosity ($\blacktriangledown$), terminal dispersion ($\blacklozenge$), and softening dispersion ($\diamond$) of atactic polypropylene from the work of Plazek and Plazek [55]. The temperature dependence of the local segmental relaxation time was determined by dynamic light scattering ($\square$) [152] and by dynamic mechanical relaxation ($\circ$) [153]. The two solid lines are separate fits to the terminal shift factor and local segmental relaxation obtained by applying the Vogel–Fulcher–Tammann–Hesse equation.

from above, but conventional glass-transition theories (Sections 2.3.1 and 2.3.2) offer no explanation, indicating that an important piece of physics has possibly been neglected in these theories.

The simplest way to see the difference between the temperature dependences of $a_{T,\alpha}$ and $a_{T,\eta}$ is from the data on high molecular weight polyethylene and hydrogenated polybutadiene [155]. These flexible polymers have low T_g s and their viscosities have Arrhenius temperature dependences instead of the WLF dependence at rheological-measurement temperatures. The Arrhenius temperature dependence is basically characterized by its activation enthalpy $E_{A,\eta}$. Polyethylene has $E_{A,\eta} = 26.8 \text{ kJ mol}^{-1}$ [156]. On the other hand, ^{13}C NMR measurements of polyethylene at high temperatures in the picosecond range [157] revealed that the local segmental relaxation is best described by an exponential correlation function,

$\exp(-t/\tau)$, and that τ has an Arrhenius temperature dependence with activation enthalpy E_A equal to 16.7 kJ mol^{-1} and smaller than $E_{A,\eta}$. This activation enthalpy of local segmental motion is similar to the activation enthalpy of $3.6 \text{ kcal mol}^{-1}$ deduced [155] for conformational transition in an isolated polyethylene chain. It turns out to be almost the same as the internal rotational barrier of low molecular weight alkanes [155]. There is a relation between E_A and $E_{A,\eta}$. This is given in [155], but will not be discussed here because it is outside the scope of this chapter.

Although the temperature dependence of τ for amorphous polymers is described well by the WLF equation, as shown in Fig. 2.19, this is usually not the case for small-molecular organic glass-formers. Over an extended temperature range with τ varying from say 10^{-11} s or shorter to 10^2 s or longer, the temperature dependence is of Arrhenius form at short τ , but at longer times it is necessary to use one VFTH equation followed by another in order to describe the temperature dependence fully [158, 159].

2.5.1.2 The dispersion of the local segmental relaxation

The KWW function $\phi(t)$ (Eq. (2.25)) can always be rewritten as $\phi(t) = \sum_i g_i \exp(-t/\tau_i)$, which may lead one to the interpretation that the dispersion of the local segmental motions originates from a sum of exponential relaxation processes with different relaxation times τ_i weighted by the factors g_i . Macroscopic mechanical and dielectric measurements can neither support nor refute this interpretation. Thus, this easy interpretation of the dispersion of the local segmental relaxation has conveniently been used to rationalize the dispersion. This interpretation is, however, not correct in the light of microscopic probing of the local segmental relaxation. Results from multidimensional NMR experiments [41, 160] on poly(vinyl acetate) showed that the structural relaxation is dynamically heterogeneous. There are rapidly and slowly moving molecular units but they exchange roles on a timescale of the order of τ . Neutron-scattering measurement of the local segmental motion [13], having the advantage of studying the dependence of τ on q , the magnitude of the scattering wave vector, revealed the $q^{-2/(1-n)}$ -dependence of τ in the KWW function [161, 162]. On the other hand, τ_i in an exponential relaxation function, $\exp(-t/\tau_i)$, has the normal q^{-2} -dependence [15]. If $\phi(t)$ were the sum $\sum_i g_i \exp(-t/\tau_i)$, then either the average or the most probable relaxation time of $\phi(t)$ will have the q^{-2} -dependence, at odds with experimental data.

The KWW exponent, $1 - n_\alpha \equiv \beta_\alpha$, usually tends to increase with temperature, although the amount of change depends on the glass-former. Hence, comparison of β_α for various polymers should be made at the glass-transition temperature. Amorphous polymers of different chemical structures in general have different values of $\beta_\alpha(T_g)$ at the glass-transition temperature [163, 164]. A smaller $\beta_\alpha(T_g)$ corresponds to a larger width of the dispersion. The following questions naturally arise. (1) How does chemical structure enter into determining the width of the local

segmental relaxation characterized by $\beta_\alpha(T_g)$? (2) Is there a correlation between $\beta_\alpha(T_g)$ and the temperature dependence (or other dependences) of τ_α ? (3) Are there any correlations between $\beta_\alpha(T_g)$ and other viscoelastic properties such as the breadth of the softening (glass–rubber-transition) dispersion, and the extent of failure of time–temperature superposition (see Fig. 2.11)? Neither the free-volume theory nor the entropy theory (Sections 2.3.1 and 2.3.2) for the glass transition addresses the dispersion of the local segmental relaxation. The dispersion comes as an afterthought and therefore they offer no help in answering these questions. This deficiency in the conventional theories of the glass transition begs another question. (4) Is β_α an indicator of a missing but important piece of physics that must be included, in parallel with volume and entropy considerations, before a satisfactory theory of the glass transition can be reached? Some qualitative answers can be given to the above questions.

(1) From empirical observations [165] it seems that a chemical structure with a higher capacity of intermolecular coupling between the repeat units will exhibit broader dispersion (i.e. has a smaller $\beta_\alpha(T_g)$). Intermolecular coupling is enhanced if the chain is made stiffer or more inflexible, such as by introducing phenyl rings into the backbone (e.g. bisphenol A polycarbonate), or if there is a bulky and rigid substituent group such as a phenyl ring on a backbone carbon atom (e.g. polystyrene).

(2) Comparison of temperature dependences of τ of polymers on a plot of $\log \tau_\alpha$ versus T_g/T shows a pattern [163–165]. The pattern can be characterized by a single parameter, which is the steepness index, S , or

$$m = d[\log \tau_\alpha(T)]/d(T_g/T)|_{T=T_g} \quad (2.27)$$

A correlation between n_α or $1 - \beta_\alpha(T_g)$ and the steepness index m has been found to exist [163–165]. The anomalous q^{-2/β_α} -dependence of τ_α from neutron-scattering experiments mentioned above is another concurrent correlation [162] between τ_α and β_α .

(3) It was recognized already in the early days of viscoelastic measurements that the time or frequency dependence of the softening zone can vary considerably with the chemical structure of the polymer. Tobolsky [2] and Ferry [1] found as early as in 1956 that the softening dispersions of polyisobutylene (PIB) and polystyrene (PS) contrast sharply. The glassy compliance (modulus) and the plateau compliance (modulus) for PIB and PS are similar, but the width of the glass–rubber-softening dispersion of PIB is several decades broader in time or frequency than that of PS. Ferry remarked in his 1991 review [166] that the origin of this difference is still not known. Other differences between the viscoelastic properties of PIB and PS can be found in reviews [10, 11]. The terminal dispersion as well as the $M^{3.4}$ molecular weight dependence of the viscosity of monodisperse entangled linear polymers do not depend on the chemical structure of the repeat units.

Nevertheless, the difference between the temperature dependences of the terminal dispersion (or the viscosity) and the local segmental motion is significantly less for PIB than it is for PS. Dielectric-relaxation and PCS measurements (to be discussed later) have revealed that $\beta_\alpha(T_g)$ varies from polymer to polymer [34, 164, 165, 167, 168]. For example, polystyrene and polyisobutylene have $\beta_\alpha(T_g)$ equal to 0.36 and 0.55, respectively [34, 167, 168]. This difference between the values of the stretching exponent $\beta_\alpha(T_g)$ for polyisobutylene and polystyrene has been identified as the origin of their contrasting viscoelastic properties [169, 170].

(4) The observation that $\beta_\alpha(T_g)$ varies in a systematic way with chemical structure like T_g itself (see Section 2.4.6) can be considered as a hint that the dispersion of the local segmental relaxation or $\beta_\alpha(T_g)$ is an indicator that intermolecular coupling must be built in for a consistent theory. The control that $\beta_\alpha(T_g)$ exerts directly over various properties of the local segmental relaxation and other viscoelastic properties points to the primary role played by intermolecular coupling, without which the other challenging experimental observations would not be explained. Suitably taking into account intermolecular coupling will introduce effects of many-molecule dynamics that cannot possibly be captured by free-volume, entropy, or other “mean-field” or thermodynamic theories. Exactly how intermolecular coupling is to be incorporated into a theory is a challenging problem on the frontier of basic research. There is an attempt called the “coupling model” [170–173], which has wide applications. In this approach, one accepts at the outset the important role of entropy S and volume V (or free-volume fraction f) in determining the local segmental mobility. Thus, before bringing in intermolecular coupling, the local segmental relaxation time $\tau_{0\alpha}$ is already a function of S, V (or f), and explicitly temperature T if the process involves thermal activation over an energy barrier. Through the dependences of S, V , or f on temperature T and pressure P , $\tau_{0\alpha}$ has already acquired nontrivial dependences on T and P . Since intermolecular coupling has not yet been introduced, $\tau_{0\alpha}$ is referred to as the independent, primitive or uncoupled relaxation time. Intermolecular coupling makes the actual molecular-relaxation process more complicated. Not all independent relaxations with relaxation time $\tau_{0\alpha}$ can be successful because motions of mutually interacting or constraining molecules require cooperativity between them. Roughly described in the simplest terms, cooperativity means that some molecules do not move (or move slower) in order that some others can move (or move faster), and they exchange roles with time (i.e. dynamic heterogeneous relaxation, as discussed before in Section 2.2.7.3). A consequence of cooperativity on the average is the slowing down of the independent relaxation rate $1/\tau_{0\alpha}$ to $1/\tau_\alpha$ and broadening of the dispersion from $\exp(-t/\tau_0)$ to the KWW stretched exponential $\exp[-(t/\tau_\alpha)^{\beta_\alpha}]$ (Eq. (2.25)). The slowing down to the $\exp[-(t/\tau_\alpha)^{\beta_\alpha}]$ decay starts only after a time t_c , before which independent relaxation with the $\exp(-t/\tau_{0\alpha})$ decay still holds. The crossover time t_c depends on the intermolecular-interaction potential but not on temperature [174]. For some

polymers, a value of 2×10^{-12} s was determined by neutron-scattering experiments [161, 162]. The crossover from $\exp(-t/\tau_{0\alpha})$ to $\exp[-(t/\tau_\alpha)^{\beta_\alpha}]$ in a small neighborhood about t_c leads to the key relation between τ and τ_0 :

$$\tau_\alpha = [t_c^{-n_\alpha} \tau_{0\alpha}]^{1/\beta_\alpha} \quad (2.28)$$

where $n_\alpha \equiv 1 - \beta_\alpha$. Naturally, one may expect that, the stronger the intermolecular coupling, the longer the cooperative local segmental relaxation time τ_α compared with $\tau_{0\alpha}$ and the broader the dispersion (or smaller β_α). These expected behaviors were confirmed by results from simplified models [173]. Recalling that the dependences on S, V , and T have been taken into account in $\tau_{0\alpha}$, τ_α in Eq. (2.28) is the final result when the slowing-down effect of intermolecular coupling has also been included. The explicit dependence of τ_α on β_α fulfills the expected important role played by intermolecular coupling in determining the relaxation time. It shows that τ_α of polymers with different chemical structures exhibit different dependences on controllable parameters. This is because β_α in Eq. (2.28) decreases with intermolecular coupling/constraint, which in turn depends on the chemical structure of the repeat unit. Furthermore, it has the potential to explain the existence of correlations of various properties of τ_α with β_α , for a family of glass-formers. In fact Eq. (2.28) shows that, for any dependence of $\tau_{0\alpha}$ on any variable Θ , the corresponding dependence for τ_α is

$$\tau_\alpha(\Theta) \propto [\tau_{0\alpha}(\Theta)]^{1/\beta_\alpha} \quad (2.29)$$

Equation (2.29) transforms a normal dependence of $\tau_{0\alpha}$ on Θ into an abnormal dependence of τ_α on Θ , and has the potential to rationalize the anomalous dependences of τ_α found experimentally. For example, from the normal q^{-2} -dependence of $\tau_{0\alpha}$ on the scattering wave vector q , the anomalous q^{-2/β_α} -dependence [161, 162, 174] follows as a consequence of Eq. (2.29).

It is commonly assumed regarding the viscoelasticity of polymers that the “monomeric” friction coefficient $\zeta_0(T)$ governs the temperature dependences of *all* the viscoelastic mechanisms, including the local segmental relaxation, the Rouse modes, and the terminal modes, [1–4]; see also Chapter 3 by W. W. Graessley. The temperature dependence of $\zeta_0(T)$ usually is considered to come only from free volume or entropy (see Sections 2.3.1 and 2.3.2). From the coupling-model standpoint, this is not true for local segmental motion because of the inherent intermolecular coupling. However, it is true for the Rouse modes modified for undiluted polymers [1] because, by their very definition, they are not intermolecularly coupled. Certainly $\zeta_0(T)$ solely governs the temperature dependence of $\tau_{0\alpha}$ because consideration of intermolecular coupling has not yet entered into $\tau_{0\alpha}$, but the same does not hold for τ_α . According to Eq. (2.29), the temperature dependence of τ_α is given by $[\zeta_0(T)]^{1/\beta_\alpha}$, which can be much stronger than $\zeta_0(T)$ for the Rouse modes. The

difference between the temperature dependences of the Rouse modes and the local segmental relaxation is summarized as follows [175]:

$$\tau_{\alpha}(T) \propto [\zeta_0(T)]^{1/\beta_{\alpha}} \quad \tau_R \propto \zeta_0(T) \quad (2.30)$$

This difference has been used to explain the dependence of the breadth of the softening dispersion on β_{α} and several other anomalous viscoelastic properties [162, 169, 170, 176].

The coupling model will not be discussed further here because the chapter is meant to provide a conceptual introduction to the glass transition in polymers. The coupling model should be considered as one among possibly other approaches by which to incorporate intermolecular coupling into entropy or volume theories of the glass transition, with the benefit of explaining more data, especially the anomalous properties. At the time of writing, the author does not know of any other attempt. Effort in this direction, which is deemed beneficial, should be encouraged.

2.5.2 Secondary relaxation

In polymers there are molecular motions, which are even more local than the local segmental relaxation process. They are called secondary or β -relaxations. Their relaxation times, τ_{β} , are shorter than the local segmental relaxation time τ_{α} , and are conveniently observed by mechanical or dielectric measurements in some temperature range below T_g without the interference from the usually more-dominant primary or local segmental relaxation. The temperature dependence of τ_{β} is of Arrhenius form for $T < T_g$. Some polymers have more than one secondary relaxation. The secondary relaxation may be some local motion of a side group. An example is the flip motion between the “chair” conformation and the “boat” conformation of the cyclohexyl side group attached to the main chain in poly(cyclohexyl methacrylate) (PCHMA) [177]. The observed activation enthalpy of 46.9 kJ mol^{-1} of this secondary relaxation has been identified with the energy barrier for the chair–boat flip. Another type of secondary relaxation originates from some subgroup of the main chain such as that involving the two phenyl rings of compounds in the bisphenol A polycarbonate family [178–180]. It seems that the occurrence of these secondary relaxations makes the glassy polymer more ductile, a desirable mechanical property. There is a large amount of literature on secondary relaxations in polymers and the reader is referred to some reviews for information [6, 181, 182].

Some secondary relaxations in amorphous polymers have fundamental implications for the dynamics of the glass transition. There are several characteristics of this class of β -relaxations in polymeric as well as in nonpolymeric glass-formers. One characteristic is the tendency of the β -relaxation spectrum to merge into the

α -relaxation spectrum as the temperature is increased above T_g . In other words, τ_α continuously approaches τ_β and they appear to become equal at some temperature. Some polymers such as 1,4-polybutadiene have all atoms of a repeat unit in the main chain. There is no side group yet the polymer has a strong β -relaxation that tends to merge with the α -relaxation. The β -relaxation in PEMA and, by implication, those in other poly(alkyl methacrylates) are found to involve not only the side group but also rotation of the main chain [183]. There are rigid small-molecular glass-formers with no intramolecular degrees of freedom and yet a β -relaxation tending to merge with the α -relaxation still occurs. These results on nonpolymeric glass-formers, first found by Johari and Goldstein [184–186], suggest that the β -relaxations are of intermolecular origin. In the literature, secondary relaxations having any of the above properties are collectively called Johari–Goldstein (J–G) β -relaxations. Attention is paid to the properties of these J–G relaxations because their origin is intriguing and they may help us to understand the microscopic dynamics of the glass transition. It was recently found empirically [187] that the logarithm of their relaxation times at T_g , $\log_{10}[\tau_\beta(T_g)]$, correlates with the exponent β in the KWW function (Eq. (2.25)) that characterizes the dispersion of the α -relaxation. This is a *cross*-correlation between α - and β -relaxation properties, suggesting that the J–G relaxation may play a fundamental role in the dynamics of the glass transition. Inferences of this possibility are the findings that τ_β is not too different in order of magnitude from τ_0 calculated from τ_α by Eq. (2.27) at T_g [185] and above T_g [188]. Another inference is from the temperature dependence of the dielectric strength of the J–G relaxation mimicking that of enthalpy and volume [186].

2.5.3 Short-time dynamics

By the introduction of quasi-elastic-neutron-scattering (QENS) and dynamic-light-scattering techniques into the investigation of the dynamics of polymers and glass-formers [13, 66, 67, 161, 162, 189–196] in general, their relaxation properties at short times from say 10^{-13} to 10^{-9} s (or correspondingly high frequencies) have been acquired. Measurements with dielectric-relaxation techniques can now routinely go up in frequency to a few times 10^9 Hz with commercial instruments, and special instrumentation can be used to tackle the previously inaccessible high-frequency range of 10^9 Hz $< \nu < 10^{14}$ Hz [197]. Using these new techniques, relaxation dynamics in the short-time range can be studied at all temperatures. At elevated temperatures, at which τ becomes short, the techniques can be used to study the dynamics of the local segmental relaxation time in polymers and the structural relaxation in nonpolymeric materials. Some of these studies at high temperatures [161, 162] (mentioned before in Section 2.5.1.2) have led to results including the

crossover from $\exp(-t/\tau_0)$ to $\exp[-(t/\tau)^\beta]$ at about 2 ps for polymers and the $q^{-2/\beta}$ -dependence of τ .

At lower temperatures [66, 67, 190–196], the techniques measure the other relaxation processes which are faster than the primary and secondary relaxations. Measurements have found such a fast relaxation process or processes. From the incoherent-neutron-scattering function, $S(q, \omega, T)$, the elastic part of the scattering, $S_{el}(q, \Delta\omega, T)$, is operationally defined by the integral of $S(q, \omega, T)$ over ω within $-\Delta\omega < \omega < \Delta\omega$, where q is the momentum transfer and $\Delta\omega$ is the resolution frequency width of the spectrometer. After normalizing $S_{el}(q, \Delta\omega, T)$ measured at temperature T by its value at $T = 0$, $S_{el}(q, \Delta\omega, T = 0)$, one defines a Debye–Waller factor $W(q, \Delta\omega, T)$ and a mean-square displacement $\langle u^2(T) \rangle$ of the fast relaxation by

$$\frac{S_{el}(q, \Delta\omega, T)}{S_{el}(q, \Delta\omega, T = 0)} = \exp[-2W(q, \Delta\omega, T)] = \exp[-\langle u^2(T) \rangle q^2/3] \quad (2.31)$$

Thus, $\langle u^2(T) \rangle$ is a measure of the intensity of the fast relaxation. In order to isolate the fast relaxation we have to exclude the contribution to $\langle u^2(T) \rangle$ from the α -relaxation and the secondary relaxation by not considering results obtained at temperatures much higher than T_g . Of fundamental interest is the finding that, as a function of temperature, the intensity of the fast process undergoes a change of slope at T_g , just like volume V , enthalpy H , and the strength of secondary relaxations [186]. This intriguing similarity in behavior of fast relaxation supposedly of microscopic nature and macroscopic V and H was found by QENS first by Buchenau and Zorn [190] for selenium, a natural polymer, and by others for polymeric and nonpolymeric glass-formers (for references see [198]). These findings for several glass-formers are shown collectively in Fig. 2.21 by the mean squared displacement $\langle u^2 \rangle$ normalized by its value at T_g , $\langle u^2(T_g) \rangle$, as a function of T/T_g . The polymers are selenium [190], polyisobutylene (PIB), and 1,4-polybutadiene (PB) [13, 191]. The nonpolymeric glass-formers are 1,2-diphenylbenzene (OTP), 0.4Ca(NO₃)₂·0.6KNO₃ (CKN), glycerol, B₂O₃, and SiO₂. The data on silica are from molecular-dynamics simulations. Figure 2.21 clearly shows the larger changes in slope at T_g for glass-formers such as PB, PIB, Se, OTP, and CKN with a smaller stretching exponent β_α in Eq. (2.25) or larger steepness index m (Eq. (2.26)). The changes are smaller for glycerol, B₂O₃, and SiO₂. These data indicate that the change at T_g decreases with decreasing $1 - \beta_\alpha$ or m .

Previously discussed in Section 2.3.1 were the similar temperature dependences of the free-volume fraction deduced from PALS and the intensity (or $\langle u^2 \rangle$) of the fast relaxation measured by QENS and light scattering for PMMA at temperatures below T_g . The fast relaxations are local or not cooperative processes measured on picosecond time scales. The fact that they also sense the glass transition as

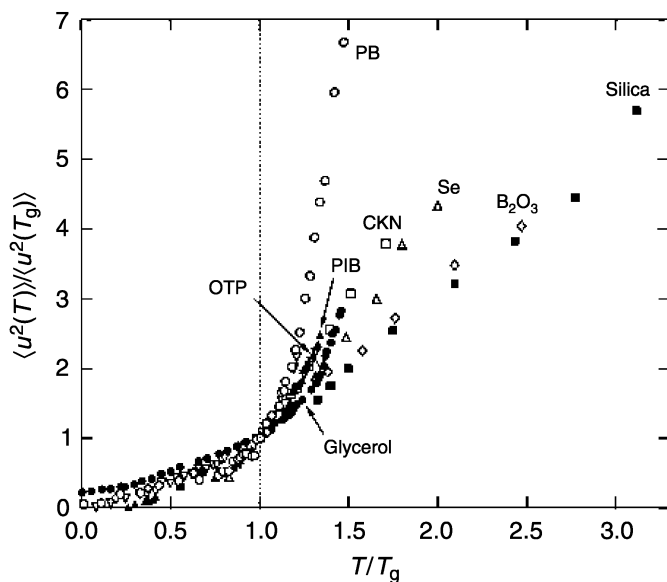


Fig. 2.21. The mean-squared displacement $\langle u^2 \rangle$ normalized by its value at T_g , $\langle u^2(T_g) \rangle$, as a function of T/T_g measured by neutron scattering for polymeric and nonpolymeric glass-formers.

the temperature crosses T_g , which corresponds to the α -relaxation of 10^2 – 10^3 s at commonly used cooling rates, is intriguing [198] and may have some impact on glass-transition theory. Somehow the free-volume or configurational-entropy theory of the glass transition has to rationalize why these local fast relaxation processes are affected by the change in free volume or configurational entropy at T_g . Some detailed dielectric measurements of secondary relaxation show that its dielectric strength also undergoes a more rapid increase with temperature above T_g than it does below T_g [186, 200, 201]. Again, the more local and faster secondary relaxation processes sense also the glass transition.

2.6 The impact on viscoelasticity

In most, if not all, textbooks on the viscoelasticity of polymers, once the location of T_g is known, the glass transition and its phenomenology become subjects of peripheral interest. At best, one is reminded of the glass transition in discussions of the temperature dependence of the shift factor a_T used to construct the master viscoelastic-response curve by time–temperature superposition of experimental data, especially so if T_g is chosen as the reference temperature T_0 in the WLF equation (2.16) for a_T . To justify time–temperature superposition of data, one makes the assumption that all viscoelastic mechanisms are governed by one and

the same friction coefficient, namely that of the local segmental relaxation, which is responsible for the glass transition, and hence individual shift factors all have the same temperature dependence. However, the assumption is not valid [10, 11], as we now show by quoting some representative experimental data. Previously, in Section 2.5.1.1 and Figs. 2.19 and 2.20, we have shown the different temperature dependences of the local segmental relaxation time and the terminal flow. Before we proceed, the reader may wonder why this disconcerting breakdown of the simplifying assumption is not mentioned at all in most standard textbooks or reviews. Perhaps it is not difficult to understand this trend. First, authors of all texts on viscoelasticity of polymers would like to start by showing the reader the complete viscoelastic response of a polymer continuously from the glassy region to the terminal-flow region as a function of time or frequency at one temperature. The only way to do so is to employ time–temperature superposition of data taken over a fixed time or frequency window. Often a good master curve was obtained by this procedure, although integrity of the master curve is not guaranteed because the assumption is not valid. Secondly, it is difficult for any author to explain why the viscoelastic mechanisms have different shift factors. Had this fact been put in the forefront of the discussion, the author would have been obliged to explain it. Since there is no easy explanation, it interrupts the flow in presenting the viscoelastic properties of polymers to the readers. We buck the trend by paying attention to this fact because the breakdown has an impact on viscoelastic properties and their interpretations. It may be pivotal to a satisfactory fundamental understanding of the viscoelastic mechanisms. It also can be used as a critical test for any theory proposed for the glass transition in amorphous polymers.

2.6.1 Low molecular weight amorphous polymers

The most spectacular observations of breakdown of time–temperature superposition occur for polymers of low molecular weight. The effect was first seen in shear-creep compliance $J(t)$ measurements on polystyrene (PS) [10, 11, 90]. Shown in Fig. 2.22 is the recoverable compliance, $J_r(t) = J(t) - t/\eta$, for PS of molecular weight 3400 plotted against the logarithm of the reduced time, t/a_T . Here η is the viscosity. It can be seen that there is a dramatic change in shape of the curve of recoverable compliance as the temperature is lowered toward T_g . At the same time the steady-state recoverable compliance J_e^0 decreases 30-fold to a value only about five times the glassy compliance, J_g . Clearly reduction to a master curve by time–temperature superposition (i.e. thermorheological simplicity) fails. The sample has a tail of high molecular weight that gives rise to a further increase of J_r at longer times. The data for a nearly monodisperse PS sample with molecular weight 12 300 and $M_w/M_n = 1.06$ exhibit the same effect

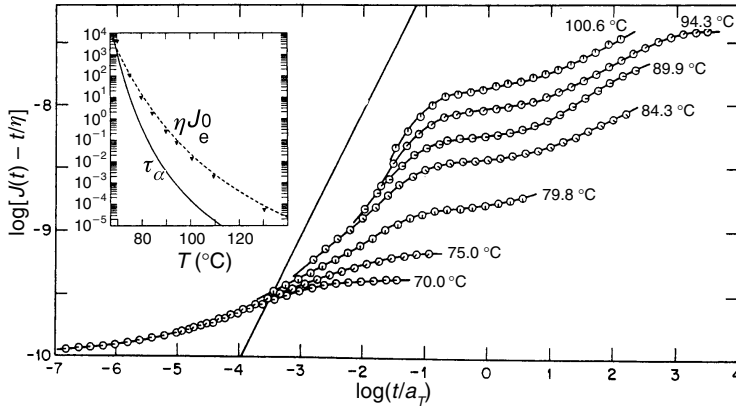


Fig. 2.22. A bilogarithmic plot of the recoverable compliance versus reduced time, t/a_T for PS with $M = 3400$. The reference temperature is 100°C . The straight line is the viscous contribution to the total creep at 100.6°C . Note the large decrease of J_e as T decreases. The inset shows the local segmental retardation time, τ , having a stronger temperature dependence than the Rouse time, τ_R , given by the product, ηJ_e^0 .

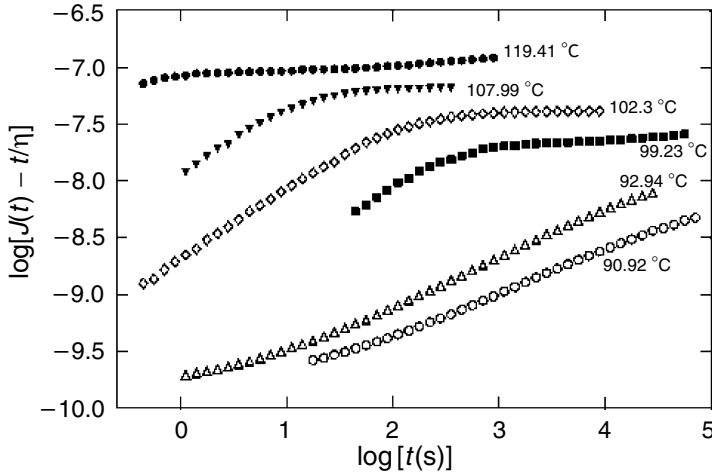


Fig. 2.23. A bilogarithmic plot of the recoverable compliance against time at several temperatures for a nearly monodisperse sample of PS (TAPS 28S FR14) with molecular weight 12300 and $M_w/M_n = 1.06$.

and are shown in Fig. 2.23. This remarkable effect was confirmed by measurements of the complex shear modulus by Gray, Harrison, and Lamb [202]. The real part of the complex shear compliance, $J'(\omega)$, data is plotted against frequency ω for PS of 3500 molecular weight at several temperatures in Fig. 2.24, where J_e^0 can be identified with the limiting value of $J'(\omega)$ at low frequencies. The

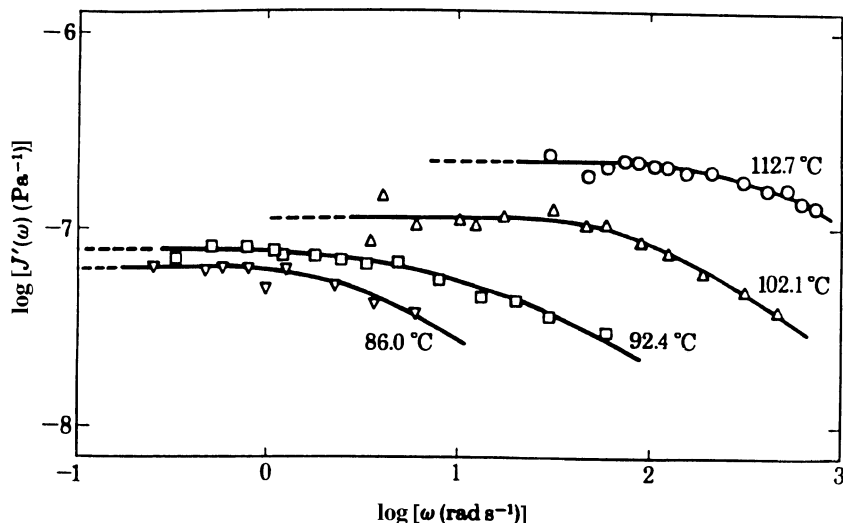


Fig. 2.24. The logarithm of $J'(\omega)$ plotted against the logarithm of angular frequency for the PS sample of molecular weight 3500 at several temperatures. From Gray *et al.* by permission [202].

variations of J_e^0 with temperature for three molecular weights are shown in Fig. 2.25. In this figure taken from Gray *et al.* [202], J_e stands for the steady-state recoverable compliance instead of J_e^0 . At sufficiently high temperatures, J_e^0 becomes weakly temperature-dependent. This plateau value increases with molecular weight and the measured values are in close agreement with the expression $J_e^0 = 0.4M/(\rho RT)$, where ρ is the density, predicted by the Rouse model modified for an undiluted polymer [1]. On decreasing the temperature toward T_g there is a marked decrease in J_e^0 . Via the relation

$$J(t) = J_r(t) + t/\eta = \int_{-\infty}^{\infty} L(\lambda)(1 - e^{-t/\lambda}) d \ln \lambda + t/\eta \quad (2.32)$$

a numerical method was used to obtain the retardation spectra $L(\lambda)$ from the isothermal $J_r(t)$ data in Fig. 2.22. Some of the results are shown in Fig. 2.26. At 100.6 °C, the peak at long λ corresponds to the Rouse modes. The peak is reduced both in height and in area with decreasing temperature, indicating a loss of the Rouse retardation mechanisms. At 70 °C, which turns out to be the measured T_g of the sample, the original tall peak completely disappears and thus all viscoelastic mechanisms associated with it cease to operate. Consequently, at $T = T_g = 70$ °C, the remnant broader L peak is contributed entirely by the local segmental motion, and J_e^0 at $T = 70$ °C is to be identified with $J_{e\alpha}$, the equilibrium compliance of the local segmental (α -) relaxation of polystyrene. From this we obtain the estimate $J_{e\alpha} \approx 4J_g$. Thus the contributions from the local segmental relaxation in polystyrene to the recoverable compliance $J_r(t)$ are restricted to the range $J_g \leq J_r(t) \leq J_{e\alpha} \approx 4J_g$.

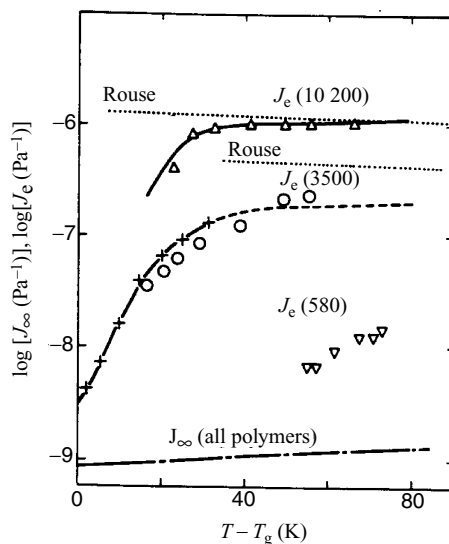


Fig. 2.25. The equilibrium compliance J_e and high-frequency limiting compliance J_∞ plotted as functions of $T - T_g$. J_e values for various molecular weights (580 (∇), 3500 ($\circ$), and 10 200 (Δ)) are from cyclic shear data of Gray *et al.* [202]. J_e for molecular weight 3400 (+) is from creep-recovery data of Plazek and O'Rourke [90]. Curves for the $M = 3500$ and 10 200 samples are calculated from the equation given in table 5 of [90]. The dashed curve is an extrapolation outside the range of measurement. The dotted lines are the J_e values predicted by the Rouse theory, $0.4M/(\rho RT)$. Values of J_∞ for all polymers were obtained from measurements at temperatures from T_g to $T_g + 20$ K and extrapolated to higher temperatures.

The retardation time τ_R for the Rouse modes is determined by the product ηJ_e^0 as a function of temperature. The temperature dependence of the local segmental relaxation time τ is given by that of the shift factor a_T used to reduce the data in the low-compliance region in Fig. 2.22. It is found that τ has a stronger temperature dependence than does τ_R (see the inset of Fig. 2.22), proving that the Rouse modes and the local segmental relaxation do not have the same friction coefficient. This fundamental result has an immediate explanation from Eq. (2.30) and the discussion that follows it. The key to that explanation is the intermolecular coupling of the local segmental relaxation with $\beta_\alpha(T_g)$ equal to 0.36 for PS (see Section 2.5.1.2). Intermolecular coupling between repeat units of PS certainly will be reduced on diluting the polymer with a solvent with a much lower T_g such as tri-*m*-tolyl phosphate [10]. The explanation by Eq. (2.30) implies that the effects observed in bulk polystyrene will be weakened by addition of tri-*m*-tolyl phosphate. This expected change has indeed been observed [10]. Polyisobutylene (PIB) has a larger $\beta_\alpha(T_g)$ (equal to 0.55) than that of polystyrene [167, 168] and again from Eq. (2.30) we expect that the effects should be weaker in PIB, which has also been observed [10, 170].

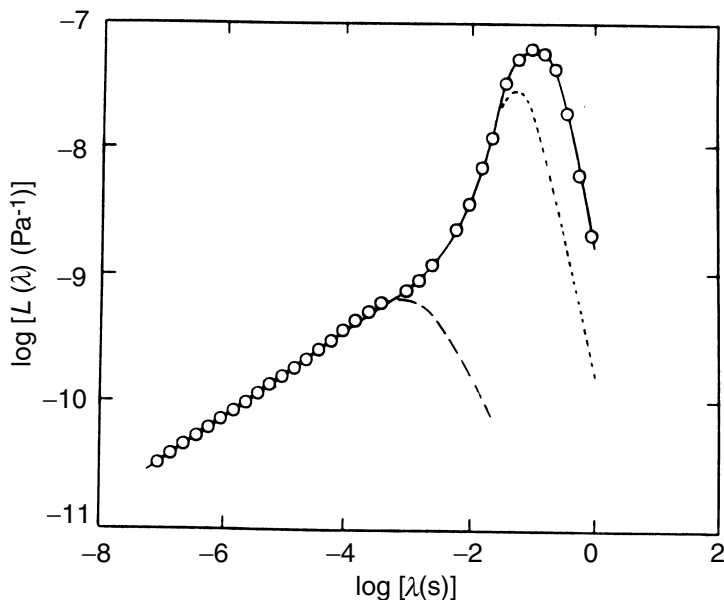


Fig. 2.26. The retardation spectrum $L(\lambda)$ for a PS sample of molecular weight 3400 with a narrow molecular weight distribution plotted bilogarithmically as a function of the retardation time λ . The data are shifted to a reference temperature $T_0 = 100^\circ\text{C}$. The original temperatures of measurement are 100.6°C ($-\circ-$), 89.9°C ($\cdots$), and 70.0°C ($---$). A dramatic loss of long-time viscoelastic mechanisms is evident when the temperature is decreased toward T_0 .

The prominent effect in the viscoelastic response of low molecular weight PS found is a general phenomenon. It is found also for other polymers, including polypropylene glycol [203], poly(methylphenyl siloxane) [204], and selenium [205]. Figure 2.27 shows similar behavior of $J_r(t)$ and L measured for a near-monodisperse sample of poly(methylphenyl siloxane) with molecular weight 5000 plotted against the logarithm of the reduced time, t/a_T . The fact that the temperature dependence of τ_α is stronger than that of τ_R for polypropylene glycol and polyisoprene was confirmed by measurements of dielectric relaxation [206]. Naturally, the origin of the effect has been traced [10, 90, 203–205] to the fact that the temperature dependence of the shift factor of the local segmental modes is stronger than that of the Rouse modes. Consequently, as the temperature is decreased, the local segmental modes encroach on the longer-timescale Rouse modes. Reconciliation of the different temperature dependences of the friction factors of the local segmental motion and the Rouse modes requires a renormalization of the degree of polymerization of the polymer, effectively reducing it and hence also J_e^0 with decreasing temperature [170].

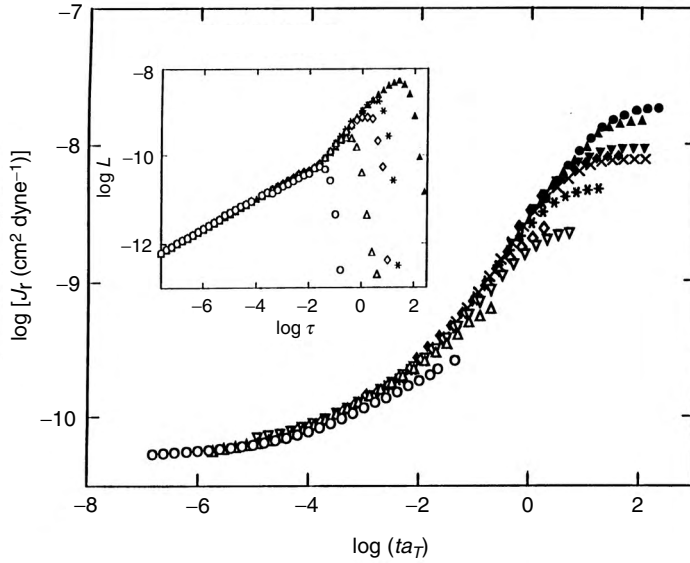


Fig. 2.27. Recoverable-compliance, $J_r(t)$, data of PPMS 5000 at temperatures -32.2°C ($\bullet$), -35.0°C ($\blacktriangle$), -38.6°C ($\blacktriangledown$), -40.0°C ($\blacklozenge$), -41.1°C ($\times$), -42.6°C ($*$), -44.5°C ($\diamond$), -45.2°C (∇), -46.9°C ($\triangle$), and -50°C ($\circ$). The data taken at different temperatures have been shifted horizontally along the $\log t$ axis by a temperature-dependent shift factor $\log a_T$ in order to superpose the curves at the short-time end with the data for -35.0°C . The inset shows the retardation spectrum, L , as a function of the reduced retardation time λ with reference temperature $T_o = -35.0^\circ\text{C}$, which was obtained numerically from $J_r(t)$ data.

2.6.2 High molecular weight amorphous polymers: softening dispersion

Equation (2.32) indicates that the strains arising from various molecular mechanisms add simply in the compliances and in principle can be separated. On the other hand, the stresses do not add and the various mechanisms cannot be easily resolved in modulus functions. To understand the individual contributions to the viscoelastic response, this additivity property of the creep compliance $J(t)$ is helpful. The effect in low molecular weight polymers discussed in Section 2.6.1 has helped to determine the maximum compliance $J_{e\alpha}$ contributed by the local segmental (α) modes over and above J_g . For high molecular weight polystyrene there is a characteristic of the retardation spectrum, $L(\lambda)$, that allows another determination of $J_{e\alpha}$ [207], in good agreement with the value obtained from low molecular weight polystyrene by the other method (Section 2.6.1). The time dependence of the compliance of the α -relaxation is given by [207, 208]

$$J_\alpha(t) = J_g + (J_{e\alpha} - J_g)\{1 - \exp[-(t/\tau_\alpha)^{1-n_\alpha}]\} \quad (2.33)$$

where $0 < (1 - n_\alpha) \leq 1$. Here, $1 - n_\alpha$ is the analog of the fractional exponent in the relaxation function, Eq. (2.25). The increase in the compliance from $J_g \approx 10^{-10} \text{ cm}^2 \text{ dyne}^{-1}$ (10^{-9} Pa^{-1}) to $J_{e\alpha} \approx 4J_g$ is small compared with the rise of $J_r(t)$ from J_g to the rubbery level at about $10^{-6} \text{ cm}^2 \text{ dyne}^{-1}$ (10^{-5} Pa^{-1}), as shown in Fig. 2.11. Often the greater part of this increase in compliance in the softening (glass–rubber-transition) region is attributed to the Rouse modes modified for undiluted polymers [1]. However, the extended Rouse model has limitations. It has been recognized by M.L. Williams [209] that, on taking the short-time limit of the contribution of extended Rouse modes to the modulus [1], one obtains $G(0) = N\rho RT/M$, where N is the number of Gaussian submolecules in a polymer molecule, ρ the density, M the molecular weight, R the gas constant, and T the temperature. The number of monomers in a submolecule, z , is given by P/N , where P is the number of monomers in a polymer chain. For a polymer of molecular weight 150 000 and density 1.5 g cm^{-3} , assuming that the smallest submolecule that can still be Gaussian consists of five monomer units (i.e. $z = 5$), Williams found that $G(0) = 7.5 \times 10^6 \text{ Pa}$ ($J(0) = 1.3 \times 10^{-7} \text{ Pa}^{-1}$). This value is about two orders of magnitude smaller (larger) than the experimentally determined value of the glassy modulus G_g (glassy compliance J_g), which typically falls in the neighborhood of 10^9 Pa (10^{-9} Pa^{-1}). Thus the extended Rouse model cannot account for the shorter-time portion of the glass–rubber dispersion of entangled polymers because here the modulus (compliance) decreases (increases) continuously from about 10^9 Pa (10^{-9} Pa^{-1}) to the plateau value of about 10^5 Pa (10^{-5} Pa^{-1}). These deficiencies of the extended Rouse model are not surprising because, after all, according to the model the submolecule is the shortest length of chain which can undergo relaxation and the motions of shorter segments within the submolecules are not taken into consideration. We know from Eq. (2.33) that the local segmental motions contribute to the compliance at short times. However, this contribution in polystyrene covers only the narrow range approximately from 10^{-9} to $4 \times 10^{-9} \text{ Pa}^{-1}$. Therefore the compliance range approximately from 4×10^{-9} to $1.3 \times 10^{-7} \text{ Pa}^{-1}$ remains to be accounted for by some other viscoelastic mechanism. The missing molecular mechanisms have length-scales smaller than the length of the Gaussian submolecule of the Rouse model but larger than the length-scale of local segmental motion, which naturally is called the “sub-Rouse modes.”

A judicious choice of polymer has to be made before carrying out an experiment to resolve the sub-Rouse modes from neighboring mechanisms. A good choice is a polymer with a very broad softening dispersion, such as polyisobutylene (PIB). On the other hand, polystyrene is a bad choice because of its narrow softening dispersion, due to the local segmental relaxation encroaching on the Rouse modes. Clear evidence for the occurrence of sub-Rouse modes in polyisobutylene was found by viscoelastic measurement [210] and by dynamic light scattering [167,

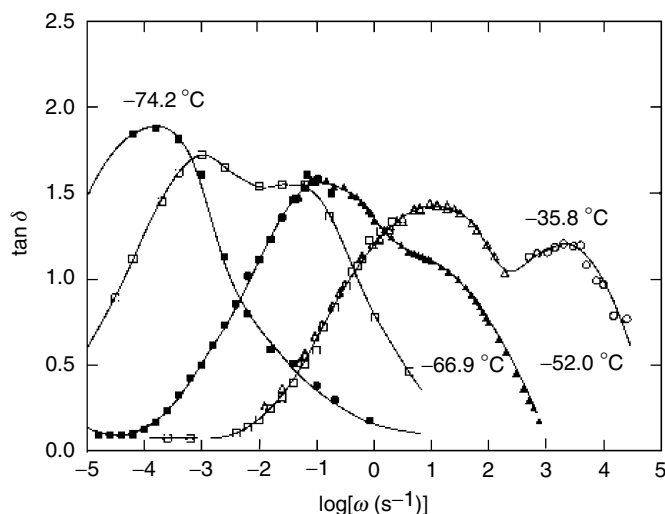


Fig. 2.28. A plot of $\tan \delta$ as a function of actual frequencies at several temperatures for NBS-PIB. The data were obtained by using several instruments spanning the frequency range as shown in the abscissa. The high-frequency data at -35.8°C (open circles) are from Fitzgerald *et al.*, *J. Appl. Phys.* **24** (1953), 640. The rest of the data were obtained by a combination of creep-compliance and dynamic-modulus measurements [209]. From Plazek *et al.* by permission [209].

168]. Shown in Fig. 2.28 are *real* time/frequency *isothermal* shear-mechanical measurements of the softening dispersion of a high molecular weight PIB (NBS-PIB) obtained using three different techniques to enhance the width of the time/frequency window and plotted as $\tan \delta = G''(\omega)/G'(\omega) = J''(\omega)/J'(\omega)$ versus frequency. The data at four temperatures from -74.2°C to -35.8°C [210] reveal the presence of two groups of viscoelastic mechanisms, which shift along the real frequency/time axis differently with temperature. Of the two peaks, the lower-frequency one originates from the Rouse modes. The high-frequency peak or shoulder is attributed to the sub-Rouse modes. The softening dispersion thus has three contributions: (i) the local segmental motion responsible for $J(t)$ from $J_g \approx 10^{-9} \text{ Pa}^{-1}$ up to about $J_{s\alpha} \approx (4-5) \times 10^{-9} \text{ Pa}^{-1}$, (ii) the sub-Rouse modes from $J_{s\alpha}$ up to somewhere near $J_{sR} \approx 10^{-7} \text{ Pa}^{-1}$, and (iii) the modified Rouse modes from $J_{sR} \approx 10^{-7} \text{ Pa}^{-1}$ up to the rubbery plateau level. These estimates may vary somewhat for polymers with different chemical structures.

Although the local segmental relaxation occurs at higher frequencies than those covered by the frequency range of the mechanical measurements in Fig. 2.28, it was subsequently measured in the same sample by PCS, which extends measurement to times as short as $1 \mu\text{s}$ [167, 168]. The measured correlation function has the KWW time dependence of Eq. (2.25) with the exponent $1 - n$ equal to 0.55. The local segmental relaxation times τ , rewritten here as τ_α , are plotted against temperature in

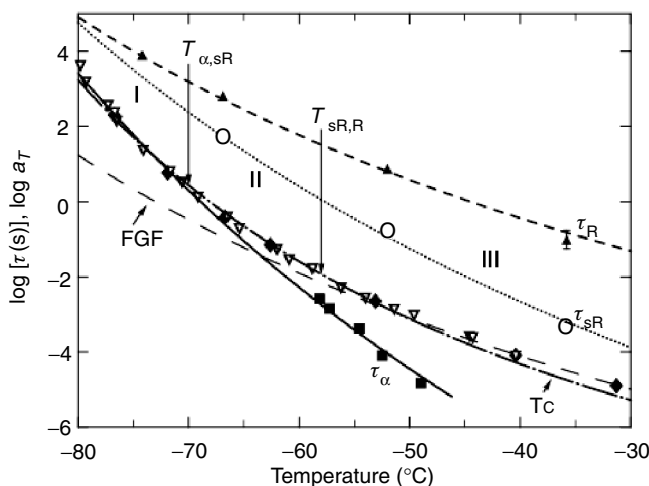


Fig. 2.29. The Rouse relaxation time, τ_R (open triangles) and the sub-Rouse relaxation time, τ_{sR} (open circles) of NBS-PIB for several temperatures obtained from the low-frequency and high-frequency $\tan \delta$ peaks in Fig. 2.28. The curves that interpolate the data points are the WLF fits. The local segmental relaxation times, τ_α (filled squares), are obtained from PCS measurements [168]. Also shown are the shift factors of Tobolsky and Catsiff (TC) from their stress-relaxation data (inverted open triangles), and of Plazek *et al.* from their creep data (filled diamonds). The two vertical arrows partition the temperature into three regions, I, II, and III, in which the viscoelastic response is respectively, contributed mainly by the local segmental motion ($J_g < J(t) < 10^{-9.5} \text{ cm}^2 \text{ dyne}^{-1}$), the sub-Rouse modes ($10^{-9.5} \text{ cm}^2 \text{ dyne}^{-1} < J(t) < 10^{-8} \text{ cm}^2 \text{ dyne}^{-1}$), and the Rouse modes ($10^{-8} \text{ cm}^2 \text{ dyne}^{-1} < J(t) < J_{\text{plateau}}$). The dashed-dotted line through the inverted open triangles is according to the WLF equation given by TC. The dashed line is the WLF equation given by Fitzgerald, Grandine and Ferry (FGF). The thick solid line, passing close by the mechanical data points (inverted open triangles and filled diamonds) in the lowest-temperature region I and the photon-correlation data (filled squares) corresponding to local segmental motion was calculated (see the text).

Fig. 2.29 (■). In the same figure are shown the Rouse relaxation times, τ_R (▲), and the sub-Rouse relaxation times, τ_{sR} (○), obtained from the peaks of $\tan \delta$ in Fig. 2.28. The dashed and dotted curves drawn through them are fits to τ_R and τ_{sR} data produced by using the WLF equation. The two vertical arrows at $T = T_{\alpha,sR}$ and $T = T_{sR,R}$ divide the temperature into three regimes, I, II, and III. In regime I, the mechanical responses obtained by measurements of creep compliance [210] or stress relaxation [2] are mainly in the range $J_g < J(t) < 10^{-8.5} \text{ Pa}^{-1}$, and hence contributed by the local segmental relaxation. Thus it is appropriate to fit the creep data in regime I to Eq. (2.33) with $1 - n_\alpha = 0.55$ to determine τ_α . Shift factors a_T used for time-temperature superpositioning of the creep data [210] and the stress-relaxation data

[2] on the same sample (NBS-PIB) are shown as filled diamonds and open inverted triangles respectively in Fig. 2.29. A constant shift has been applied to a_T to make a_T coincide with τ_α in regime I. The dash-dotted curve is the WLF equation given by Tobolsky and Catsiff [2] to describe the temperature dependence of their a_T . Regime II corresponds to $10^{-8.5} \text{ Pa}^{-1} < J(t) < 10^{-7.0} \text{ Pa}^{-1}$, and the viscoelastic responses come mainly from the sub-Rouse modes. Regime III corresponds to $10^{-7.0} \text{ Pa}^{-1} < J(t) < J_{\text{plateau}}$, and the dominant contributors are the Rouse modes. The solid curve describes well τ_α from mechanical data in regime I and τ_α at higher temperatures from the PCS data. It is obtained by the following procedure. First, from the shift factor $a_{T,R} \equiv \tau_R(T)/\tau_R(T_0)$ of the WLF fit to the Rouse-mode relaxation time we obtain the temperature dependence of the friction factor $\zeta_0(T)$ that governs also that of τ_0 . Secondly, scaling it as $a_{T,R}^{1/\beta}$ according to Eq. (2.30) gives the shift factor of τ_α and, because $\beta \equiv 1 - n_\alpha = 0.55$ for PIB, the scaled quantity is $a_{T,R}^{1/0.55}$. Finally, the solid curve matching approximately the τ_α data in Fig. 2.29 is obtained after the application of a constant shift to $a_{T,R}^{(1/0.55)}$. The fact that τ_{SR} has a stronger temperature dependence than does τ_R (Fig. 2.29) indicates that the sub-Rouse modes have some degree of intermolecular coupling, which is reasonable because they have length-scales intermediate between those of the local segmental mode (with intermolecular coupling) and the Rouse modes (without intermolecular coupling). Neutron scattering can probe modes of different length-scales, L , by detecting different momentum transfers, Q , where $L = Q^{-1}$. Thus, when Q^{-1} falls below the length-scale of the smallest Gaussian submolecule, Rouse dynamics will give way to the slower sub-Rouse dynamics. This was observed [211, 212] in polyisobutylene by neutron-spin-echo measurements, which revealed a significant slowing down of the relaxation in comparison with the Rouse-model predictions at $Q^{-1} < 6.7 \text{ \AA}$. The slowing down of modes with $Q^{-1} < 6.7 \text{ \AA}$ was interpreted [211, 212] not as intermolecular coupling of the sub-Rouse modes but rather by the introduction of an additional dissipative mechanism (internal viscosity) into a Rouse-like single-chain theory of polymer-melt dynamics. Others [213] gave reasons why this is a many-particle effect (i.e. intermolecular coupling, which is consistent with the sub-Rouse-modes interpretation given here), which cannot be explained in terms of an effective single-particle theory as suggested in [211, 212].

From the results in Fig. 2.29, the three groups of viscoelastic mechanisms, namely local segmental, sub-Rouse, and Rouse modes, all have different temperature shift factors and the sensitivities of their relaxation times to temperature decrease in that order. The shift factors a_T used for time-temperature superpositioning of the creep or stress-relaxation data in temperature regimes I, II, and III are, respectively, that of the local segmental relaxation, that of the sub-Rouse modes, and that of the Rouse modes. Over the entire temperature range a_T is not the shift factor of any one of the three mechanisms.

We have taken advantage of the fact that PIB has a broad softening dispersion to resolve the sub-Rouse mechanism. It would be difficult to do so for other polymers with narrower softening dispersions. However, the sub-Rouse modes seem to manifest their occurrence in polystyrene by the failure of time–temperature superpositioning of data in the neighborhood of the viscoelastic-response region where the sub-Rouse modes cross over to the Rouse modes. Such failure is not unexpected because the two mechanisms have different shift factors (Fig. 2.29). Actually, this fact was shown first by creep-compliance measurements on polystyrene (PS) in the softening dispersion [214] long before sub-Rouse modes had clearly been resolved in polyisobutylene (PIB). It has been confirmed for PS by dynamic modulus measurements [215], for PS and tetramethyl polycarbonate [10], and for polybutadiene [216]. These data are partly reproduced in a review [10]. An example concerning PS is shown in Fig. 2.30. The lack of reduction of the data is clear from the change in

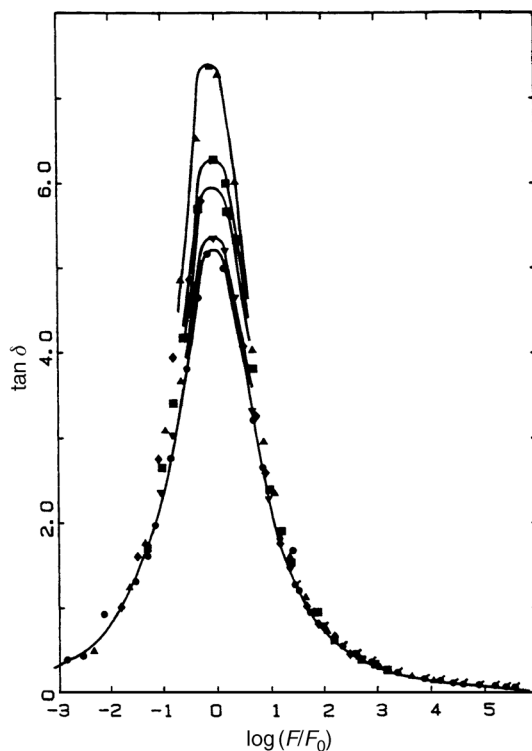


Fig. 2.30. A bilogarithmic plot of isothermal $\tan \delta$ ($= G''/G'$) versus the reduced frequency for a monodisperse atactic PS of molecular weight 98 000 measured in the frequency range 10^{-5} –10 Hz and the temperature range 359–374 K; (●) 359.7 K, (▲) 364.5 K, (■) 367.5 K, (◆) 369.0 K, (▼) 371.6 K and (●) 373.9 K. The curves have been shifted horizontally along the frequency axis by 5.02, 3.48, 2.79, 2.34, and 1.88 for temperatures of 359.7, 364.5, 367.5, 369.0, and 373.9 K respectively. From Cavaille *et al.* by permission [214].

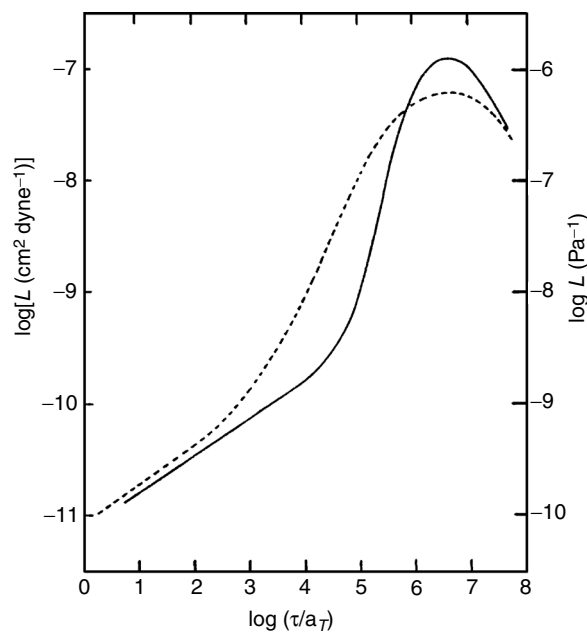


Fig. 2.31. The logarithm of the retardation spectrum L of poly(methyl methacrylate) as a function of the logarithm of the reduced retardation time τ/a_T . The solid curve was calculated from the reduced $J_r(t)$ curve obtained from creep data taken at lower temperatures (14.4–34.7 °C) and longer times ($10^0 \text{ s} < t < 10^5 \text{ s}$) and shifted to 13.1 °C. The dashed line was calculated from the dynamic compliances obtained by Williams and Ferry at higher temperatures and frequencies; T_0 was chosen to be 10.8 °C. From [217] by permission.

the $\tan \delta$ peak with temperature. The $\tan \delta$ peak occurs over a frequency region that corresponds to compliances in the range from 10^{-5} Pa^{-1} down to about 10^{-7} Pa^{-1} .

Significant narrowing of the softening dispersion of poly(methyl methacrylate) and poly(vinyl acetate) with decreasing temperature was found by comparing the retardation spectrum obtained from the complex-compliance $J^*(\omega)$ measurements of William and Ferry [217] at higher temperatures (higher frequencies, $10 \text{ Hz} < \omega/(2\pi) < 6 \times 10^3 \text{ Hz}$) with that obtained by Plazek *et al.* [218] from their $J(t)$ data at lower-temperature (longer times, $1 \text{ s} < t < 10^6 \text{ s}$) data. The retardation spectra L of the softening dispersion from the two measurements on poly(methyl methacrylate) (PMMA) shown in Fig. 2.31 are significantly different, demonstrating once more the failure of time–temperature superposition (i.e. breakdown of thermorheological simplicity) for the softening dispersion. As we know from PIB data directly, the shift factors of local segmental relaxation, the sub-Rouse modes, and the Rouse modes are all different. Hence, as the temperature is decreased, the viscoelastic mechanism in the softening dispersion having a *shorter* relaxation time shifts to longer times *more*, as exemplified by Figs. 2.11, 2.28,

and 2.31 for high molecular weight samples of PS, PIB, and PMMA respectively, and by Figs. 2.22 and 2.27 for low molecular weight samples of PS and PMPS. The phenomenon is appropriately described as “encroachment” of the shorter-time mechanism on the longer-time one. Consequently the separations among the three groups of viscoelastic mechanisms are decreased with decreasing temperature, explaining the narrowing of the softening dispersion when it is probed at longer times or lower temperatures [218].

It has previously been shown for PS, poly(vinyl acetate), and atactic polypropylene that the shift factor of the terminal relaxation or the viscosity $a_{T,\eta}$ has a weaker temperature dependence than do the softening dispersion $a_{T,S}$ (Fig. 2.11) and the local segmental relaxation $a_{T,\alpha}$ (Figs. 2.19 and 2.20). Therefore, in practice the shift factors a_T used to obtain master curves for polymers by time–temperature superposition are actually combinations of the individual shift factors of the several different viscoelastic mechanisms. At low temperatures, a_T is principally determined by the shift factor of the local segmental mode $a_{T,\alpha}$. With increasing temperature, a_T is principally determined sequentially by the shift factors of the sub-Rouse modes, $a_{T,sR}$, the Rouse modes, $a_{T,R}$, modes in the rubbery plateau, and, finally, the terminal modes, $a_{T,\eta}$. Hence, it is not correct to assume that a_T describes the temperature dependence of *any* or *all* of the viscoelastic mechanisms in a polymer.

In addition to timescale shifts with temperature, the magnitude of the compliance or modulus can change. The kinetic theory of rubber-like elasticity suggests that the entropically based contribution of the modulus to the viscoelastic response should increase in direct proportion to the absolute temperature. Correspondingly, the reciprocal of the steady-state recoverable compliance should be directly proportional to the absolute temperature. This is true at temperatures that are greater than $2T_g$, but, between $1.2T_g$ and $2T_g$, the steady-state recoverable compliance J_s is essentially independent of temperature. At still lower temperatures a strong decrease of J_s is seen [51].

2.6.3 The pressure dependence

A dielectric-relaxation study of the dependences of the local segmental relaxation and chain dynamics on pressure has been carried out [219] as a function of the molecular weight for polyisoprene (PI). The dipole moment of the polymer has components parallel and perpendicular to the chain backbone. Consequently, both the end-to-end vector motions and the local segmental motions of the polymer are probed dielectrically. Five *cis*-PI samples with number-averaged molecular weights of 1200, 2500, 3500, 10 600, and 26 000 and polydispersity indices less than 1.1 were used in this study. The entanglement molecular weight of PI is 5400 and thus the samples of lower molecular weights are not entangled.

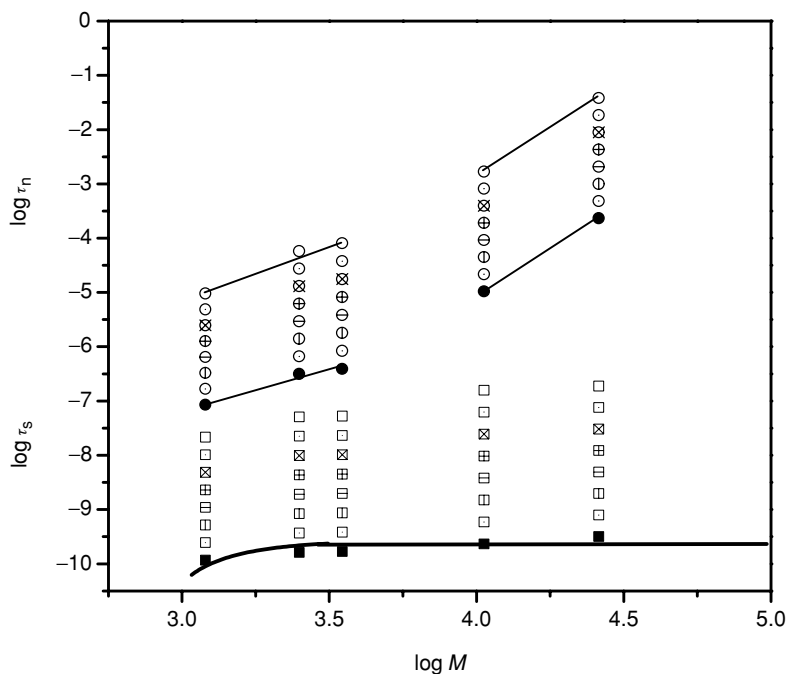


Fig. 2.32. Molecular weight dependences of the segmental (squares) and longest normal (circles) modes for the five PIs investigated plotted for various pressures at 320 K. The shortest time corresponds to the data at 1 bar and the rest are interpolated data shown at intervals of 0.5 kbar. The line through the segmental times at atmospheric pressure is a guide for the eye. From Floudas *et al.* by permission [218].

The dependences of the segmental and longest normal modes on the molecular weight at 320 K and various pressures are shown in Fig. 2.32. Notice that the segmental modes (by virtue of their higher apparent activation volume) exhibit a stronger P -dependence than do the corresponding normal modes. At any given P , the longest normal-mode times exhibit the M^2 -dependence for $M < M_e$ of Rouse dynamics (after correction of T_g has been performed for the samples of the smaller molecular weights to account for chain-end effects), and the $M^{3.4}$ -dependence for $M > M_e$, where M_e is the molecular weight for entanglement (see Chapter 3 by W. W. Graessley).

Individually, the spectral shape of the normal modes or the local segmental mode is invariant with changes in T and P within the range of the experiment. However, they shift differently with pressure, the local segmental relaxation time being more sensitive to changes in pressure. Hence, time–pressure superposition of the *entire* dielectric spectrum fails. Time–temperature superposition also fails for low and high molecular weight polymers as shown in Sections 2.6.1–2.6.3.

2.6.4 Dependences of viscoelastic and dynamic properties on chemical structure

As mentioned before in Section 2.5.1.2, the glassy compliance (modulus) and the plateau compliance (modulus) for PIB and PS are similar, but the width of the softening dispersion (glass–rubber transition) of PIB is several decades broader in time or frequency than that of PS [1, 2, 10]. This difference in the width of the softening dispersion is shown in Fig. 2.33 in terms of the retardation spectra $L(\lambda)$ of high molecular weight samples of PS and PIB obtained from recoverable-creep-compliance $J_r(t/\lambda)$ data by numerically solving Eq. (2.32) [11, 220]. The softening dispersion of $L(\lambda)$ marked by the rise from short λ (τ/a_T in Fig. 2.33) up to the first peak is broader in PIB than is that in PS. This difference of a viscoelastic property

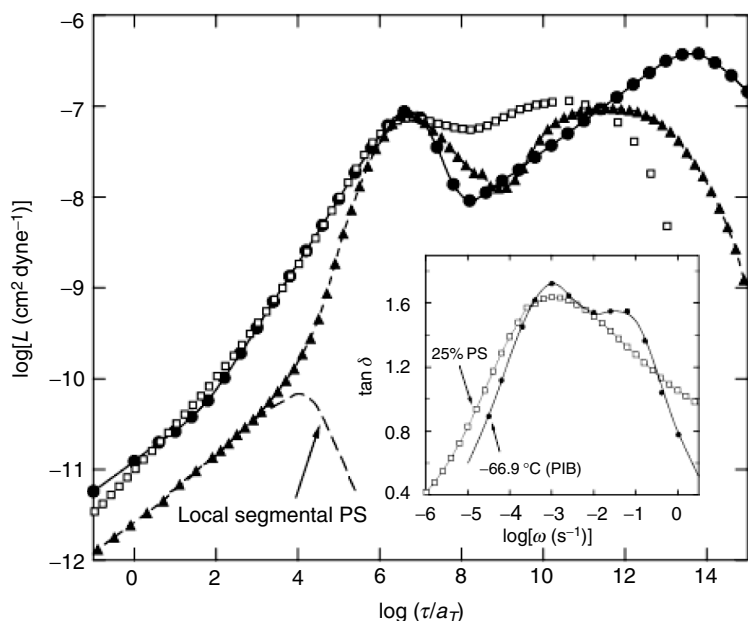


Fig. 2.33. A comparison of the retardation spectra L of a high molecular weight PS (filled triangles), a solution of 25% PS in TCP (open squares) and PIB (filled circles). The shift factors are arranged such that the maximum of the first peak occurs at the same reduced frequency for all three samples. Downward vertical shifts by 0.869 and 1.39 of $\log_{10} L$ have been applied to data for PS and the 25% PS solution, respectively, in order to make all data have about the same height at the first maximum. The disparity in width of the softening dispersion of bulk PS and PIB is clear. The small peak near the bottom (dashed line) is the contribution to L from the local segmental motion in bulk PS. The inset shows isothermal $\tan \delta$ data of PIB in the softening region at -66.9°C , and $\tan \delta$ of the solution of 25% PS in TCP obtained from a reduced recoverable-compliance curve after applying time–temperature superposition to the limited isothermal data.

between PS and PIB naturally leads one to ask the following question: what causes this difference? This elementary question begs an explanation, but has seldom been addressed.

We have touched upon this difference in choosing PIB rather than PS in order to resolve the sub-Rouse modes from the local segmental relaxation and the Rouse modes by experiment. The data on PIB in Fig. 2.29 show that the temperature dependence of the local segmental relaxation time $\tau_\alpha(T)$ is stronger than that of the Rouse relaxation time $\tau_R(T)$, which has quantitatively been accounted for by invoking their separate dependences on the friction factor $\zeta_0(T)$ given by Eq. (2.30). PCS measurements found that PS and PIB have β_α equal to 0.36 and 0.55, respectively [34, 167, 168]. Thus, according to Eq. (2.30), the effect that $a_{T,\alpha}$ has a much stronger temperature dependence than does $a_{T,R}$ is more prominent in PS than it is in PIB. The encroachment of $\tau_\alpha(T)$ on $\tau_R(T)$ is more severe in PS than it is in PIB, resulting in PS having a narrower softening dispersion. This explanation leads to another prediction. If we can decrease intermolecular coupling (or increase β_α) in PS by some means, then the softening dispersion should broaden. One way to decrease intermolecular coupling is by dissolving PS in a solvent with lower T_g such as *m*-tricresyl phosphate (TCP). The intermolecular coupling decreases with increasing solvent content and the width of the softening dispersion at some polymer concentration will match that of PIB. The softening dispersion of the solution of 25% PS in TCP [94] shown in Fig. 2.33 is indeed broader than that of PS and not too different from that of PIB. The loss tangent of the solution of 25% PS in PIB in the softening dispersion is also similar in width to that of PIB, but the sub-Rouse peak has not yet been resolved. A better match with PIB is expected from solutions with PS concentrations lower than 25% [220]. The isothermal $\tan \delta$ data of a solution of 17% PS in TCP shown in Fig. 2.34 have both the sub-Rouse and the Rouse peaks matching those for bulk PIB. The T_g -scaled temperature dependence of the shift factor of the softening dispersion of the solution of 17% PS in TCP (see Eq. (2.27)) also resembles that of bulk PIB. Thus several characteristic properties of the softening dispersion of PS, which differ greatly from those of the softening dispersion of PIB, are made the same as those for PIB by reducing the intermolecular coupling in PS by the addition of a diluent [220].

The chains of siloxane polymers such as poly(dimethyl siloxane) (PDMS) are very flexible because of the oxygen linkages in the backbone and the large Si—O—Si bond angles (see Chapter 1, by J. E. Mark). One consequence of the flexibility is the low T_g of these polymers, as discussed in Section 2.4.6. Another consequence of the greater chain flexibility is that the size of the smallest submolecule that can still be Gaussian, z , would be smaller for the siloxane polymers than it would for PIB and PS. Hence we can expect that the Rouse model [1] is valid down to shorter length-scales in PDMS than it is in PIB and PS. Indeed, neutron-scattering data

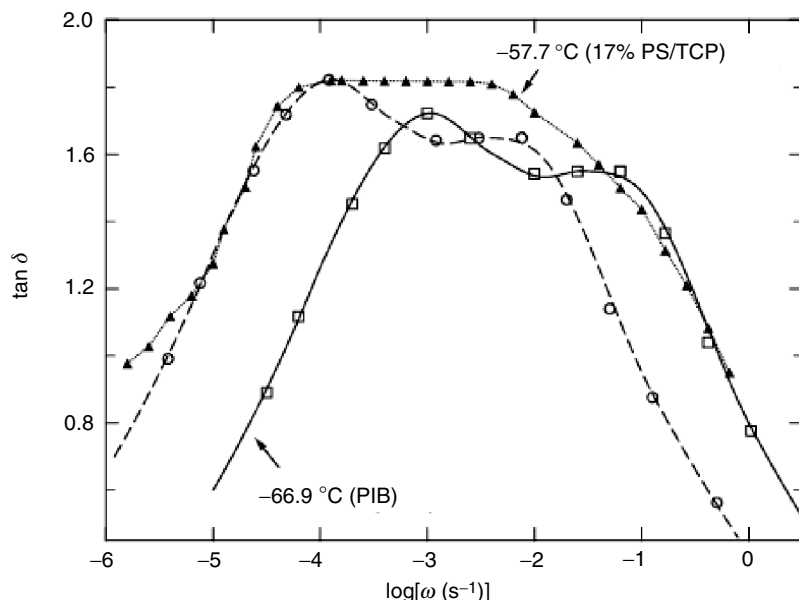


Fig. 2.34. A comparison of isothermal $\tan \delta$ of the solution of 17% PS in TCP at -57.7°C (filled triangles) and isothermal $\tan \delta$ of PIB at -66.9°C (open squares) in the softening region. The open circles are $\tan \delta$ of PIB at -66.9°C after the first peak has been shifted horizontally and scaled vertically to match the position and height of the first peak of the 17% PS solution. The lines connecting the data points of each set are drawn to guide the eye.

have shown that the Rouse dynamics continued to be observed down to distance of $2.5 \text{ \AA}$ in PDMS but only down to $6.7 \text{ \AA}$ in PIB [211, 212]. Creep-compliance measurements on amorphous poly(methylphenyl siloxane) and poly(methyl-*p*-tolyl siloxane), compounds in the same family as PDMS, do indeed show that the Rouse mode starts at a lower level compliance than it does in PIB [220].

2.7 Conclusion

Many of the macroscopic phenomena of the glass transition, particularly those of kinetic nature discussed in Section 2.2, are understood well on the basis of some properties of the structural relaxation above and below T_g . However, the microscopic molecular motions leading to these properties of the structural relaxation are far from being completely understood and are currently the subject of much research. A fundamental and in-depth understanding of the glass transition requires some knowledge of the physics that governs the molecular motions and the effects associated with them. Therefore it is important also to investigate and explain the molecular-dynamic properties of the equilibrium liquid on all timescales, with the aim of capturing the physics.

Theoretical approaches founded either on free volume or on configurational entropy can account for the changes of mobility with temperature and pressure, and explain the dependences of T_g on various parameters (Section 2.4). The research community is divided into two groups, believing that either free volume or configuration entropy is the only quantity that controls mobility. While, on the one hand, more sophisticated statistical-mechanical theories have been constructed in order to support the theory based on configurational entropy, on the other hand, recent pressure experiments on dynamics have found evidence of specific-volume contributions to the determination of molecular mobility. Thus there is no unique understanding of the theoretical basis even within these thermodynamic or mean-field treatments of the glass transition. Possibly both volume and entropy play their roles in the glass transitions of some polymeric and nonpolymeric liquids.

Lacking from these traditional theories and some modern mean-field theories of the glass transition is the consideration of possible effects due to the complex molecular dynamics. The objective of these theories is to explain the temperature dependence of the molecular mobility. Once the temperature has been fixed, these theories cease to offer any significant prediction of the structural-relaxation properties. Noticeably absent from these theories is the treatment of the dispersion (time or frequency dependence) of the molecular dynamics of the equilibrium liquid state. Even where the dispersion has been considered in ancillary developments, the results were given as an afterthought, and the dispersion obtained has no implication for other properties. Many empirical facts given in this chapter have shown that the shape of the dispersion characterized by the Kohlrausch–Williams–Watts fractional exponent β correlates or anti correlates with other properties. In particular, β enters into the anomalous dependences of the structural-relaxation time on various parameters. For polymers, β of the local segmental relaxation also influences various viscoelastic properties of longer length-scales. Among these is the failure of time–temperature and time–pressure superposition of viscoelastic data contributed by more than one mechanism, which shakes the foundation of viscoelasticity and casts doubt on any model in which it is assumed that different viscoelastic mechanisms have the same friction factor. Thus, the empirical facts suggest that the dispersion plays a fundamental role, implying that the dispersion is the manifestation of a hidden physical ingredient, which takes part in conjunction with volume and entropy in determining other properties. The hidden physical ingredient seems to be intermolecular interaction or coupling. It is the origin of the complex molecular motions and the dispersion of structural relaxation in equilibrium liquids.

How best to incorporate intermolecular coupling into structural relaxation is an open question. A first step has been made with the coupling model, which identifies the dispersion as a reflection of the intermolecular coupling. By taking advantage

of an ostensibly general physical principle, the coupling model generates many predictions that have explained the effects, correlations, and anomalous properties. Nevertheless, there are shortcomings of the coupling model, such as the lack of a description of the complex molecular motions. The field would benefit from other, more-sophisticated attempts to incorporate intermolecular coupling into a theory of molecular liquids. On the other hand, an expedient attempt such as using the spatial and dynamic heterogeneity of relaxation as a basis on which to explain other properties cannot accomplish the goal. This is because dynamic heterogeneity is just one among other parallel consequences of intermolecular coupling and hence it is not fundamental. It certainly is consistent with other consequences such as the non-exponential time dependence of the relaxation function, but it can contradict other experimental facts because it is not fundamental.

The task of this chapter is to provide a conceptual introduction to the glass transition and glassy-state phenomena in polymers, and a stepping-stone for discussion of viscoelastic and flow properties. It is written differently from other texts on the same subject by virtue of telling the reader not only about the macroscopic kinetic properties that are understood but also about the microscopic dynamics that are still not understood well. The chapter draws attention to the challenging problems that remain, particularly the importance of including intermolecular coupling in considering the dynamics of local segmental relaxation. The reader is exposed to overwhelming experimental measurements proving that polymers are not thermorheologically simple. This property caused principally by intermolecular coupling in local segmental relaxation should be taken into consideration in any model or theory of the viscoelasticity of polymers.

Acknowledgments

I am grateful to Connie T. Moynihan, Don J. Plazek, and C. M. Roland for many helpful discussions. I thank Greg McKenna for sending his reviews and the late Professor John D. Ferry for encouragement. The work was supported in part by the Office of Naval Research, USA.

References

- [1] J. D. Ferry, *Viscoelastic Properties of Polymers*, 3rd edition (John Wiley, New York, 1980).
- [2] A. V. Tobolsky, *Properties and Structure of Polymers* (John Wiley, New York, 1960).
- [3] J. J. Aklonis and W. J. MacKnight, *Introduction to Polymer Viscoelasticity*, 2nd edition (John Wiley, New York, 1983).
- [4] G. Strobl, *The Physics of Polymers*, 2nd edition (Springer, Berlin, 1997).

- [5] M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Clarendon Press, Oxford, 1986).
- [6] N. G. McCrum, B. E. Read, and G. Williams, *Anelastic and Dielectric Effects in Polymeric Solids* (John Wiley, New York, 1967).
- [7] G. Williams, *Adv. Polym. Sci.*, **33** (1979), 60.
- [8] G. B. McKenna, in *Comprehensive Polymer Science, Volume 2, Polymer Properties*, edited by C. Booth and C. Price (Pergamon, Oxford, 1989), p. 311.
- [9] C. A. Angell, K. L. Ngai, G. B. McKenna, P. F. McMillan, and S. W. Martin, *J. Appl. Phys.*, **88** (2000), 3113.
- [10] K. L. Ngai and D. J. Plazek, *Rubber Chem. Technol., Rubber Rev.*, **68** (1995), 376.
- [11] D. J. Plazek, *J. Rheol.*, **40** (1996), 987.
- [12] G. B. McKenna, in *Encyclopedia of Polymer Science and Technology* (John Wiley, New York, 2002).
- [13] F. Mezei, in *Liquids, Freezing and Glass Transition*, edited by J. P. Hansen, D. Levesque, and J. Zinn-Justin (North Holland, Amsterdam, 1991), p. 629.
- [14] K. Schmidt-Rohr and H. W. Spiess, *Multidimensional Solid State NMR and Polymers* (Academic Press, London, 1994).
- [15] R. Pecora (ed.), *Dynamic Light Scattering* (Academic Press, New York, 1986).
- [16] K. Binder (ed.), *Monte Carlo and Molecular Dynamics Simulations in Polymer Science* (Oxford University Press, Oxford, 1995).
- [17] W. Paul, G. D. Smith, Y. Yoon, D. B. Farago, S. Rathgeber, A. Zirkel, L. Willner, and D. Richter, *Phys. Rev. Lett.*, **80** (1998), 2346.
- [18] H. Takeuchi and R. J. Roe, *J. Chem. Phys.*, **94** (1991), 7446 and 7458.
- [19] R. H. Boyd, R. H. Gee, J. Han, and Y. J. Jin, *J. Chem. Phys.*, **101** (1994), 788.
- [20] T. Pakula, *J. Molec. Liquids*, **86** (2000), 109.
- [21] D. N. Theodorou and U. W. Suter, *Macromolecules*, **18** (1985), 1206.
- [22] J. Baschnagel, *et al.*, *Adv. Polym. Sci.*, **152** (2000), 41.
- [23] R. Greiner and F. R. Schwarzl, *Rheol. Acta*, **23** (1984), 378.
- [24] D. J. Plazek and K. L. Ngai, in *Physical Properties of Polymer Handbook*, edited J. E. Mark (AIP Press, Woodbury, New York, 1996), p. 139.
- [25] C. T. Moynihan, E. J. Easteal, and M. A. DeBolt, *J. Am. Cer. Soc.*, **59** (1976), 12.
- [26] C. T. Moynihan, S.-K. Lee, M. Tatsumisago, and T. Minami, *Thermochim. Acta*, **280/281** (1996), 153.
- [27] A. Q. Tool, *J. Am. Ceram. Soc.*, **29** (1946), 240.
- [28] A. J. Kovacs, *Fortschr. Hochpolym.-Forsch.*, **3** (1964), 394.
- [29] G. W. Scherer, *J. Am. Cer. Soc.*, **69** (1986), 374.
- [30] O. S. Narayanaswamy, *J. Am. Cer. Soc.*, **54** (1971), 491.
- [31] C. T. Moynihan, *et al.*, *Ann. N. Y. Acad. Sci.*, **279** (1976), 15.
- [32] A. J. Kovacs, J. J. Aklonis, J. M. Hutchinson, and A. R. Ramos, *J. Polym. Sci.: Polym. Phys. Ed.*, **17** (1979), 1097.
- [33] G. Williams and D. C. Watts, *Trans. Faraday Soc.*, **66** (1971), 80; G. Williams, D. C. Watts, S. B. Dev, and A.M.D.C. North, *Trans. Faraday Soc.*, **67** (1971), 1323.
- [34] G. D. Patterson, in [15], p. 260.
- [35] I. Hodge, *J. Non-Cryst. Solids*, **266** (1994), 169; G. W. Scherer, *J. Am. Ceram. Soc.*, **67** (1984), 504.
- [36] G. Adam and J.H. Gibbs, *J. Chem. Phys.*, **43** (1965), 139.
- [37] W. Kauzmann, *Chem. Rev.*, **43** (1948), 219.
- [38] J. M. Hutchinson, S. Montserrat, Y. Calventus, and P. Cortés, *J. Non-Cryst. Solids*, **307–310** (2002), 412.
- [39] I. M. Hodge, *Macromolecules*, **16** (1983) 898.

- [40] S. L. Simon, J. W. Sobieski, and D. J. Plazek, *Polymer*, **42** (2001), 2555.
- [41] K. Schmidt-Rohr and H. W. Spiess, *Phys. Rev. Lett.*, **66** (1991), 3020.
- [42] R. Böhmer, *et al.*, *J. Non-Cryst. Solids*, **235–237** (1998), 1.
- [43] C. T. Moynihan and J.-H. Whang, *Master. Res. Soc. Symp. Proc.*, **455** (1977), 133.
- [44] L. C. E. Struik, *Physical Aging in Amorphous Polymers and Other Materials* (Elsevier, Amsterdam, 1978); *J. Non-Cryst. Solids*, **131–133** (1991), 395.
- [45] A. K. Doolittle, *J. Appl. Phys.*, **22** (1951), 1031.
- [46] J. H. Gibbs and E. A. DiMarzio, *J. Chem. Phys.*, **28** (1958), 373.
- [47] J. H. Gibbs and E. A. DiMarzio, *J. Chem. Phys.*, **28** (1958), 807.
- [48] M. Mezard and G. Parisi, *Phys. Rev. Lett.*, **82** (1999), 747.
- [49] M. Goldstein, *J. Chem. Phys.*, **51** (1969), 3728.
- [50] M. H. Cohen and D. Turnbull, *J. Chem. Phys.*, **31** (1959), 1164.
- [51] D. J. Plazek and A. J. Chelko Jr, *Polymer*, **18** (1977), 15.
- [52] M. L. Williams, R. F. Landel, and J. D. Ferry, *J. Am. Chem. Soc.*, **77** (1955), 3701.
- [53] D. J. Plazek, *J. Phys. Chem.*, **69** (1965), 3480.
- [54] D. J. Plazek, *Polymer J.*, **12** (1980), 43.
- [55] D. L. Plazek and D. J. Plazek, *Macromolecules*, **16** (1983) 1469.
- [56] D. J. Plazek, *J. Polym. Sci.: Polym. Phys. Ed.*, **20** (1982), 729.
- [57] S. J. Tao, *J. Chem. Phys.*, **56** (1972), 5499.
- [58] M. Eldrup, D. Lightbody, and J. N. Sherwood, *Chem. Phys.*, **63** (1981), 51.
- [59] Y. Y. Wang, H. Nakanishi, Y. C. Jean, and T. C. Sandreczki, *J. Polym. Sci. B, Polym. Phys.*, **28** (1990), 1431.
- [60] H. A. Hristov, B. Bolan, A. F. Yee, L. Xie, and D. W. Gidley, *Macromolecules*, **29** (1996), 8507.
- [61] J. Bartos and J. Kristiak, *J. Phys. Chem.*, **104** (2000), 5666.
- [62] Y. Kobayashi, W. Zheng, E. F. Meyer, J. D. McGervey, A. M. Jamieson, and R. Simha, *Macromolecules*, **22** (1989) 2302.
- [63] X. S. Li and M. C. Boyce, *J. Polym. Sci. B Polym. Phys.*, **31** (1993), 869.
- [64] K. L. Ngai, L.-R. Bao, A. F. Yee, and C. L. Soles, *Phys. Rev. Lett.*, **87** (2001), 215 901.
- [65] J. Bartos, O. Sausa, P. Bandzuch, J. Zrucova, and J. Kristiak, *J. Non-Cryst. Solids*, **307–310** (2002), 417.
- [66] A. Mermet, E. Duval, N. V. Surovtev, J. F. Jal, A. J. Dianoux, and A. F. Yee, *Europhys. Lett.*, **38** (1997), 515.
- [67] J. Bartos, J. Kristiak, and T. Kanaya, *Physica B*, **234** (1997), 435.
- [68] P. J. Flory, *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, New York, 1953).
- [69] J. H. Magill, *J. Chem. Phys.*, **47** (1967), 2802.
- [70] S. S. Chang and A. B. Bestul, *J. Chem. Phys.*, **56** (1972), 505.
- [71] O. Yamamuro, I. Tsukushi, A. Lindqvist, S. Takahara, M. Ishikawa, and T. Matsuo, *J. Phys. Chem.*, **102** (1998), 1605.
- [72] C. M. Roland, P. Santangelo, and K. L. Ngai, *J. Chem. Phys.*, **111** (2000), 5593.
- [73] G. P. Johari, *J. Chem. Phys.*, **116** (2002), 2043.
- [74] K. L. Ngai and C. M. Roland, *Polymer*, **43** (2002), 567.
- [75] C. A. Angell, *J. Res. Natl. Inst. Stand. Technol.*, **102** (1997), 171.
- [76] R. Richert and C. A. Angell, *J. Chem. Phys.*, **108** (1998), 9016.
- [77] K. L. Ngai, *J. Phys. Chem.*, **103** (1999), 5895.
- [78] H. Vogel, *Phys. Z.*, **22** (1921), 645.
- [79] G. S. Fulcher, *J. Am. Ceram. Soc.*, **8** (1928), 339.
- [80] G. Tammann and W. Hesse, *Z. Anorg. Allg. Chem.*, **156** (1926), 245.

- [81] T. G. Fox and P. J. Flory, *J. Appl. Phys.*, **21** (1950), 581.
- [82] T. G. Fox and L. Loshack, *J. Polym. Sci.*, **15** (1995), 371.
- [83] E. A. DiMarzio and C. M. Guttman, *Macromolecules*, **20** (1987), 1403.
- [84] A. J.-M. Yang and E. A. DiMarzio, *Macromolecules*, **24** (1991), 6012.
- [85] S. J. Clarson, K. Dodgson, and J. A. Semlyen, *Polymer*, **26** (1985), 930.
- [86] K. U. Kirst, F. Kremer, T. Pakula, and J. Hollingshurst, *J. Coll. Polym. Sci.*, **272** (1994), 1420.
- [87] S. J. Clarson, J. A. Semlyen, and K. Dodgson, *Polymer*, **32** (1991), 2823.
- [88] P. G. Santangelo, C. M. Roland, T. Chang, D. Cho, and J. Roovers, *Macromolecules*, **34** (2001), 9002.
- [89] A. K. Rizos and K. L. Ngai, *Macromolecules*, **31** (1998), 6217.
- [90] D. J. Plazek and V. M. O'Rourke, *J. Polym. Sci., Part A-2*, **9** (1971), 209.
- [91] E. Jenkel and R. Heusch, *Kolloid Z.*, **130** (1953), 19.
- [92] D. J. Plazek, C. Seoul, and C. A. Bero, *J. Non-Cryst. Solids*, **131–133** (1991), 570.
- [93] F. N. Kelly and F. Beuche, *J. Polym. Sci.*, **50** (1961), 549.
- [94] D. J. Plazek, E. Riande, H. Markovitz, and N. Raghupathi, *J. Polym. Sci.: Polym. Phys. Ed.*, **17** (1979), 2189.
- [95] J. L. Schrag, *et al.*, *J. Non-Cryst. Solids*, **131–133** (1991), 537.
- [96] R. L. Morris, S. Amelar, and T. P. Lodge, *J. Chem. Phys.*, **89** (1988), 6523.
- [97] D. J. Gisser and M. D. Ediger, *Macromolecules*, **25** (1992), 1248.
- [98] A. K. Rizos and K. L. Ngai, *Phys. Rev. B*, **46** (1992), 8127.
- [99] A. K. Rizos and K. L. Ngai, *Macromolecules*, **27** (1994), 4493.
- [100] P. G. Santangelo, C. M. Roland, K. L. Ngai, A. K. Rizos, and H. Katerinopoulos, *J. Non-Cryst. Solids*, **172–174** (1994), 1084.
- [101] C. M. Roland, P. G. Santangelo, Z. Baram, and J. Runt, *Macromolecules*, **27** (1994), 5382.
- [102] R. E. Wetton, W. J. MacKnight, J. R. Fried, and F. E. Karasz, *Macromolecules*, **11** (1978), 158.
- [103] A. Zetsche and E. W. Fischer, *Acta Polym.*, **45** (1994), 168.
- [104] S. Kamath, R. H. Colby, S. K. Kumar, K. Karatasos, G. Floudas, G. Fytas, and J. E. L. Roovers, *J. Chem. Phys.*, **111** (1999), 6121.
- [105] J. B. Miller, K. J. McGrath, C. M. Roland, C. A. Trask, and A. N. Garroway, *Macromolecules*, **23** (1990), 4543.
- [106] K. Schmidt-Rohr, J. Clauss, and H. W. Spiess, *Macromolecules*, **25** (1992), 3273.
- [107] A. Alegria, J. Colmenero, K. L. Ngai, and C. M. Roland, *Macromolecules*, **27** (1994), 4486.
- [108] K. L. Ngai and C. M. Roland, *Macromolecules*, **28** (1995), 4033.
- [109] G.-C. Chung, J. A. Kornfield, and S. D. Smith, *Macromolecules*, **27** (1994), 5729.
- [110] S. Hoffmann, L. Willner, D. Richter, A. Arbe, J. Colmenero, and B. Farago, *Phys. Rev. Lett.*, **85** (2000), 772.
- [111] M. Doxastakis, M. Kitsiou, G. Fytas, D. N. Theodorou, N. Hadjichristidis, G. Meier, and B. Frick, *J. Chem. Phys.*, **112** (2000), 8687.
- [112] C. M. Roland and K. L. Ngai, *Macromolecules*, **24** (1991), 2261.
- [113] C. M. Roland and K. L. Ngai, *J. Rheol.*, **36** (1992), 1691.
- [114] T. P. Lodge and T. C. McLeish, *Macromolecules*, **33** (2000), 5278.
- [115] T. Inoue, M. T. Cicerone, and M. D. Ediger, *Macromolecules*, **28** (1995), 3425.
- [116] D. Bainbridge and M. D. Ediger, *Rheol. Acta*, **36** (1997), 209.
- [117] K. L. Ngai, *J. Phys. Chem. B*, **103** (1999), 10684.
- [118] E. A. DiMarzio, *J. Res. Natl. Bur. Stand. A*, **68** (1964), 611.
- [119] M. J. Schroeder and C. M. Roland, *Macromolecules*, **35** (2002), 2676.

- [120] J.-F. Shi, L. C. Dickinson, W. J. MacKnight, and J. C. W. Chien, *Macromolecules*, **26** (1993), 5908.
- [121] K. L. Ngai and C. M. Roland, *Macromolecules*, **25** (1994), 2454.
- [122] H. A. Flocke, *Kolloid Z. Z. Polym.*, **180** (1962), 188.
- [123] B. G. Rånby, K. S. Chan, and H. Brumberger, *J. Polym. Sci.*, **58** (1962), 545
- [124] G. Floudas, P. Placke, W. Brown P. Stepanek, and K. L. Ngai, *Macromolecules*, **28** (1995), 6799.
- [125] K. L. Ngai, S. Etienne, Z. Z. Zhong, and D. E. Schuele, *Macromolecules*, **28** (1995), 6423.
- [126] F. E. Karasz and W. J. MacKnight, *Macromolecules*, **1** (1968), 537.
- [127] G. P. Mikhailov and T. I. Borisova, *Polym. Sci. USSR*, **2** (1961), 387.
- [128] D. J. Plazek, V. Tan, and V. M. O'Rourke, *Rheol. Acta*, **13** (1974), 367.
- [129] A. Eisenberg, *J. Phys. Chem.*, **67** (1967), 1333.
- [130] J. E. McKinney and M. Goldstein, *J. Res. Natl. Bur. Stand. A*, **78A** (1974), 331.
- [131] G. Goldbach and G. Rehage, *Rheol. Acta*, **6** (1967), 30.
- [132] C. M. Roland and R. Casalini, *Macromolecules*, **36** (2003), 1361.
- [133] M. Paluch, R. Casalini, and C. M. Roland, *Phys. Rev. B*, **66** (2002), 092 202.
- [134] J. L. Keddie, R. A. L. Jones, and R. A. Cory, *Europhys. Lett.*, **27** (1994), 59.
- [135] K. Tanaka, A. Takahara, and T. Kajiyama, *Macromolecules*, **33** (2000), 6439; K. Fukao and Y. Miyamoto, *Phys. Rev. E*, **61** (2000), 1743.
- [136] J. A. Forrest, K. Dalnoki-Veress, J. R. Stevens, and J. R. Dutcher, *Phys. Rev. Lett.*, **77** (1996), 2002; J. A. Forrest, K. Dalnoki-Veress, and J. R., Dutcher, *Phys. Rev. E.*, **58** (1998), 6109; J. A. Forrest and Dalnoki-Veress, *Adv. Coll. Interf. Sci.*, **94** (2001), 167.
- [137] K. L. Ngai, A. K. Rizos, and D. J. Plazek, *J. Non-Cryst. Solids*, **235–237** (1998), 435.
- [138] K. L. Ngai, *Euro. Phys. J. E*, **8** (2002), 225.
- [139] J. Baschnagel, C. Mischler, and K. Binder, *J. Physique IV*, **10** (2000), 7–9.
- [140] C. Mischler, J. Baschnagel, and K. Binder, *Adv. Coll. Interf. Sci.*, **94** (2001), 197.
- [141] S. H. Anastasiadis, K. Karatasos, G. Vlachos, E. Manias, and E. P. Giannelis, *Phys. Rev. Lett.*, **84** (2000), 915.
- [142] D. S. Fryer, P. F. Nealey, and J. J. de Pablo, *Macromolecules*, **33** (2000), 6439.
- [143] G. B. McKenna, *J. Physique IV*, **10** (2000), 7–53.
- [144] C. L. Jackson and G. B. McKenna, *J. Chem. Phys.*, **93** (1991), 9002.
- [145] M. Arndt, R. Stannarius, H. Groothues, E. Hempel, and F. Kremer, *Phys. Rev. Lett.*, **79** (1997), 2077.
- [146] K. L. Ngai, *J. Phys.: Condens. Matter*, **11** (1999), A119.
- [147] A. Schönhals, H. Goering, and Ch. Schick, to be published (2003).
- [148] K. L. Ngai, *J. Non-Cryst. Solids*, **275** (2000), 7.
- [149] R. Kohlrausch, *Pogg. Ann. Phys.* **12** (1847), 393; *Pogg. Ann. Phys.*, **91** (1854), 56 and 179.
- [150] H. W. Spiess, *J. Non-Cryst. Solids*, **131–133** (1991), 766; S. Kaufmann, S. Wefing, D. Schaefer, and S.W. Spiess, *J. Chem. Phys.*, **93** (1990), 197.
- [151] K. L. Ngai and D. J. Plazek, in *Physical Properties of Polymers Handbook*, edited by J. E. Mark (AIP Press, Woodbury, New York, 1996), p. 341.
- [152] G. Fytas and K. L. Ngai, *Macromolecules*, **21** (1988), 804.
- [153] P. G. Santangelo, K. L. Ngai, and C. M. Roland, *Macromolecules*, **29** (1996), 3651.
- [154] C. M. Roland, K. L. Ngai, P. G. Santangelo, X. H. Qiu, M. D. Ediger, and D. J. Plazek, *Macromolecules*, **34** (2001), 6159.
- [155] G. B. McKenna, K. L. Ngai, and D. J. Plazek, *Polymer*, **26** (1985), 1651; K. L. Ngai and D. J. Plazek, *J. Polym. Sci.: Polym. Phys. Ed.*, **23** (1985), 2159.
- [156] R. A. Mendelsohn, W. A. Bowles, and G. L. Finger, *J. Polym. Sci. A-2*, **8** (1970), 105.

- [157] M. D. Qiu, X. H. Ediger, *Macromolecules*, **33** (2000), 490.
- [158] F. Stickel, E. W. Fischer, and R. Richert, *J. Chem. Phys.*, **104**, (1996), 2043.
- [159] K. L. Ngai, J. H. Magill, and D. J. Plazek, *J. Chem. Phys.*, **112** (2000), 1887.
- [160] A. Heuer, M. Wilhelm, H. Zimmermann, and H. W. Spiess, *Phys. Rev. Lett.*, **75** (1997) 2851.
- [161] J. Colmenero, A. Alegria, A. Arbe, and B. Frick, *Phys. Rev. Lett.*, **69** (1992), 478; J. Colmenero, A. Arbe, and A. Alegria, *J. Non-Cryst. Solids*, **172–174** (1994), 126; R. Zorn, A. Arbe, J. Colmenero, B. Frick, D. Richter, and U. Buchenau, *Phys. Rev. E*, **52** (1995), 781; J. Colmenero, A. Arbe, G. Coddens, B. Frick, C. Mijangos, and H. Reinecke *Phys. Rev. Lett.*, **78** (1997) 1928.
- [162] K. L. Ngai, J. Colmenero, A. Arbe, and A. Alegria, *Macromolecules*, **25** (1992), 6727.
- [163] D. J. Plazek and K. L. Ngai, *Macromolecules*, **24** (1991), 1222. Werner Oldekop [*Glaßtechnische Berichte*, **30** (1957), 8] and later W. T. Laughlin and D. R. Uhlmann [*J. Phys. Chem.*, **76** (1972), 2317.] were the first to use T_g as a corresponding state parameter for liquid viscosity η to compare the flow behavior of different liquids. Later on C. A. Angell introduced the terms “fragile” and “strong” to classify non-polymeric liquids that have different curvatures in this plot [C. A. Angell, in *Relaxations in Complex Systems*, edited by K. L. Ngai and G. B. Wright (US Government Publishing House, 1984), pp. 3–16; *J. Non-Cryst. Solids*, **131–133** (1991), 13.].
- [164] R. Böhmer, K. L. Ngai, C. A. Angell, and D. J. Plazek, *J. Chem. Phys.*, **99** (1993), 4201.
- [165] K. L. Ngai and C. M. Roland, *Macromolecules*, **26** (1993), 6824.
- [166] J. D. Ferry, *Macromolecules*, **24** (1991), 5237.
- [167] A. K. Rizos, T. Jian, and K. L. Ngai, *Macromolecules*, **28** (1995), 517.
- [168] K. L. Ngai, D. J. Plazek, and A. K. Rizos, *J. Polym. Sci. Pt B: Polym. Phys.*, **35** (1997), 599.
- [169] D. J. Plazek, X. D. Zheng, and K. L. Ngai, *Macromolecules*, **25** (1992), 4920.
- [170] K. L. Ngai and D. J. Plazek, C. Bero, *Macromolecules*, **26** (1993), 1065.
- [171] K. L. Ngai, *Comments Solid State Phys.*, **9** (1979), 127 and 141.
- [172] K. L. Ngai, A. K. Rajagopal, and S. Teitler, *J. Chem. Phys.*, **88** (1988), 6088.
- [173] K. L. Ngai and K. Y. Tsang, *Phys. Rev. E*, **60** (1999), 4511.
- [174] K. L. Ngai and R. W. Rendell, in *Supercooled Liquids, Advances and Novel Applications*, edited by J. T. Fourkas, D. Kivelson, U. Mohanty, and K. Nelson, (American Chemical Society, Washington, 1997), p. 45.
- [175] K. L. Ngai, R. W. Rendell, and D. J. Plazek, *Rheol. Acta.*, **36** (1997), 307.
- [176] K. L. Ngai and D. J. Plazek, *Macromolecules*, **35** (2002), 9136.
- [177] J. Heijboer, *Kolloid Z.*, **148** (1956), 36.
- [178] E. W. Fischer, G. P. Hellmann, H. W. Spiess, F. J. Horth, U. Ecarius, and M. Wehrle, *Makromol. Chem., Suppl.*, **12** (1985), 189.
- [179] A. A. Jones, J. F. O’Gara, P. T. Inglefield, J. T. Bendler, A. F. Yee, and K. L. Ngai, *Macromolecules*, **16** (1983), 658.
- [180] J. J. Connolly and A. A. Jones, *Macromolecules*, **18** (1985), 910.
- [181] A. Eisenberg and B. C. Eu, *Ann. Rev. Mater. Sci.*, **6** (1976), 335.
- [182] J. R. Fried, in *Physical Properties of Polymers Handbook*, edited by J. E. Mark (AIP Press, Woodbury, New York, 1996), p. 161.
- [183] K. Schmidt-Rohr, A. S. Kulik, H. W. Beckham, A. Ohlemacher, U. Pawelzik, C. Boeffel, and H. W. Spiess, *Macromolecules*, **27** (1994), 4733.
- [184] G. P. Johari, *Annals New York Acad. Sci.*, **279** (1976), 117.
- [185] M. Goldstein, *Ann. N.Y. Acad. Sci.*, **279** (1976), 68.

- [186] G. P. Johari, G. Power, and J. K. Vij, *J. Chem. Phys.*, **116** (2002), 5908.
- [187] K. L. Ngai, *J. Chem. Phys.* **109** (1998), 6982; *Macromolecules*, **32** (1999), 7140.
- [188] K. L. Ngai, *J. Phys.: Condens. Matter*, **15** (2003), S1107.
- [189] F. Fujara and W. Petry, *Europhys. Lett.*, **4** (1987), 921.
- [190] U. Buchenau and R. Zorn, *Europhys. Lett.*, **18** (1992), 523.
- [191] B. Frick and D. Richter, *Phys. Rev. B*, **47** (1993), 14 795.
- [192] W. Petry and J. Wuttke, *Trans. Theor. Statist. Phys.*, **24** (1995), 1075.
- [193] J. Gapinski, W. Steffen, A. Patkowski, A. P. Sokolov, A. Kisliuk, U. Buchenau, M. Russina, F. Mezei, and H. Schober, *J. Chem. Phys.*, **110** (1999), 2312.
- [194] H. C. Barshilia, G. Li, G. Q. Shen, and H. Z. Cummins, *Phys. Rev. E*, **59** (1999), 5625.
- [195] F. Mezei and M. Russina, *J. Phys.: Condens. Matter*, **11** (1999), A341.
- [196] T. Kanaya, T. Tsukushi, K. Kaji, J. Bartos, and J. Kristiak, *Phys. Rev. E*, **60** (1999) 1906.
- [197] P. Lunkenheimer, U. Schneider, R. Brand, and A. Loidl, *Contemp. Phys.*, **41** (2000), 15.
- [198] R. Casalini and K. L. Ngai, *J. Non-Cryst. Solids*, **293–295** (2001), 318.
- [199] C. A. Angell, *J. Phys.: Condens. Matter*, **12** (2000), 6463.
- [200] S. Yagihara, M. Yamada, M. Asano, Y. Kanai, N. Shinyashiki, S. Mashimo, and K. L. Ngai, *J. Non-Cryst. Solids*, **235–237** (1998), 412.
- [201] S. Corezzi, M. Beiner, H. Huth, K. Schröter, S. Capaccioli, R. Casalini, D. Fioretto, and E. Donth, *J. Chem. Phys.*, **117** (2002), 2435.
- [202] R. W. Gray, G. Harrison, and J. Lamb, *Proc. R. Soc. London, A Ser.*, **356** (1977), 77.
- [203] J. Cochrane, G. Harrison, J. Lamb, and D. W. Phillips, *Polymer*, **21** (1980), 837.
- [204] D. J. Plazek, C. Bero, S. Neumeister, G. Floudas, G. Fytas, and K. L. Ngai, *J. Colloid Polymer Sci.*, **272** (1994), 1430.
- [205] D. J. Plazek, A. Schönhal, E. Schlosser, and K. L. Ngai, *J. Chem. Phys.*, **98** (1993), 6488.
- [206] K. L. Ngai, A. Schönhal, and E. Schlosser, *Macromolecules*, **25** (1992), 4915.
- [207] K. L. Ngai, I. Echeverria, and D. J. Plazek, *Macromolecules*, **29** (1997), 7937.
- [208] B. E. Read, P. E. Tomlins, and G. D. Dean, *Polymer*, **31** (1990), 1204.
- [209] M. L. Williams, *J. Polym. Sci.*, **62** (1962), 57.
- [210] D. J. Plazek, I.-C. Chay, K. L. Ngai, and C. M. Roland, *Macromolecules*, **28** (1995), 6432.
- [211] D. Richter, M. Monkenbusch, J. Allgeier, A. Arbe, J. Colmenero, B. Farago, Y. Choel Bae, and R. Faust, *J. Chem. Phys.*, **111** (1999), 6107.
- [212] A. Arbe, M. Monkenbusch, J. Stellbrink, D. Richter, B. Farago, M. Almdal, and R. Faust, *Macromolecules*, **34** (2001), 1281.
- [213] S. Krushev, W. Paul, and G. D. Smith, *Macromolecules*, **35** (2002), 4198.
- [214] D. J. Plazek, *J. Polym. Sci. Pt A-2*, **6** (1968), 621.
- [215] J.-Y. Cavaille, C. Jordan, J. Perez, L. Monnerie, and G. Johari, *J. Polym. Sci.: Pt B: Polym. Phys.*, **25** (1987), 1235.
- [216] L. I. Palade, V. Verney, and P. Attané, *Macromolecules*, **28** (1995), 7051.
- [217] M. L. Williams and J. D. Ferry, *J. Colloid Sci.*, **10** (1955), 474.
- [218] D. J. Plazek, M. J. Rosner, and D. L. Plazek, *J. Polym. Sci., Part B: Polym. Phys.*, **26** (1988), 473.
- [219] G. Floudas, C. Gravalides, T. Reisinger, and G. J. Wegner, *J. Chem. Phys.*, **111** (1999), 9847.
- [220] K. L. Ngai and D. J. Plazek, *Macromolecules*, **35** (2002), 9136.

3

Viscoelasticity and flow in polymeric liquids

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3.1 Introduction

This chapter deals with viscoelastic behavior in the liquid state, particular emphasis being placed upon those aspects associated with the flow properties of polymer melts and concentrated solutions. The time-dependent response of polymers in the glassy state and near the glass transition, one variety of viscoelasticity, was discussed in Chapter 2. The concern in this chapter is the response at long times and for temperatures well above the glass transition. The elastic behavior of polymer networks well above the glass transition was discussed in Chapter 1. The conditions here are similar, and elastic effects may be very important in polymeric liquids, but steady-state flow can now also occur because the chains are not linked together to form a network. All the molecules have finite sizes, and, for flexible-chain polymers, the materials of interest in this chapter, the molecules have random-coil conformations at equilibrium (see Chapters 1 and 7).

The discussion in this chapter covers linear viscoelasticity [1], a primary means of rheological characterization for polymer liquids, and simple shear flow under steady-state conditions [2, 3], a relatively well-understood bridge into nonlinear viscoelastic behavior. The effects of large-scale chain structure – molecular weight, molecular weight distribution, and long-chain branching – will be discussed, and some theoretical ideas about molecular aspects will be described. The general mathematical framework of the subject [4, 5], and applications to the solution of practical flow problems [6–8] are more advanced topics and will not be discussed here. Some other important topics have also been omitted or considered only briefly, but sources of information on these are included in the references. The primary aim of this chapter is to provide some physical understanding of the viscoelastic behavior in polymer liquids both from the macroscopic viewpoint and from the molecular viewpoint.

3.2 Concepts and definitions

3.2.1 Deformation and stress

To deform a body of material means to change its shape [9]. A liquid deforms when it flows in a tube (Poiseuille flow), as depicted in Fig. 3.1. Whether the liquid elements are driven by pressure or gravity, they move in straight lines parallel to the axis of the tube. Those on the centerline of the tube have the largest velocity, those at the wall do not move at all. For long tubes and a constant driving force, all elements move at constant velocity, slightly slower than adjacent elements nearer the centerline and slightly faster than those nearer the wall. Tube flow exemplifies a *simple shear deformation*. The layers of liquid along the direction of flow slide over one another without stretching. Other examples of simple shear shown in Fig. 3.1 are the flows induced by relative rotation of coaxial cylinders (Couette flow), coaxial parallel plates (torsional flow), and coaxial cone and plate.

Simple extension belongs to a different class of deformations. As depicted in the lower part of Fig. 3.1, liquid elements are stretched along the direction of flow without sliding relative to adjacent elements. Extensional flow, sometimes called elongational flow, is an important component in many polymer-processing operations, for example in fiber spinning and film formation. Extensional flows are difficult to generate and sustain in a controlled way, however. Most laboratory methods used to characterize polymer-flow properties involve simple shear flows. The effects of these two classes of deformation on chain conformations, caused by the respective relative motions, are sketched in Fig. 3.2. For simplicity and brevity only the response in shear flow will be discussed in this chapter.

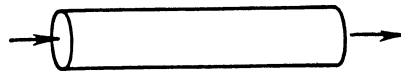
Deformation always involves a change in distance between the parts of a body, which induces a resisting force. The flow velocities in a tube, for example, result from the balance of two forces. The force from an applied *pressure difference* driving the flow is opposed by a force from the *shear stress*, generated by the relative motion of the liquid elements and acting between adjacent layers of liquid. The applied torque in the various coaxial geometries shown in Fig. 3.1 is similarly opposed by a shear stress originating from relative motion. In more general terms, the *stress* in a body of material is the *force per unit area* transmitted through contact between adjacent layers of particles. The relationship between stress and deformation is a property of the material itself. *Rheology* is the study of stress–deformation relationships, although that term is usually reserved for discussions of materials that are more complicated in their behavior than ordinary liquids and solids.

3.2.2 Viscoelasticity

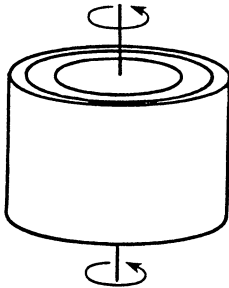
Liquids have no preferred shape. Except for a pressure contribution acting equally in all directions, the stress in a *perfectly viscous liquid* depends only on the *rate*

Simple Shear Deformation:

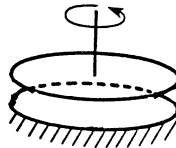
Layers of liquid slide over one another without stretching



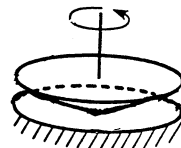
Flow through a tube



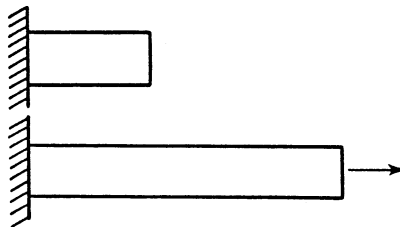
Coaxial Cylinders



Parallel Plates



Cone and Plate

Simple Extensional Deformation:

Layers of liquid are stretched without sliding

Fig. 3.1. Types of deformation.

of deformation. The stress at each moment depends on how rapidly the liquid is being deformed at that moment alone. In a perfectly viscous liquid, the past history of deformation is irrelevant. A perfectly viscous liquid has no memory. All the mechanical work expended on producing the deformation is dissipated, converted instantaneously to thermal energy.

A solid, on the other hand, has a preferred shape, the shape it assumes spontaneously when no forces are applied, also called its *rest shape*. In a *perfectly*

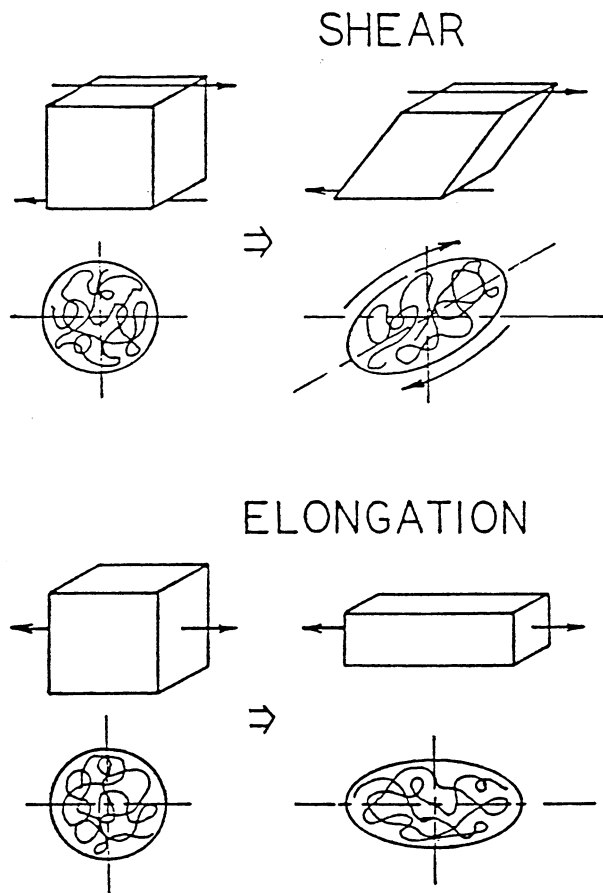


Fig. 3.2. Effects of shear and extensional flow on chain conformations.

elastic solid, the stress (again, except for the pressure) depends only on the amount of deformation from that preferred shape. All the mechanical work expended on deforming a perfectly elastic solid from its rest state is stored as elastic energy.

The mechanical behavior of a *viscoelastic material* exhibits both dissipation and storage of energy. In a viscoelastic liquid, the stress depends on the history of the deformation. Some finite time must elapse for a viscoelastic liquid to “forget” the sequence of shapes that it had in the past.

All real substances are viscoelastic. How they respond in particular situations depends on the rate of testing compared with the rate of spontaneous structural reorganization at the molecular level [1]. As depicted in Fig. 3.3, the neighbors of molecules in an ordinary liquid well above its glass-transition temperature T_g change rapidly through the action of Brownian motion. Local structural “memory” – the

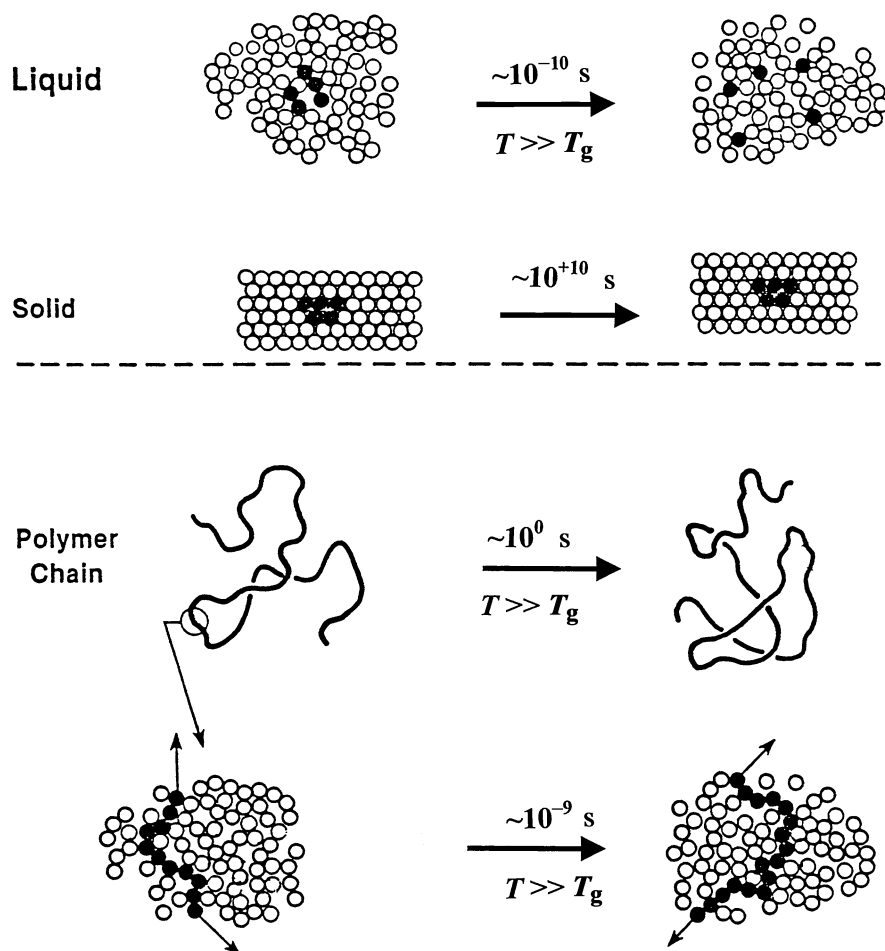


Fig. 3.3. Molecular rearrangement and the associated timescale for ordinary liquids, solids, and polymer melts.

average lifetime of adjacent pairings – is very short ($\sim 10^{-10}$ s, perhaps). Any deformation-induced changes in intermolecular separation, and hence in intermolecular potential energy, relax quickly back to equilibrium. Accordingly, the mechanical response of an ordinary liquid to deformation is essentially viscous, unless the testing rate is extraordinarily rapid. In ordinary solids, on the other hand, the corresponding relaxation of local structure is very slow ($\sim 10^{10}$ s, perhaps). Structural memory is very long, so deformation-induced changes in intermolecular potential energy are preserved. Thus, the mechanical response of an ordinary solid to deformation – for small deformations at least – is essentially elastic, unless the testing rate is extraordinarily slow.

One property that sets polymeric liquids apart is the enormously wide range of times from the onset of significant conformational rearrangement until the return to full equilibrium. The distribution of conformational relaxation over many orders of magnitude in time is a natural consequence of macromolecular structure and local chain flexibility. Rearrangement of flexible chains on the scale of a monomeric unit is very rapid ($\sim 10^{-9}$ s, perhaps). The local-rearrangement time for macromolecules – the *primitive time* – is affected by the rotational energies of the backbone bonds and, to some extent, by the need for local cooperation with adjacent units along the same chain. The primitive time is independent of chain length for long chains, and it decreases with increasing temperature. It seems not to be significantly different from the local-rearrangement time for ordinary liquids at the same temperature relative to T_g . However, as illustrated in Fig. 3.3, the complete rearrangement of chain conformation requires much longer times ($\sim 10^1$ s is not uncommon, for example). The chain units must not only rearrange locally but also diffuse over progressively longer distances in order to rearrange the conformations of progressively longer segments of the chain. The time required for complete rearrangement is many multiples of the primitive time and depends strongly on the large-scale chain architecture. These relatively sluggish processes, the *terminal relaxations* or *slow dynamics*, strongly influence the flow properties of polymer melts and solutions. It is for this reason that molecular weight, molecular weight distribution, and long-chain branching play such important roles in the rheological behavior of polymers.

A second property that sets polymeric liquids and networks apart from ordinary liquids and solids is the ease of evoking *finite-deformation* effects. Thus, deformation can displace chain conformations significantly from equilibrium both in polymeric liquids and in networks. Nonlinear elastic responses are produced by these large conformational distortions and are as readily demonstrated in polymeric liquids as in networks [10]. The combination of both time-dependent and deformation-dependent properties gives rise to *nonlinear viscoelastic behavior*, simple examples of which are discussed later in the chapter. On the other hand, if the deformations are small, or applied sufficiently slowly, the molecular arrangements are never far from equilibrium. The mechanical response is then just a reflection of dynamic processes happening at the molecular level of any system, even one at full mechanical and thermal equilibrium. This is the domain of *linear viscoelasticity*. Stress and strain in this case are related linearly, but in a special sense that is explained below. Within very broad limits, the linear viscoelastic behavior of any liquid can be described completely by a single function of time. The properties of this function can be obtained by a variety of experimental procedures, as discussed in the following section.

3.3 Linear viscoelasticity

Consider the simple shear deformation depicted in Fig. 3.4. The *shear stress* σ is F/A , the shear force F per unit area of the surface A that is acted upon (the shear plane). Deformation is specified by the shear strain γ , which is Δ/H , the relative displacement Δ per unit distance H from the shear plane. The deformation rate is specified by the *shear rate* $\dot{\gamma}$, which is $(d\Delta/dt)/H$, the rate of change of shear strain with time. The shear rate can also be expressed as the *velocity gradient* V/H , where V is $d\Delta/dt$, the relative velocity. For the example shown, σ , γ , and $\dot{\gamma}$ are the same everywhere in the material: the deformation is *homogeneous*.

3.3.1 Stress–strain relationships

The stress–strain relationship is a physical property of the material. For Hookean solids and Newtonian liquids, the classical models for a purely elastic response and for a purely viscous response, the following stress–strain relationships apply in simple shear:

$$\sigma(t) = G\gamma(t) \quad \text{Hooke's law} \quad (3.1)$$

$$\sigma(t) = \eta\dot{\gamma}(t) \quad \text{Newton's law} \quad (3.2)$$

In these equations, $\gamma(t)$ and $\dot{\gamma}(t)$ are the shear strain and shear rate at any time t , and $\sigma(t)$ is the shear stress at the same time. A single constant completely defines the mechanical response in each case, the *shear modulus* G for the solid and the *shear viscosity* η for the liquid. To reiterate, the current stress depends only on the current strain for the solid and only on the current strain rate for the liquid. The history of loading plays no part in either case. Hooke's law accurately describes the small-strain behavior of many solid materials, and Newton's law is broadly applicable to small-molecule liquids except near the glass transition.

3.3.1.1 Relaxation of stress

The history of loading comes into play for a viscoelastic substance [1]. The response to a sudden deformation is solid-like at short times and moves to liquid-like at long

Shear Deformation

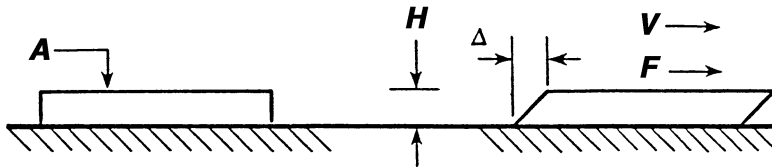


Fig. 3.4. The geometry of a simple shear deformation.

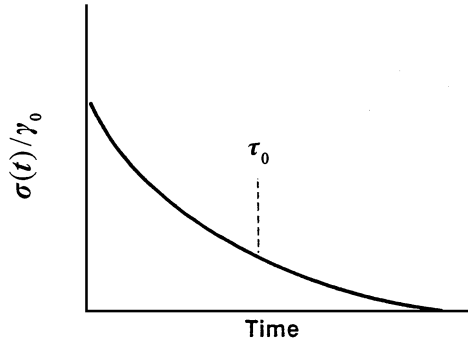


Fig. 3.5. Relaxation of stress after a small step-shear deformation. $\gamma = \gamma_0$ (at $t \geq 0$).

times, and the loading history – the time lapse since the deformation was imposed in this case – is crucial. In a stress-relaxation experiment, for example in simple shear, some small but otherwise arbitrary shear strain γ_0 is imposed instantaneously (in principle), and the shear stress at subsequent times is recorded, the strain being held fixed. The stress would be a constant, $\sigma(t) = G\gamma_0$, for a Hookean solid, because the strain is constant. The stress would be zero for a Newtonian liquid (except for an initial spike), because the strain rate is zero. The stress for a viscoelastic substance begins at some initial value – the liquid-like spike typically happens too quickly to be recorded – that decreases with time and finally reaches an equilibrium value for a solid or zero for a liquid. If the strain is small enough, the ratio of stress to strain is a function of time alone. The response is linear in the disturbance, and the ratio of response to disturbance is a linear viscoelastic property of the material. For a simple shear step strain, the result is $G(t)$, the *shear-stress-relaxation modulus*:

$$G(t) = \sigma(t)/\gamma_0 \quad (3.3)$$

The result of a typical stress-relaxation experiment is sketched in Fig. 3.5.

3.3.1.2 Creep and recovery

The roles of stress and strain are reversed in a creep experiment: stress is the disturbance and strain the response. In simple shear, a constant shear stress σ_0 is imposed and the time dependence of strain $\gamma(t)$ is recorded. In the creep recovery phase, the sample is unloaded (the shear stress is set to zero), and the strain at subsequent times is recorded. Because the stress is constant, the creep strain $\gamma(t)$ would be a constant, $\gamma(t) = \sigma_0/G$, for the Hookean solid and directly proportional to time, $\gamma(t) = (\sigma_0/\eta)t$, for the Newtonian liquid. In the recovery phase, the strain recoils immediately to zero for the solid and remains fixed at $(\sigma_0/\eta)t_1$ for the liquid, t_1 being the time at which recovery began.

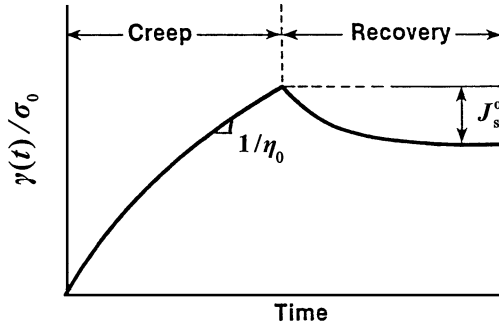


Fig. 3.6. Shear deformation after a constant stress has been imposed, reaching steady state, then recoil following removal of the stress. $\sigma = \sigma_0$ (at $t \geq 0$); $\sigma = 0$ (after steady state has been attained).

For a viscoelastic liquid in the creep phase, the strain begins at some small value, then builds up rapidly but at a decreasing rate until finally reaching a steady state at which strain simply increases linearly with time. In the recovery phase, a viscoelastic liquid recoils back toward zero and finally reaches equilibrium at some smaller total strain than that at the time of unloading. The response over the entire range of time is linear if the shear stress is chosen small enough. In the linear range, the ratio of shear strain to shear stress in the creep phase is a material function of time alone, the *shear creep compliance* $J(t)$:

$$J(t) = \gamma(t)/\sigma_0 \quad (3.4)$$

The general characteristics of creep compliance to steady state and recovery from the steady state are sketched in Fig. 3.6.

The linear viscoelastic properties $G(t)$ and $J(t)$ are closely related. Both the stress-relaxation modulus and the creep compliance are manifestations of the same dynamic processes at the molecular level in the liquid at equilibrium, and they are closely related. It is not the simple reciprocal relationship $G(t) = 1/J(t)$ that applies to Newtonian liquids and Hookean solids. They are related through an integral equation obtained by means of the Boltzmann superposition principle [1], a link between such linear response functions. An example of such a relationship is given below.

The characteristics of $G(t)$ for melts of nearly monodisperse linear polymers, illustrating the glassy, transition, plateau, and terminal zones of response, are sketched in Fig. 3.7. Deformation carries the chains into distorted conformations, as depicted in Fig. 3.8. At very short times, the response is glassy. The modulus for an organic glass is large, $G_g \sim 10^9$ Pa, and relatively insensitive to temperature. The modulus begins to decrease from G_g in the same range of times as that during which the chains begin to relax locally, and it continues to decrease as the relaxation propagates

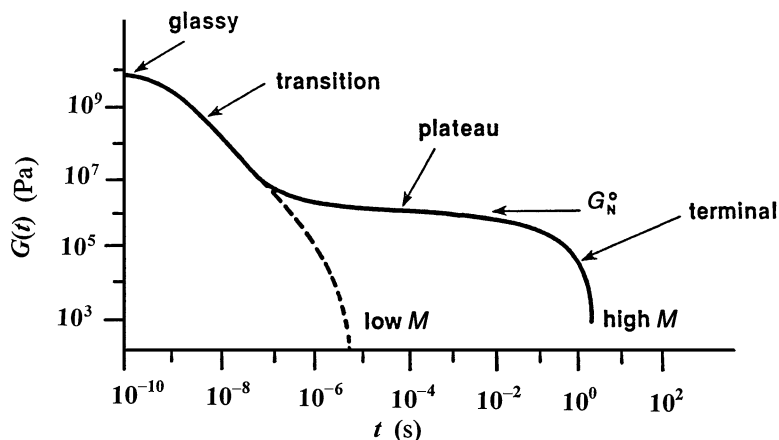


Fig. 3.7. The shear-stress-relaxation modulus over an extended time range for a typical polymer melt.

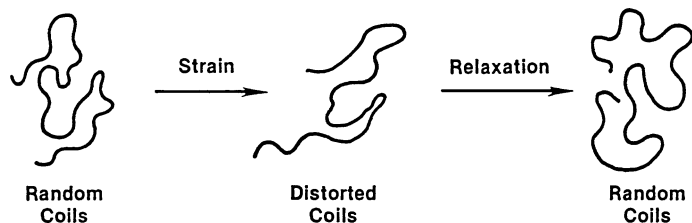


Fig. 3.8. Distortion of the chain conformation by a step shear strain, followed by relaxation back to equilibrium at the new shape.

over progressively longer chain distances. For relatively short-chain polymers, the relaxation simply proceeds smoothly and uneventfully to zero. For long chains, however, the relaxation rate, $d \log G(t)/d \log t$, begins to slow perceptibly at some intermediate time, and the modulus remains relatively constant over some range of times before resuming a more rapid rate of relaxation to full equilibrium.

The intermediate zone, or plateau, separates the short-time-relaxation region, the transition zone, where the large-scale chain architecture has little effect, and the long-time-relaxation region, the terminal zone, where such architectural features as molecular weight, molecular weight distribution, and long-chain branching have profound effects. The mechanical response in the plateau zone resembles that of a rubber network. The width of the plateau zone increases rapidly with chain length, but the plateau modulus itself, $G_N^0 \sim 10^5\text{--}10^6$ Pa depending on polymer species and concentration, is independent of large-scale chain architecture and insensitive to temperature. The existence of a plateau is attributed to chain entanglement, or, more precisely, to the mutual uncrossability of molecular backbones, as sketched

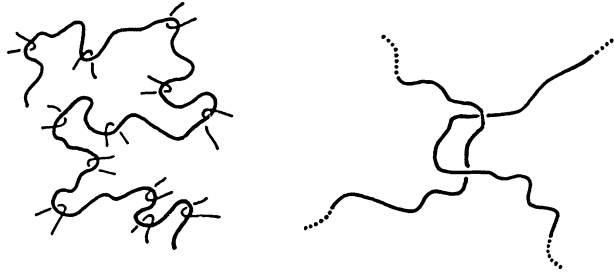


Fig. 3.9. Chain-entanglement interaction, arising from coil overlap and the mutual uncrossability of backbones.

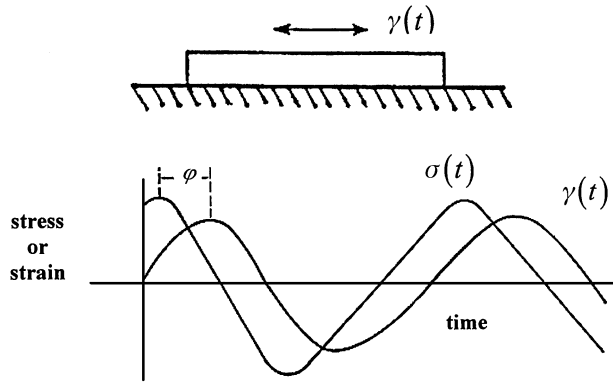


Fig. 3.10. The steady-state response of stress to a small-amplitude, oscillatory shear deformation.

in Fig. 3.9. Entanglement is an important feature in the molecular interpretation of polymeric viscoelasticity and is discussed in more detail below.

3.3.1.3 The dynamic modulus

Although stress-relaxation and creep measurements are used extensively, measuring oscillatory shear is the most commonly used method for characterizing the linear viscoelastic properties of polymer melts and concentrated solutions. As indicated in Fig. 3.10, the liquid is strained sinusoidally at some frequency ω , and in the linear region (small-enough strain amplitude γ_0). The stress response at steady state is also sinusoidal, but usually out of phase with the strain by some phase angle φ . The steady-state stress signal is resolved into in-phase and out-of-phase components, and these are recorded as functions of frequency:

$$\gamma(t) = \gamma_0 \sin(\omega t) \quad \text{input} \quad (3.5)$$

$$\sigma(t)/\gamma_0 = G'(\omega) \sin(\omega t) + G''(\omega) \cos(\omega t) \quad \text{output} \quad (3.6)$$

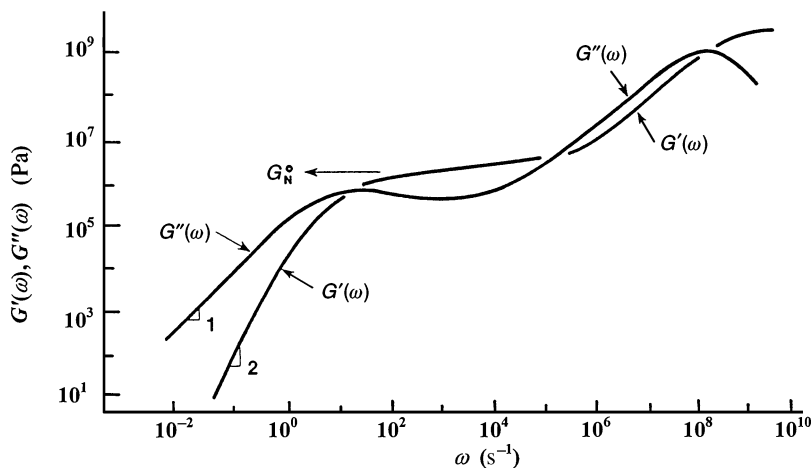


Fig. 3.11. Dynamic storage and loss moduli over a wide frequency range for a typical polymer melt.

in which $G'(\omega)$ is the *dynamic storage modulus* and $G''(\omega)$ the *dynamic loss modulus*. For a Hookean solid (Eq. (3.1)), the stress would be in phase with the strain to give $G'(\omega) = G$ and $G''(\omega) = 0$ at all frequencies. For a Newtonian liquid (Eq. (3.2)), the stress would be 90° out of phase with the strain (in phase with the strain rate, $\gamma_0 \omega \cos(\omega t)$) to give $G'(\omega) = 0$ and $G''(\omega) = \eta \omega$. For a viscoelastic substance, as might be expected, the frequency dependences of $G'(\omega)$ and $G''(\omega)$ are amalgams of solid-like and liquid-like responses. For viscoelastic liquids, Boltzmann superposition leads to relationships between the dynamic moduli and the stress-relaxation modulus [1]:

$$\begin{aligned} G'(\omega) &= \omega \int_0^\infty G(t) \sin(\omega t) dt \\ G''(\omega) &= \omega \int_0^\infty G(t) \cos(\omega t) dt \end{aligned} \quad (3.7)$$

The frequency dependences of $G'(\omega)$ and $G''(\omega)$ for a melt of long, nearly monodisperse linear chains are sketched in Fig. 3.11. Compared with $G(t)$ in Fig. 3.7, the order of appearance of the various viscoelastic zones is reversed. Low frequencies correspond to long times and high frequencies to short times. At the lowest frequencies, $G'(\omega)$ is much smaller than $G''(\omega)$: the viscous response dominates. The curves eventually cross, however, and, at intermediate frequencies, $G'(\omega)$ is larger than $G''(\omega)$: the elastic response dominates in the plateau zone. The relative magnitudes reverse again on entering the transition zone. Eventually $G'(\omega)$ levels off at the glassy modulus G_g , and $G''(\omega)$ falls again through the glassy zone. The loss modulus has two peaks, corresponding in location to the terminal zone (low frequency, relaxation processes sensitive to large-scale molecular architecture) and the transition zone (high frequency, relaxations insensitive to architecture).

3.3.1.4 Viscoelastic parameters

Two quantities that play important roles in flow behavior of polymeric liquids are the steady-state viscosity at zero shear rate, η_o , and the steady-state recoverable shear compliance, J_s^o . Both are obtained quite directly from creep results, η_o from σ_o and the shear rate $\dot{\gamma}_{ss}$ in the steady-state region of the creep phase and J_s^o from the total recoil strain (γ_r) in the recovery phase:

$$\eta_o = \sigma_o / \dot{\gamma}_{ss} \quad \text{zero-shear viscosity} \quad (3.8)$$

$$J_s^o = \gamma_r / \sigma_o \quad \text{recoverable compliance} \quad (3.9)$$

The Boltzmann superposition principle relates η_o and J_s^o to the properties of $G(t)$:

$$\eta_o = \int_0^\infty G(t) dt \quad (3.10)$$

$$J_s^o = \frac{1}{\eta_o^2} \int_0^\infty t G(t) dt \quad (3.11)$$

The dynamic moduli $G'(\omega)$ and $G''(\omega)$ are linked to $G(t)$ through Eq. (3.7). From those expressions, the zero-shear viscosity and recoverable shear compliance can be obtained from the low-frequency limiting behavior through Eqs. (3.10) and (3.11):

$$\eta_o = \lim_{\omega \rightarrow 0} G''(\omega) / \omega \quad (3.12)$$

$$J_s^o = \frac{1}{\eta_o^2} \lim_{\omega \rightarrow 0} G'(\omega) / \omega^2 \quad (3.13)$$

The recoverable compliance J_s^o is zero for a Newtonian liquid. All liquids have a viscosity, but a nonzero value for J_s^o is one clear indication of a viscoelastic nature. As shown below, J_s^o also characterizes the elastic features of the response in steady-flow situations. It is an extremely difficult quantity to measure, but even reasonable estimates can be very useful. The zero-shear viscosity η_o , which is not as difficult to measure as J_s^o but still demands care, is useful for many purposes. The product of zero-shear viscosity and recoverable compliance is the *characteristic relaxation time* [11]:

$$\tau_o = \eta_o J_s^o \quad (3.14)$$

This quantity has many uses. For example, τ_o is approximately the time required for final equilibration of flow-induced stress in the liquid. As shown below, τ_o also locates the onset of nonlinear viscoelastic response in steady-shear flows.

The plateau modulus G_N^o is already known for many polymer species [12, 13]. It can be estimated from the relatively constant values of $G(t)$ or $G'(\omega)$ in the plateau

zone for high molecular weight, nearly monodisperse samples of the species. More refined methods for obtaining values of G_N^0 are also available [1].

3.3.2 Temperature dependences

The stress-relaxation modulus and dynamic moduli, as set forth in Figs. 3.7 and 3.11, span many orders of magnitude in modulus, as well as in time or frequency scale. No single experiment could possibly cover the entire span; five orders of magnitude is a typical dynamic range for even the best instruments. Those sketches in fact represent master curves – composites of data for the same polymer measured at different temperatures. With very few exceptions, conventional low-density polyethylene being the most prominent [14, 15], homogeneous polymer liquids well above T_g obey rather well the principle of time–temperature superposition [1, 16]. A change in temperature shifts the viscoelastic functions along the log(modulus) and log(time) or log(frequency) scales without significantly altering their shapes:

$$G(t, T) = G(t/a_T, T_0)/b_T \quad (3.15)$$

$$\begin{aligned} G'(\omega, T) &= G'(a_T \omega, T_0)/b_T \\ G''(\omega, T) &= G''(a_T \omega, T_0)/b_T \end{aligned} \quad (3.16)$$

where T_0 is a reference temperature, chosen arbitrarily for mere convenience, while a_T and b_T are empirically determined ratios of the time and modulus scales for another temperature T ($a_T = b_T = 1$ at T_0) that produce superposition of the curves. Furthermore, the modulus scale shift is usually very small: the main effect of a temperature change is to rescale the time or frequency. Raising the temperature shifts the response curves to shorter times or higher frequencies. The rate of molecular rearrangement at all chain-distance scales is increased by the same factor, but the molecular organization – the physical structure of the liquid – is hardly changed at all. Measurements at different temperatures can thus be assembled to form a master curve, covering many more decades than is possible with measurements at any single temperature.

Typical behavior is shown in Fig. 3.12(a), where the storage modulus in the plateau and terminal regions for a commercial polystyrene melt is plotted against frequency at several temperatures [17]. A reference temperature is selected, in this case $T_0 = 160^\circ\text{C}$, and “best-fit” scale factors for data obtained at other temperatures are determined empirically to form Fig. 3.12(b). The timescale can shift very rapidly, as indicated by the plot of a_T versus T in Fig. 3.13 [17]. The Williams–Landel–Ferry (WLF) equation, introduced in Chapter 2 and shown for this particular sample and choice of reference temperature in Fig. 3.13, describes rather well the temperature dependence of a_T for most polymer melts and concentrated solutions.

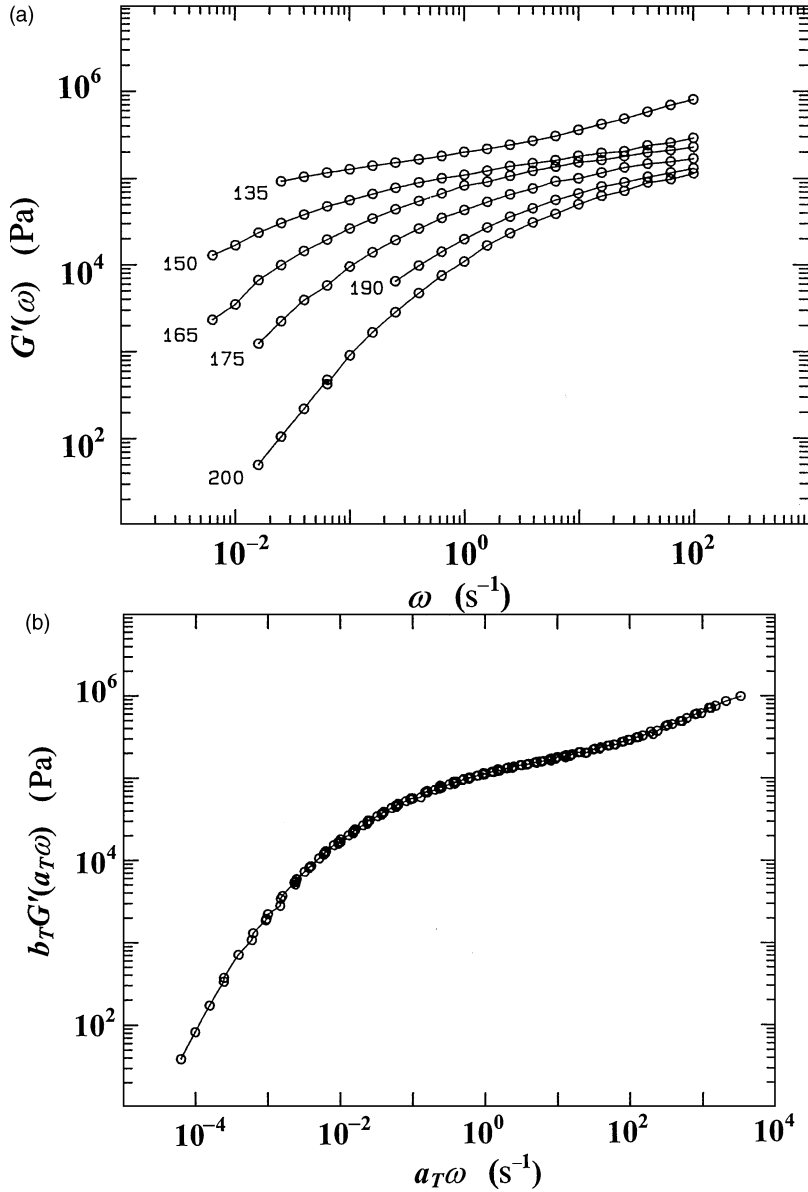


Fig. 3.12. (a) The storage modulus as a function of frequency for a commercial polystyrene sample at several temperatures [17]. (b) The master curve formed by shifts of the data in (a) along the axes to a reference temperature $T_0 = 150^\circ\text{C}$.

This subject is discussed in some detail in the treatise by Ferry [1], which also provides a wealth of a_T data for many polymer species. For the purposes of this chapter, temperature dependence is primarily a function of the local composition of the liquid. Thus, except for rather short chains, the values of a_T are independent

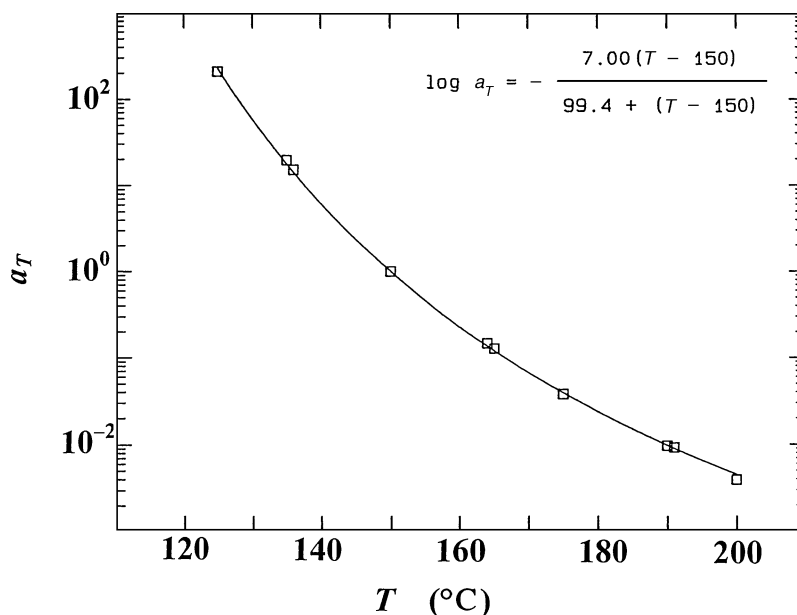


Fig. 3.13. Time–temperature shift factors obtained in forming the master curve in Fig. 3.12(b), fitted to the WLF equation.

of molecular weight and molecular weight distribution. Moreover, the temperature dependence of viscosity depends directly on a_T . Thus, with the approximation of there being no shift in modulus scale with temperature, the following relation applies:

$$\begin{aligned}
 \eta_o(T) &= \eta_o(T_0)a_T \\
 G_N^o(t) &= G_N^o(T_0) \\
 J_s^o(t) &= J_s^o(T_0)
 \end{aligned}
 \tag{3.17}$$

Indeed, well above T_g , both G_N^o and J_s^o are virtually independent of temperature. These results follow directly from the combination of Boltzmann and time–temperature superposition [16] and are extremely useful for extrapolation purposes. Thus, for example, flow-related viscoelastic properties can be measured at experimentally convenient temperatures and estimated at other, typically much higher, temperatures with reasonable confidence.

3.3.3 Effects of chain architecture

Storage-modulus master curves for narrow-distribution samples of linear polystyrenes with widely different molecular weights [18] are shown in Fig. 3.14. Note the increase in plateau width with increasing molecular weight and the

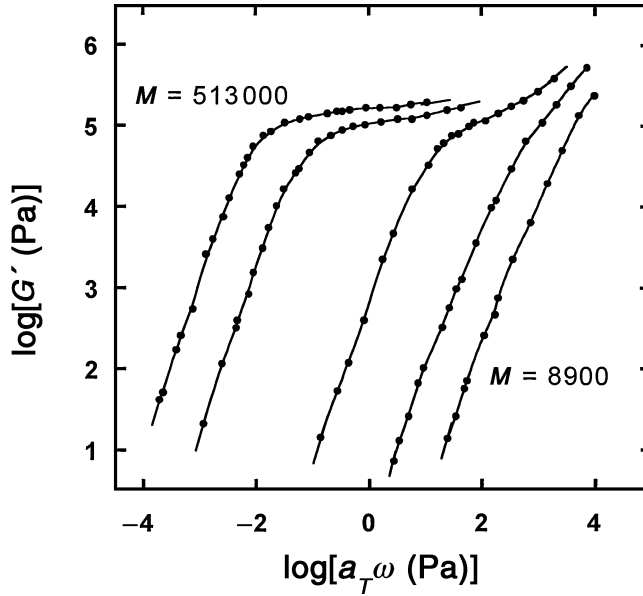


Fig. 3.14. Selected master curves ($T_0 = 160^\circ\text{C}$) for the storage modulus for a series of nearly monodisperse polystyrenes of various molecular weights [18].

similarity in shapes of the terminal regions for different molecular weights. Master curves for polystyrene samples with various molecular weight distributions [19] are shown in Fig. 3.15. The samples have similar values of η_0 , because their loss moduli merge at low frequencies (see Eq. (3.12)). However, their recoverable compliances are quite different. For samples with the same viscosity, J_s^0 depends only on $G'(\omega)$ at low frequencies (Eq. (3.13)), and those values are much larger for the sample with a broader distribution. Indeed, $G'(\omega)$ for the broad-distribution sample has not reached its limiting behavior ($G' \propto \omega^2$) at the lowest accessible frequencies. This result illustrates the general point that J_s^0 is extremely sensitive to distribution breadth and particularly to the presence of a high molecular weight tail in the distribution.

The molecular weight distribution strongly affects the shape of the terminal region. The response is “smeared out,” so to speak, because chains of different sizes relax to equilibrium at different rates. For the example in Fig. 3.15, the terminal zone for the polydisperse sample is so broad that the terminal loss peak in G'' , which is rather well defined for the narrow-distribution sample, is merely a broad shoulder on the transition loss peak. Modulus values for the two samples merge at high frequencies. The response at high frequencies depends only on local chain motions; the effects of chain length and distribution are gone.

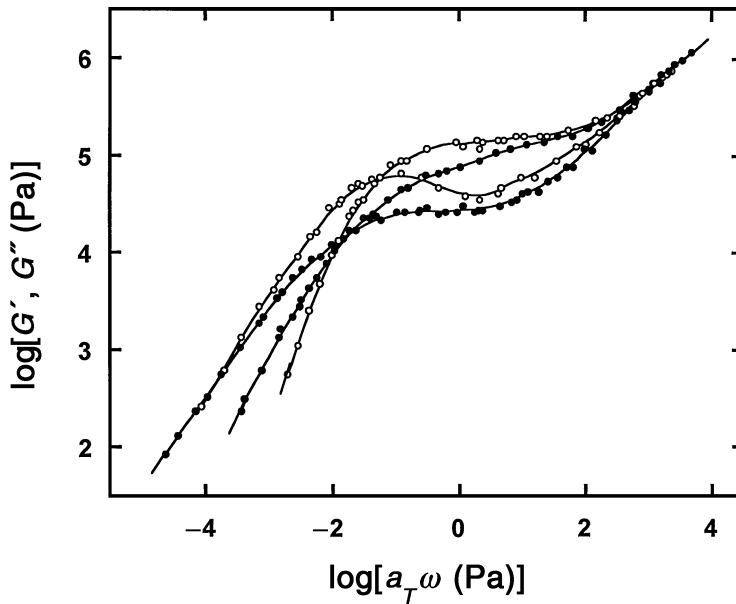


Fig. 3.15. A comparison of modulus master curves ($T_0 = 160^\circ\text{C}$) for a nearly monodisperse polystyrene ($\circ$) and a polydisperse commercial polystyrene ($\bullet$) [19].

3.4 Nonlinear viscoelasticity

This section considers the behavior of polymeric liquids in steady, simple shear flows – the shear-rate dependence of viscosity and the development of differences in normal stress. Also considered in this section is an elastic-recoil phenomenon, called die swell, that is important in melt processing. These properties belong to the realm of nonlinear viscoelastic behavior. In contrast to linear viscoelasticity, neither strain nor strain rate is always small, Boltzmann superposition no longer applies, and, as illustrated in Fig. 3.16, the chains are displaced significantly from their equilibrium conformations. The large-scale organization of the chains (i.e. the physical structure of the liquid, so to speak) is altered by the flow. The effects of finite strain appear, much as they do when a polymer network is deformed appreciably.

3.4.1 Viscosity and normal stress

If a liquid is sheared at a constant shear rate $\dot{\gamma}$, the stress that results will eventually reach a steady-state value. In the parallel-plate illustration in Fig. 3.17, the upper plate moves at constant velocity, V , in direction 1, and a constant shear stress, $\sigma = F/A$, acts in direction 1 on all planes of the liquid that are normal to direction 2.

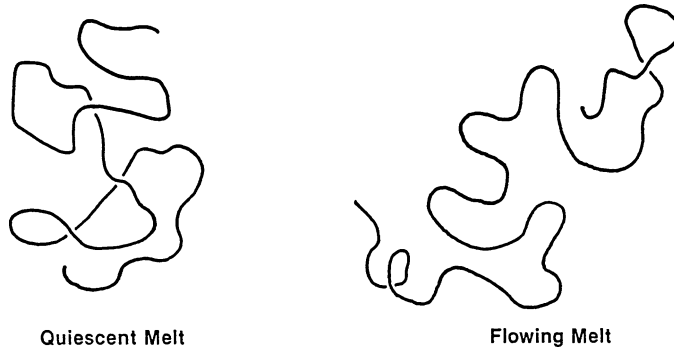


Fig. 3.16. The effect of flow on the chain conformation.

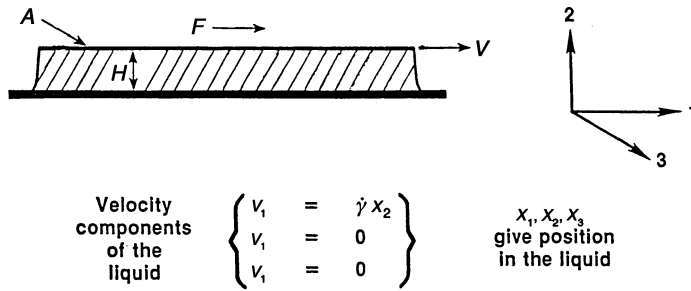


Fig. 3.17. The geometry of simple shear flow and the velocity components.

The deformation is homogeneous: the shear rate $\dot{\gamma} = V/H$ is the same everywhere in the liquid, and the components of velocity are as follows:

$$v_1 = \dot{\gamma} x_2 \quad v_2 = 0 \quad v_3 = 0 \quad (3.18)$$

The subscripts 1, 2, and 3 refer to the flow, velocity gradient, and neutral directions, respectively, and x_2 is the vertical distance measured from the fixed plate. Apart from pressure, the forces acting on each element of the liquid are also the same everywhere.

Suppose that we could isolate a very small bit of the liquid in this simple shearing flow at some instant and examine the forces acting upon it. Consider for example a small cubic element with faces parallel to one of the three coordinate directions, as sketched in Fig. 3.18. For a Newtonian liquid, the components of force that act normally to the six faces of the cube have the same magnitude, originating from the pressure. The force acting on some of the faces also has a shear component. The shear forces, which are equal in magnitude but opposed in direction, as is needed for mechanical equilibrium, originate from the viscosity and are directly proportional to the shear rate.

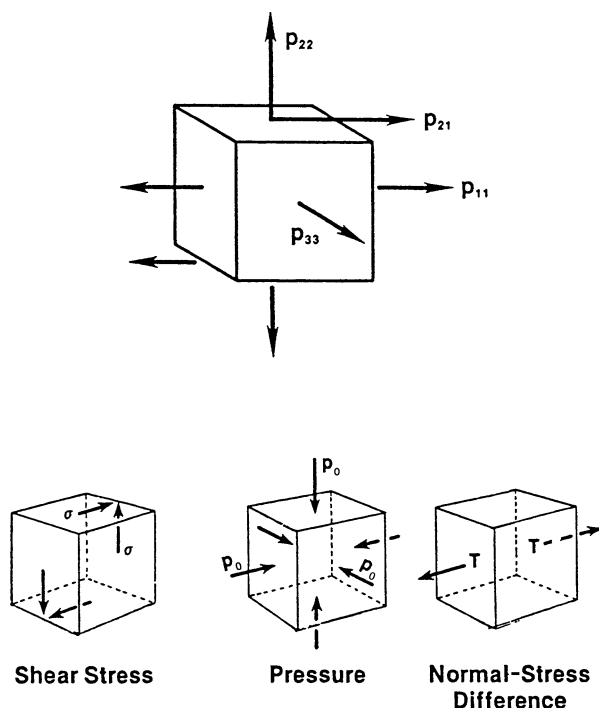


Fig. 3.18. Stress components in simple shear flow (redrawn from [9]).

The situation is changed in two important ways for a viscoelastic liquid [2]. First, the normal components of force are no longer equal in magnitude. The differences are such as to produce, as the major effect in simple shear flow, a net tension in the liquid along the direction of flow. The differences in normal force depend on the shear rate and are zero only in the $\dot{\gamma} = 0$ limit. Secondly, though they are still equal in magnitude and opposed in direction, the magnitude of the shear force is no longer directly proportional to the shear rate except in the $\dot{\gamma} = 0$ limit. The components that make up the *stress* are the components of *force per unit area* acting on the faces of the cube. Apart from pressure, the steady-state stress for any viscoelastic liquid in simple shear flow is specified completely by three shear-rate functions, namely the *shear-stress function*, and two *normal-stress-difference functions*. The shear-stress function is $\sigma(\dot{\gamma})$, shown as p_{21} in Fig. 3.18, the first and second normal-stress differences are $N_1(\dot{\gamma})$ and $N_2(\dot{\gamma})$, $p_{11} - p_{22}$ and $p_{22} - p_{33}$ as defined in the same figure. All three functions go to zero at $\dot{\gamma} = 0$. The shear stress is linear in shear rate at low enough shear rates, the linear viscoelastic regime. Also, at low enough shear rates, the normal-stress differences are small compared with the shear stress. They are nonlinear viscoelastic properties and vary quadratically with shear rate in

that range. Thus,

$$\sigma(\dot{\gamma}) = \eta(\dot{\gamma})\dot{\gamma} \quad (3.19)$$

$$N_1(\dot{\gamma}) = \theta_1(\dot{\gamma})\dot{\gamma}^2 \quad (3.20)$$

$$N_2(\dot{\gamma}) = \theta_2(\dot{\gamma})\dot{\gamma}^2 \quad (3.21)$$

where $\eta(\dot{\gamma})$ is the *steady-state viscosity*, and $\theta_1(\dot{\gamma})$ and $\theta_2(\dot{\gamma})$ are the *normal-stress coefficients*. In the low-shear-rate limit [20],

$$\eta(0) = \eta_0 \quad (3.22)$$

$$\theta_1(0) = 2J_s^0\eta_0^2 \quad (3.23)$$

Equations (3.22) and (3.23) establish direct connections to behavior in the linear viscoelastic regime.

Some generally useful facts are known about these properties for melts and concentrated solutions of non-associating polymers. Both $\eta(\dot{\gamma})$ and $\theta_1(\dot{\gamma})$ decrease with increasing shear rate, and both begin to depart from η_0 and $2J_s^0\eta_0^2$ near the same shear rate $\dot{\gamma}_0$. Moreover, this *characteristic shear rate* is closely related to the characteristic time of the liquid:

$$\dot{\gamma}_0 \sim 1/\tau_0 \quad (3.24)$$

For most polymeric liquids, the shear-rate dependence of viscosity goes over to a power law beyond $\dot{\gamma}_0$:

$$\eta(\dot{\gamma}) \propto \dot{\gamma}^{-a} \quad (3.25)$$

The power-law exponent, typically in the range $0.5 \leq a \leq 0.9$ and insensitive to temperature, varies with the concentration of polymer and large-scale molecular architecture. The ratio $N_1(\dot{\gamma})/[\sigma(\dot{\gamma})]^2$ is relatively insensitive both to shear rate and to temperature, which is a useful characteristic for extrapolation and estimation purposes. Less is known about the second normal-stress difference N_2 . However, it has been shown to be negative for homogeneous polymer liquids and closely related to N_1 . Thus, on the basis of extensive data [21, 22], $-N_2/N_1$ typically lies in the range 0.2–0.3 and is remarkably insensitive to the shear rate, polymer species, concentration of polymer, and large-scale molecular architecture.

Viscosity–shear-rate behavior is a relatively easy property to measure. Measurement of the first normal-stress difference is more difficult, especially at high shear rates ($\dot{\gamma}\tau_0 \gg 1$), and obtaining data on N_2 requires the use of specialized techniques. Figure 3.19 shows the working parts of the cone-and-plate rheometer, a device that is commonly used to measure both $\sigma(\dot{\gamma})$ and $N_1(\dot{\gamma})$ at relatively low shear rates. The liquid is placed in the gap between cone and plate, each with radius

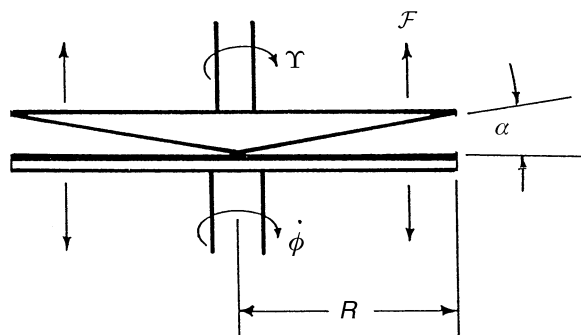


Fig. 3.19. A diagram of a cone-and-plate rheometer.

R , one equipped with force transducers and held fixed, and the other is then driven rotationally at some constant angular velocity $\dot{\phi}$. The torque Υ and axial force $\mathcal{F}$ at steady state are recorded. For a small gap angle α the shear rate is $\dot{\gamma} = \dot{\phi}/\alpha$ and is the same everywhere in the liquid. The following relationships then apply [9, 23]:

$$\sigma(\dot{\gamma}) = 3\Upsilon(\dot{\gamma})/(2\pi R^2) \quad (3.26)$$

$$N_1(\dot{\gamma}) = 2\mathcal{F}(\dot{\gamma})/(\pi R^3) \quad (3.27)$$

That there should be a relationship between the axial force and the normal-stress difference is not too difficult to understand. Much like rubber bands stretched around a cylinder, the flow-induced tension along the lines of flow causes the outer liquid elements to squeeze inward upon the inner elements. The result is a build up of pressure on the surfaces of the cone and plate from near zero at the outer edge to a maximum at the center, tending to force them apart. The axial force is simply the sum of contributions from this pressure. Equation (3.27) gives the precise connection between $\mathcal{F}$ and N_1 .

Data on $\sigma(\dot{\gamma})$ and $N_1(\dot{\gamma})$ for a 10% solution of a nearly monodisperse sample of polyisoprene [24] ($M = 1.62 \times 10^6$) are shown in Fig. 3.20. At low shear rates, σ is indeed much larger than N_1 , but because σ grows as $\dot{\gamma}$ and N_1 as $\dot{\gamma}^2$, the curves eventually cross, and N_1 becomes larger than σ at high shear rates. Near the crossing point ($\sigma \sim N_1$), σ begins to depart from its direct proportionality to $\dot{\gamma}$; that is, the steady-state viscosity $\eta(\dot{\gamma})$ begins to decrease from its low-shear-rate limit, η_0 . That qualitative characteristic appears to be quite general for flexible polymer liquids. The onset of non-Newtonian viscosity behavior occurs near the shear rate at which σ and N_1 become equal, and N_1 grows increasingly larger than σ at higher shear rates.

Figures 3.21(a) and (b) show the same data replotted as the steady shear viscosity $\eta(\dot{\gamma})$ and the steady shear compliance function $J_s^0(\dot{\gamma})$, the latter defined as

$$J_s^0(\dot{\gamma}) = N_1(\dot{\gamma})/[2\sigma(\dot{\gamma})]^2 \quad (3.28)$$

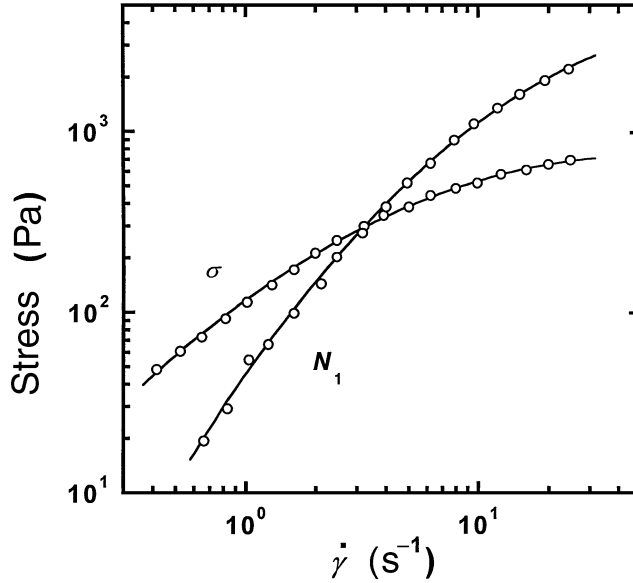


Fig. 3.20. The shear-rate dependence of shear stress and the first normal-stress difference at 25 °C for a 10-wt% solution of a nearly monodisperse 1,4-polyisoprene in tetradecane [24].

which goes to J_s^0 at $\dot{\gamma} = 0$, in accord with Eq. (3.23). For the polyisoprene solution, $\eta_0 = 115 \text{ Pa s}$ and the power-law exponent $a \sim 0.68$ from Fig. 3.21(a), and $J_s^0 \sim 1.6 \times 10^{-3} \text{ Pa}^{-1}$ from Fig. 3.21(b). From Eq. (3.14), the time constant for the solution is about 0.2 s. From the discussion above, the shear rate at which N_1 and σ cross, and at which $\eta(\dot{\gamma})$ begins to depart from η_0 , should be about $1/\tau_0 = 5 \text{ s}^{-1}$. From Figs. 3.20 and 3.21(a), that seems a little high, but certainly within the correct range.

The use of cone-and-plate rheometers for polymer melts is limited to relatively low shear rates by the onset of flow instabilities, typically occurring not far beyond the onset of shear-rate dependence for $\eta(\dot{\gamma})$ and the $\sigma \sim N_1$ crossing point. A capillary rheometer is sketched in Fig. 3.22. Stable operation at much higher shear rates is possible, but usually η_0 cannot be determined because of instrumental limitations at low shear rates. The steady-state viscosity, however, can be obtained from measurements of the volumetric flow rate, Q , and the pressure drop, $\Delta P = P - P_0$, P_0 being the ambient pressure. For long tubes ($L/D \gg 1$), the following equation applies for Newtonian liquids:

$$\eta = \frac{\pi D^4}{128L} \frac{\Delta P}{Q} \quad (3.29)$$

Being based on the assumption of a shear-rate-independent viscosity, Eq. (3.29) is not generally true for viscoelastic liquids. Unlike cone-and-plate flow, the shear

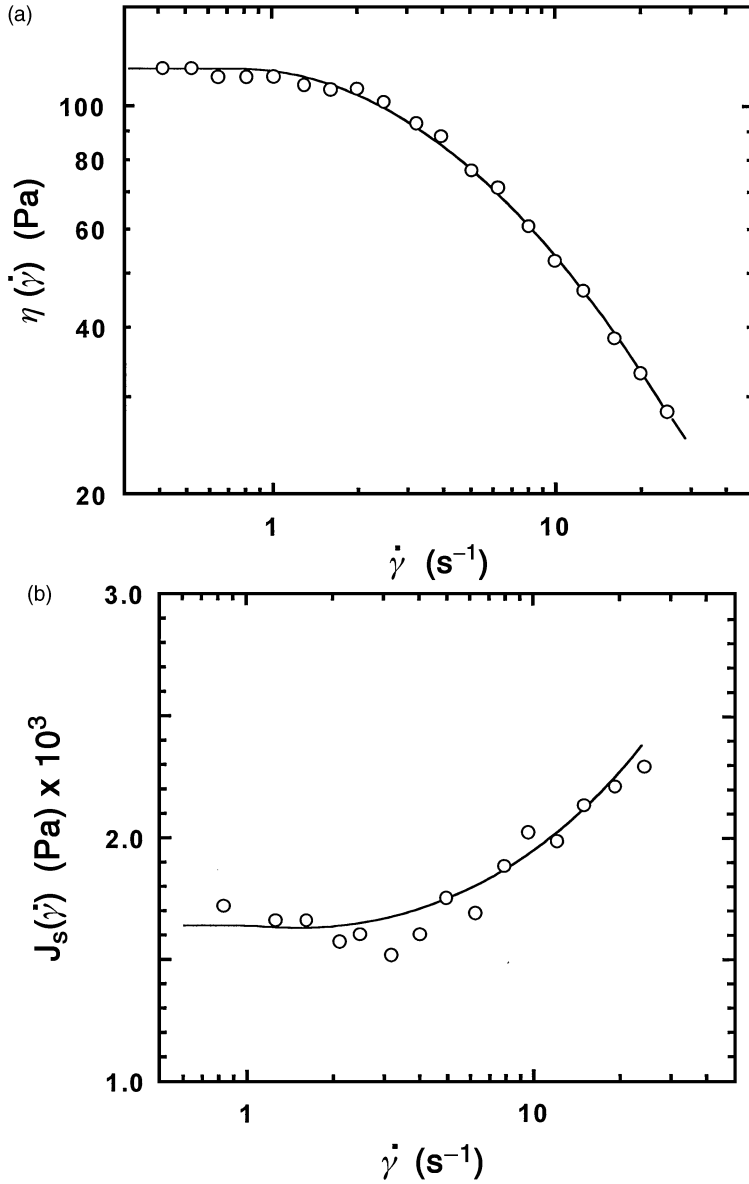


Fig. 3.21. (a) The shear-rate dependence of steady-state viscosity from the data in Fig. 3.20. (b) The steady-state normal stress compliance from the data in Fig. 3.20.

rate in tubes varies with location, specifically with distance from the centerline of the tube, so that any shear-rate dependence of $\eta(\dot{\gamma})$ rules out the use of Eq. (3.29). However, the shear stress at the capillary wall for any liquid can be calculated from the pressure drop [25]:

$$\sigma_w = \frac{D}{4L} \Delta P \quad L/D \gg 1 \quad (3.30)$$

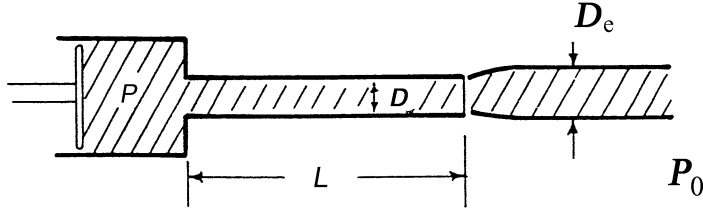


Fig. 3.22. A schematic diagram of a capillary rheometer.

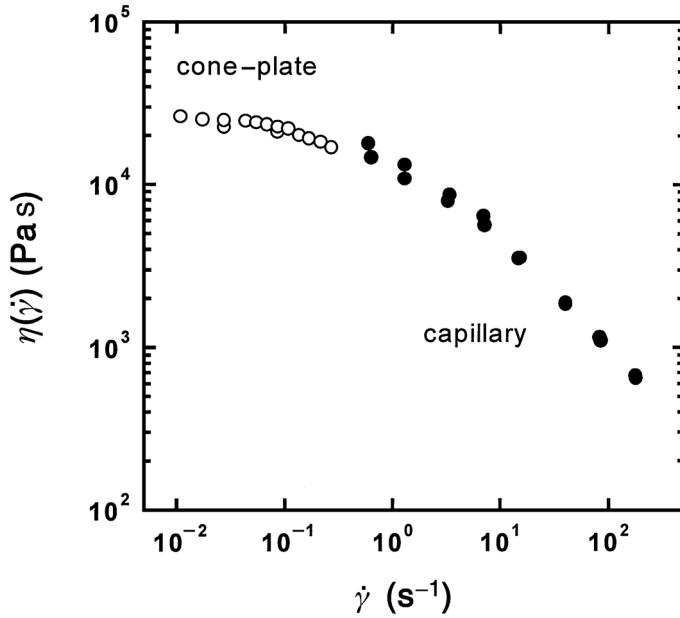


Fig. 3.23. The steady-state viscosity at 180 °C for a commercial polystyrene [26].

Likewise, the shear rate at the wall for any liquid can be obtained from an appropriate numerical differentiation of data on Q versus ΔP [25]:

$$\dot{\gamma}_w = \frac{8Q}{\pi D^3} \left(3 + \frac{d \log Q}{d \log \Delta P} \right) \quad (3.31)$$

Thus, with known values of shear stress and shear rate at the same location, the viscosity function for a viscoelastic liquid is given simply as a plot of $\sigma_w/\dot{\gamma}_w$ versus $\dot{\gamma}_w$. Results obtained for a commercial polystyrene sample [26] ($M_w = 260\,000$, $M_w/M_n \sim 2.5$; $T = 180\,^\circ\text{C}$) are shown in Fig. 3.23. Cone-and-plate measurements cover the low-shear-rate range, and capillary measurements cover the high-shear-rate range. The two instruments provide complementary information on the viscosity.

There is a surprising but useful relationship between the steady shear viscosity $\eta(\dot{\gamma})$ and the amplitude of complex dynamic viscosity (or simply the complex

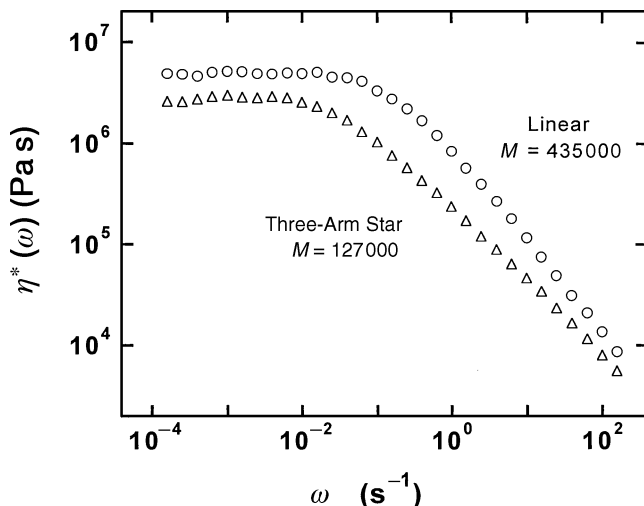


Fig. 3.24. Complex-viscosity master curves at 25 °C for nearly monodisperse samples of linear and three-arm-star 1,4-polybutadiene [28].

viscosity):

$$\eta^*(\omega) = [(G')^2 + (G'')^2]^{1/2} / \omega \quad (3.32)$$

which, although it is impossible to prove it generally, turns out to work remarkably well. It is the *Cox–Merz rule* [27], which asserts that the steady shear viscosity at any shear rate is equal to the complex viscosity at a frequency numerically equal to that shear rate:

$$\eta(\dot{\gamma}) = [\eta^*(\omega)]_{\omega=\dot{\gamma}} \quad (3.33)$$

Master curves ($T_0 = 25^\circ\text{C}$) for the complex viscosity of two nearly monodisperse 1,4-polybutadiene melts [28] are shown in Fig. 3.24. One is linear ($\eta_0 = 4.8 \times 10^6 \text{ Pa s}$, $J_s^0 = 2.1 \times 10^{-6} \text{ Pa}^{-1}$), the other a three-arm star ($\eta_0 = 2.8 \times 10^6 \text{ Pa s}$, $J_s^0 = 1.4 \times 10^{-5} \text{ Pa}^{-1}$). Their zero-shear viscosities are similar, but their recoverable compliances differ by a factor of seven and the shapes of their curves are obviously different, too. Figures 3.25(a) and (b) compare those results with steady-shear-viscosity data for nearly monodisperse polymers, showing master curves at 183 °C for five linear polystyrene samples [29] ($48\,500 \leq M \leq 242\,000$) in Fig. 3.25(a), and master curves at 106 °C for seven polybutadiene stars [30] ($45\,000 \leq M \leq 184\,000$) in Fig. 3.25(b). Values of η_0 were available for all samples, so knowledge of $\eta(\dot{\gamma})/\eta_0$ was always available. Values of J_s^0 were not generally available, so τ_0 for the shear-rate reduction was estimated from the onset of shear-rate dependence. Agreement with the Cox–Merz rule is evident even in this rather severe test of using different samples and even different species. The

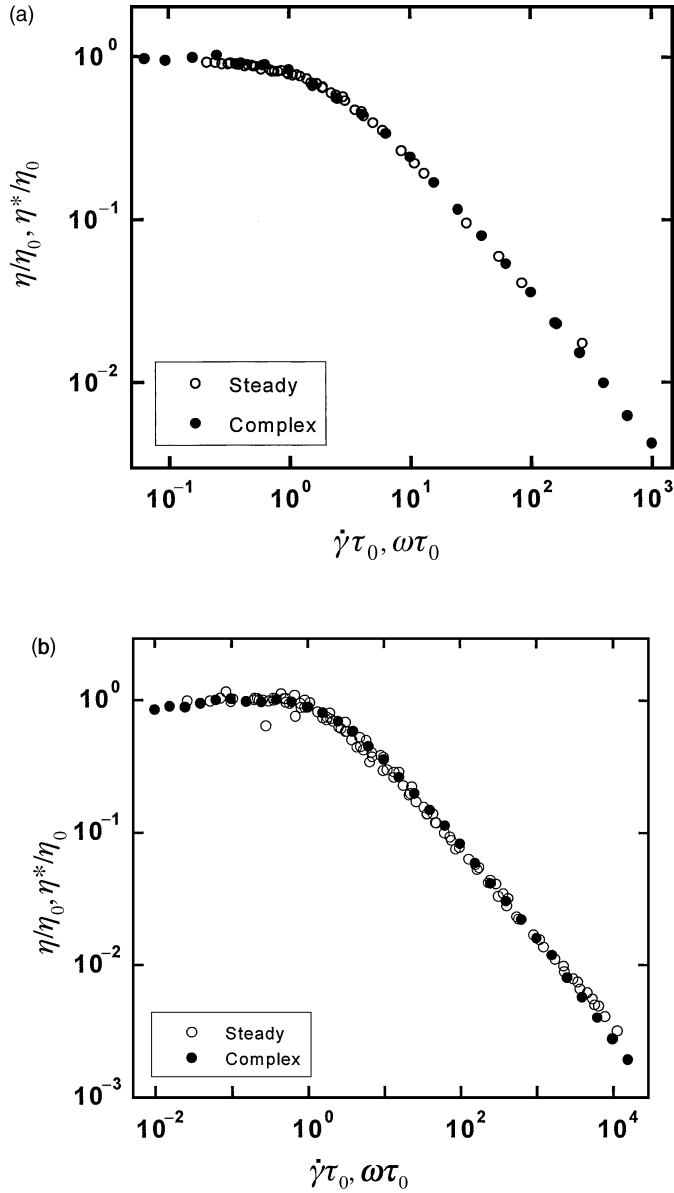


Fig. 3.25. A comparison of complex viscosity and steady-state viscosity in reduced form for (a) nearly monodisperse linear polymers and (b) nearly monodisperse star polymers.

only necessity for success, at least in these two cases, is matching polydispersities and architectures. As shown in Fig. 3.26, comparing the results for linear and star samples, there is a dependence of the reduced curve shape on the architecture.

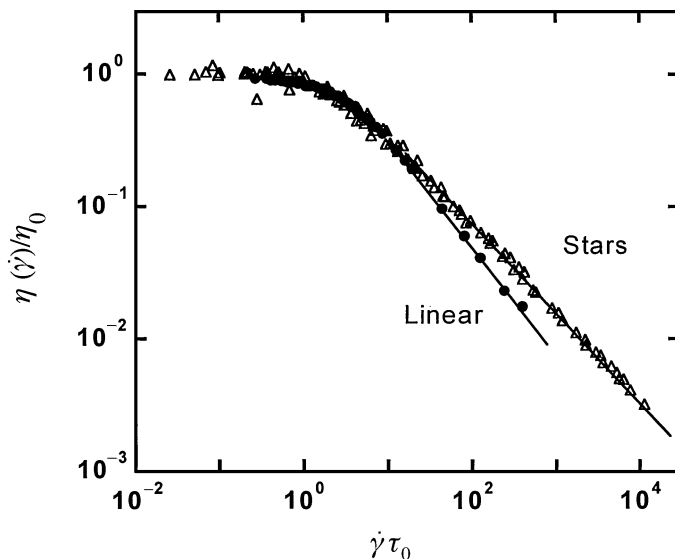


Fig. 3.26. A comparison of reduced-viscosity master curves for nearly monodisperse linear and star polymers.

3.4.2 Die-swell phenomena

Figure 3.22 illustrates die swell at the exit of a flow channel, a characteristic property of viscoelastic liquids for high-shear-rate flows ($\dot{\gamma}_w \tau_0 \gg 1$). The extrudate emerging from the flow channel, a capillary in this case, spontaneously rearranges to form a diameter larger than that of the channel [8, 31]. The *swell ratio* D_e/D increases with increasing flow rate. As depicted in Fig. 3.27, the swell ratio also depends on the length/diameter ratio of the capillary. This length dependence for short capillaries reflects a partially retained “memory” of the liquid-element shapes at the entrance to the capillary. However, D_e/D depends on Q even in the long-channel limit. For long channels, the swell ratio mainly reflects the normal-stress differences generated by the shearing flow in the channel itself. Put simply, the tension along the lines of flow inside the channel draws the extrudate back when the confining effect of the wall is left behind, producing a recoil analogous to the retraction upon release of a stretched rubber band.

Figure 3.28 compares the viscosity function and D_e/D versus $\dot{\gamma}_w$ in a long capillary for a commercial sample of polystyrene [32] with $M_w = 220\,000$, $M_w/M_n = 3.1$, $\eta_0 = 1.4 \times 10^4$ Pa s at 180°C , $J_s^0 \sim 6 \times 10^{-5}$ Pa $^{-1}$. At low shear rates, the viscosity levels off at η_0 . Normal-stress differences are small in that region, as discussed before, and D_e/D is about 1.1, the computed value for slow flows of a Newtonian liquid [33]. The swell ratio then begins to rise near the shear rate at the onset of shear-rate dependence in the viscosity, a shear rate that, from $\dot{\gamma}_w \sim \tau_0^{-1}$, based on Eq. (3.14), also locates the $\sigma \sim N_1$ crossover range, indicating

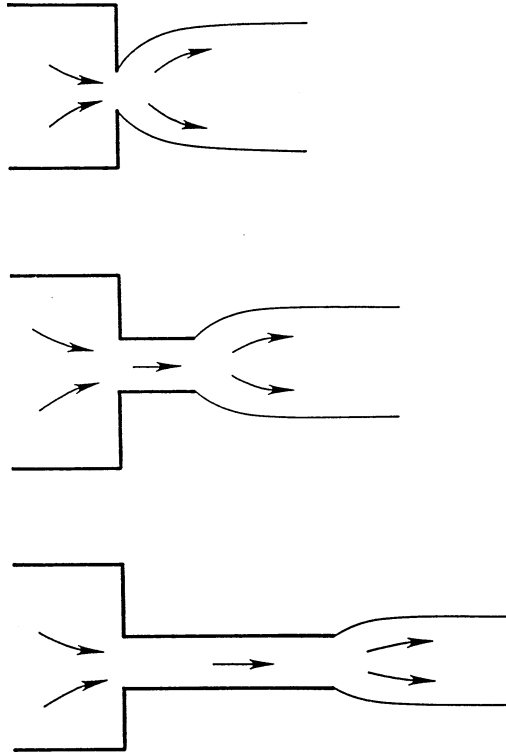


Fig. 3.27. A depiction of viscoelastic memory effects on die swell at fixed flow rate in capillaries of various lengths.

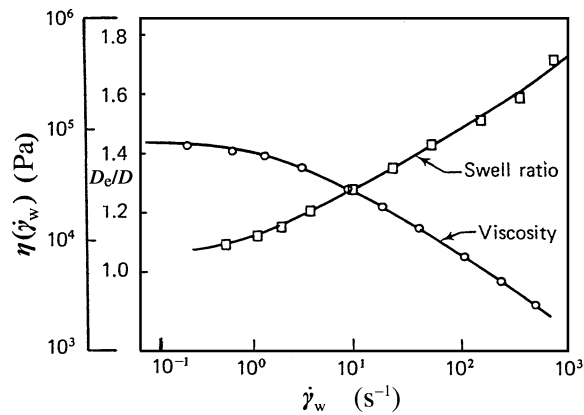


Fig. 3.28. A comparison of the shear-rate dependences of viscosity and die swell for a commercial polystyrene [32].

that normal-stress differences are becoming significant. The values of D_e/D increase steadily at still higher shear rates, at which N_1 exceeds σ by increasingly large amounts, and the viscosity assumes a power-law dependence, $\eta(\dot{\gamma}) \propto \dot{\gamma}^{-\alpha}$, where $\alpha \sim 0.65$ for this polystyrene melt.

Theories relating die swell and normal-stress difference are fairly successful. The phenomenon itself is a complicated one even for Newtonian liquids. The Tanner equation [34] captures the essential behavior for polymer melts:

$$\frac{D_e}{D} = 0.1 + \left[1 + \frac{1}{8} \left(\frac{N_1}{\sigma} \right)^2 \right]^{1/6} \quad (3.34)$$

3.4.3 The temperature dependence

As with a linear response, temperature has a large and systematic effect on non-linear viscoelastic behavior, and time–temperature superposition can again be very useful. Indeed, the temperature-shift factors are indistinguishable from those obtained from linear viscoelastic measurements on the same material. Stress plays the role of modulus, and shifts along the stress axis with temperature are relatively small. The shear rate plays the role of frequency, and shifts with temperature along the shear-rate axis are governed by a_T and typically large. Thus, for example, log–log plots of shear stress versus shear rate are shifted by temperature along the shear-rate axis without change of shape. The same data, plotted as viscosity–shear-rate curves, shift by about equal amounts along each axis, as shown for a nearly monodisperse polystyrene melt [35] ($M = 411\,000$) at various temperatures in Fig. 3.29. Reduction to master curves can be achieved by normalizing the viscosity values at each temperature with $\eta_0(T)$ and plotting as a function of $\dot{\gamma} \tau_0(t)$,

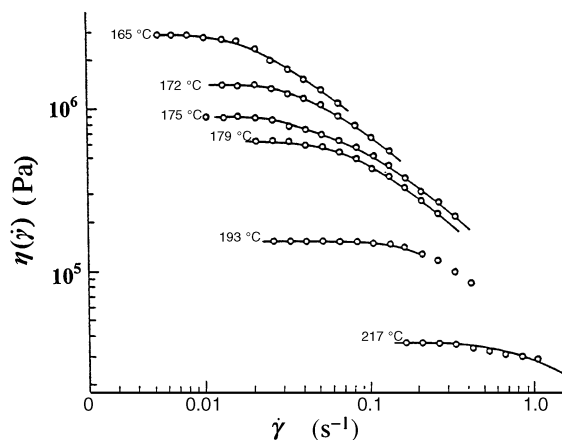


Fig. 3.29. The shear-rate dependence of viscosity for a nearly monodisperse polystyrene at several temperatures [35].

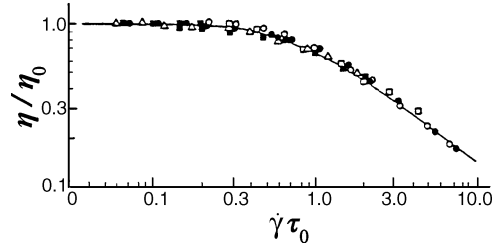


Fig. 3.30. The time-temperature master curve for a nearly monodisperse polystyrene [35].

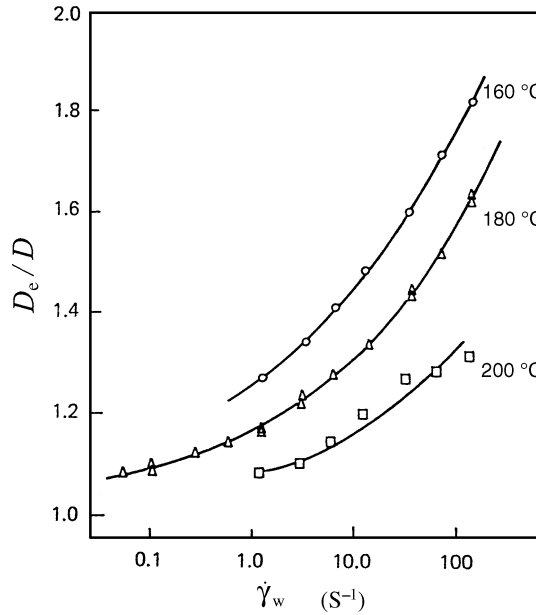


Fig. 3.31. Die swell versus wall shear rate at various temperatures for a commercial polystyrene [32].

as shown for another nearly monodisperse polystyrene melt [35] ($M = 180\,000$; $J_s^0 = 1.7 \times 10^{-6} \text{ Pa}^{-1}$ at 190°C) in Fig. 3.30. Because J_s^0 is frequently unknown and typically insensitive to temperature in any case, superposition can frequently be obtained simply by plotting $\eta(\dot{\gamma})/\eta_0$ versus $\dot{\gamma}\tau_0$.

Another useful feature, the insensitivity to temperature of the relationship between σ and N_1 , follows from the temperature-superposition principle and the insensitivity to temperature of J_s^0 . Both stress components depend on the shear rate, and hence both shift along the shear-rate axis with temperature, but, when $\dot{\gamma}$ is eliminated by plotting N_1 versus σ directly, the result is quite insensitive to temperature. The effect of temperature on die swell provides an interesting application of this principle. As shown in Fig. 3.31 for the polystyrene melt used in

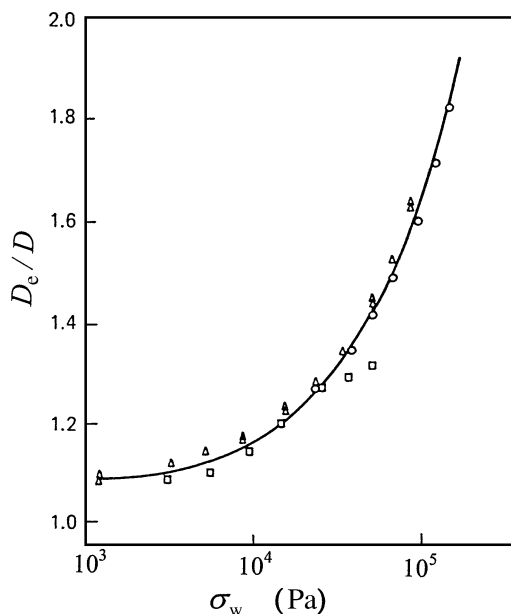


Fig. 3.32. The die-swell data in Fig. 3.31 plotted as a function of wall shear stress [32].

Fig. 3.28, at each shear rate the swell ratio decreases with increasing temperature [32]. However, as shown in Fig. 3.32, the same data superpose rather well when they are plotted instead as a function of the shear stress. That result turns out to be quite general and, of course, quite useful for extrapolation purposes. It is a natural consequence of the temperature invariance of the relationship between σ and N_1 and the idea, embodied by Eq. (3.34), that D_e/D for long capillaries depends only on a ratio of stress components in the capillary.

3.5 Structure–property relationships

The importance of the terminal zone in the viscoelastic response to flow behavior and its strong dependence on large-scale molecular architecture has already been mentioned. These relationships are considered in greater detail in this section. It is important to distinguish, as indicated in Fig. 3.33, the effects of local chain structure and large-scale molecular architecture. The details of local structure control the basic physical properties of flexible-chain polymers in the solid state. Provided that the chains are long enough, large-scale molecular architecture has relatively little direct influence on solid-state properties. The situation is reversed for melts and concentrated solutions. Local chain structure sets the relationship between chain dimensions and chain length for the species. It also sets the rate of chain rearrangement at the monomeric-unit level and controls its temperature dependence. Beyond those

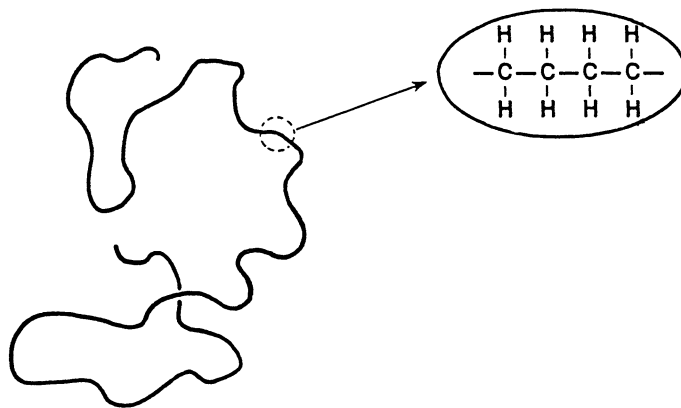


Fig. 3.33. Distinguishing chemical microstructure and large-scale molecular architecture in polymers.

two contributions, stated in an overly simplified but still essentially correct manner, the local structure would appear to have no significant effect. The laws relating flow properties and large-scale architecture – molecular weight, molecular weight distribution, and the various varieties of long-chain branching – are universal.

Commercial polyolefins, which in some cases may contain significant numbers of molecules distributed over four or more orders of magnitude in chain length, are rather extreme examples. In general, however, the molecular weight distributions of commercial polymers are relatively broad and highly variable. Some contain long branches as well, and, in many cases, the reaction mechanisms that introduce branching also broaden the distribution. Dilute-solution methods for determining the molecular weight distribution of linear polymers have improved considerably in the past decade. Size-exclusion chromatography (SEC) remains the basic technique, but that is now supplemented by in-line viscometry and light scattering, furnishing much improved resolution of the high molecular weight tail [36–38]. Universal calibration assumptions are no longer required, since light scattering provides absolute molecular weights. The availability of knowledge regarding both intrinsic viscosity and molecular weight distributions offers much better ways to detect long-chain branching and, when these approaches are supported by appropriate off-line modeling and mechanistic studies, even to quantify it.

Connecting such data to the flow behavior of polydisperse systems continues to be difficult, but even here some progress has been made. Studying model systems, in which large-scale architecture can be varied systematically, remains the main method for developing an improved understanding of flow–property relationships. This is an active area both in theory and in experiment; the following pages offer a brief survey of that aspect of polymeric viscoelasticity.

3.5.1 Molecular weight distributions

The molecular weight distribution of a commercial polymer, a sample of poly(vinyl chloride), is sketched in Fig. 3.34. The distribution function, $W(M) dM$, is the fractional mass of polymer contributed by molecules with molecular weights ranging from M to $M + dM$. The distribution is commonly characterized by its averages, M_n , M_w , M_z , and M_{z+1} defined as follows by ratios of successively higher moments of the distribution:

$$\begin{aligned}
 M_n &= \int W(M) dM / \int \frac{1}{M} W(M) dM && \text{number average} \\
 M_w &= \int M W(M) dM / \int W(M) dM && \text{mass average} \\
 M_z &= \int M^2 W(M) dM / \int M W(M) dM && z \text{ average} \\
 M_{z+1} &= \int M^3 W(M) dM / \int M^2 W(M) dM && z + 1 \text{ average}
 \end{aligned} \tag{3.35}$$

The averages for this sample, which are not particularly broad in distribution compared with those of many polyolefins, were calculated from measurements with a calibrated SEC instrument but no additional in-line detectors. The values of M_z , and especially M_{z+1} , are only estimates; the results for those averages in particular are exceedingly sensitive to the baseline determination.

Rheological properties are far more sensitive to the molecular weight distribution, and particularly to the high molecular weight tail, than are properties measured by dilute-solution methods such as SEC. It is not unusual to find, for example,

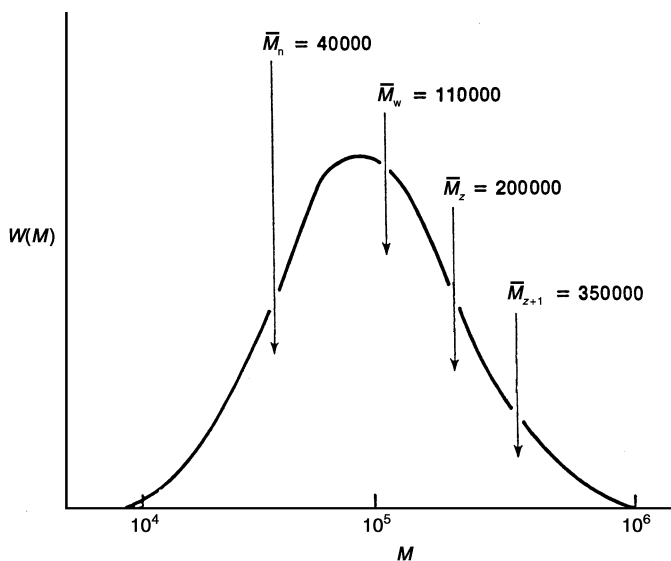


Fig. 3.34. A typical SEC curve cast in terms of molecular weight, for commercial poly(vinyl chloride), measured by size-exclusion chromatography.

two polymer samples with SEC results that are the same within the limits of reproducibility and yet differ significantly in melt-flow behavior. Sensitivity to high molecular weight components is, in fact, to be expected even from the very simplest of molecular theories. The discussion begins with the properties of nearly monodisperse linear polymers, then considers polydispersity contributions, and, finally, some effects due to long-chain branching.

3.5.2 Entanglements

The “slowing down” of relaxation rates at intermediate times, sketched earlier for the stress relaxation modulus in Fig. 3.7, is attributed to chain entanglement or, more precisely, to the mutual uncrossability of backbone-chain contours. At high concentrations of polymer, the domains of individual chains overlap extensively. After the liquid has been deformed, long chains equilibrate up to a certain average distance along their backbones called the *entanglement spacing*, corresponding macroscopically to the end of the transition zone. Further conformational equilibration is slowed because the chains must extricate themselves from the constraining mesh of surrounding chains. In order to arrive at the onset of the terminal zone, the chains must somehow contrive to diffuse around the contours of their neighbors. Beyond that time the chains proceed to their equilibrium distribution of conformations and thereby obliterate all memory of their distorted shapes. The timescale of the terminal relaxations is governed by entanglement interactions, specifically by the ratio of contour length to entanglement spacing. The entanglement interaction is essentially geometric in nature; entanglement effects are universally observed in the melt dynamics of all chains with uncrossable backbones. The plateau modulus is important in flow behavior, because it sets the modulus scale for the terminal response. The details of shape in the transition and glassy zones, on the other hand, have little influence on flow behavior of long-chain systems.

3.5.3 Nearly monodisperse linear polymers

In polymer melts and concentrated solutions, the chains are random coils at equilibrium with average coil dimensions for linear polymers related to chain length by

$$R_g = K_o M^{1/2} \quad (3.36)$$

in which R_g is the root-mean-square radius of gyration of the coils. The coefficient K_o is known for many species from dilute-solution measurements in a theta solvent [39] or small-angle neutron-scattering measurements in the melt state (see Chapter 7). Deformation distorts the distribution of conformations – the chains are

carried out of equilibrium by frictional interactions with their displaced surroundings – and Brownian motion tends to restore the equilibrium. The competition of these opposing effects determines at any moment the average conformational distortion and resulting stress.

The dynamics of polymer chains depend on the interplay of three types of forces acting on the monomeric units:

- (1) a frictional force proportional to the relative velocity of mer and surrounding medium;
- (2) a connector force between adjacent mers on the same chain, maintaining connectivity; and
- (3) a random force from collisions with the surroundings, providing Brownian motion.

The Rouse model [1, 40] describes the contribution of these forces to the slow dynamics of flexible chains, their terminal-stress response and center-of-mass diffusion coefficient. Excluded volume, uncrossability effects, and long-range hydrodynamic interactions are neglected.

The diffusion coefficient for Rouse chains (molecular weight M) is

$$\mathcal{D}_R = \frac{\mathcal{D}_o}{n} \propto M^{-1} \quad (3.37)$$

in which n is the number of mers in the chain, and $\mathcal{D}_o$ is a local dynamics parameter that depends on species and temperature, conceptually the diffusion coefficient of an unattached mer. The stress-relaxation modulus $G(t)$ for a liquid of long, monodisperse Rouse chains (mass concentration c) is given with sufficient accuracy at long times by

$$G(t) = \frac{cRT}{M} \sum_{p=1}^{\infty} \exp\left(-\frac{p^2 t}{\tau_R}\right) \quad (3.38)$$

in which RT is the product of the gas constant and the absolute temperature. The Rouse relaxation time τ_R is

$$\tau_R = \frac{1}{\pi^2} \frac{n R_g^2}{\mathcal{D}_o} \propto M^2 \quad (3.39)$$

The viscosity and recoverable compliance, obtained by applying Eqs. (3.7) and (3.8), are

$$(\eta_o)_R = \frac{1}{6} \frac{cRT}{M} \frac{n R_g^2}{\mathcal{D}_o} \propto M \quad (3.40)$$

$$(J_s^o)_R = \frac{2}{5} \frac{M}{cRT} \propto M \quad (3.41)$$

The Rouse predictions are consistent with some of the observations described earlier. Thus, the longest relaxation timescales with $\eta_o J_s^o$ ($\tau_R = (15/\pi^2)(\eta_o J_s^o)_R$),

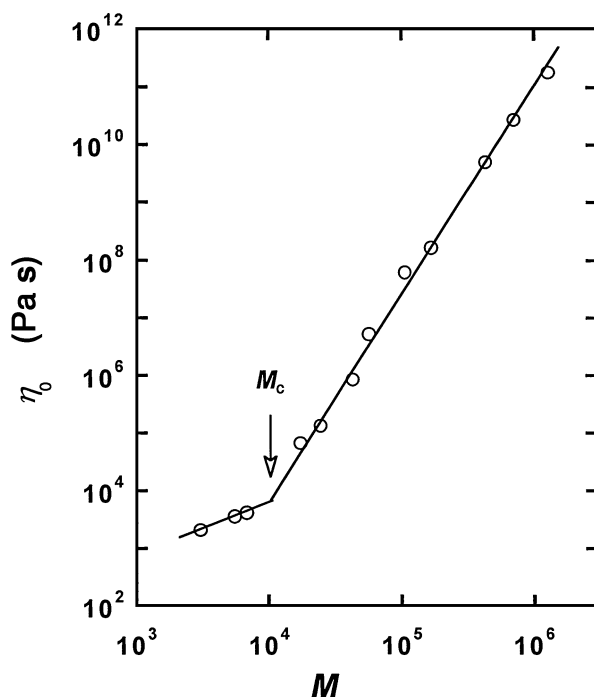


Fig. 3.35. The molecular weight dependence of viscosity for undiluted nearly monodisperse 1,4-polyisoprenes [41].

from Eqs. (3.39)–(3.41), and the temperature dependence of recoverable compliance is very weak ($(J_s^0)_R \propto (cT)^{-1}$). The temperature dependence and local-structural specificity of the diffusion coefficient, viscosity, and relaxation time reside in $\mathcal{D}_0$, the only adjustable parameter in the model and one that, aside from chain-end effects, should be independent of molecular weight for long chains. On the other hand, the model predicts that there is no shear-rate dependence of viscosity: η_R is independent of $\dot{\gamma}$ even when $\tau_R \dot{\gamma}$ is much greater than unity, contrary to the experimental observations.

How well does the Rouse model work in other respects? Viscosity and recoverable compliance as functions of molecular weight are shown in Figs. 3.35 and 3.36 for nearly monodisperse samples of 1,4-polyisoprene [41]. The behavior for other species is similar. Up to some molecular weight, M_c , the prediction of viscosity by Eq. (3.40) is fairly good: η_0 is proportional to M (after a chain-end correction), and even the magnitude (with $\mathcal{D}_0$ estimated from small-molecule diffusion data) is about right [1]. Above M_c , however, the viscosity varies with a much higher power of molecular weight [42]:

$$\eta_0 \propto \begin{cases} M & M \lesssim M_c \\ M^b & M \gtrsim M_c \end{cases} \quad (3.42)$$

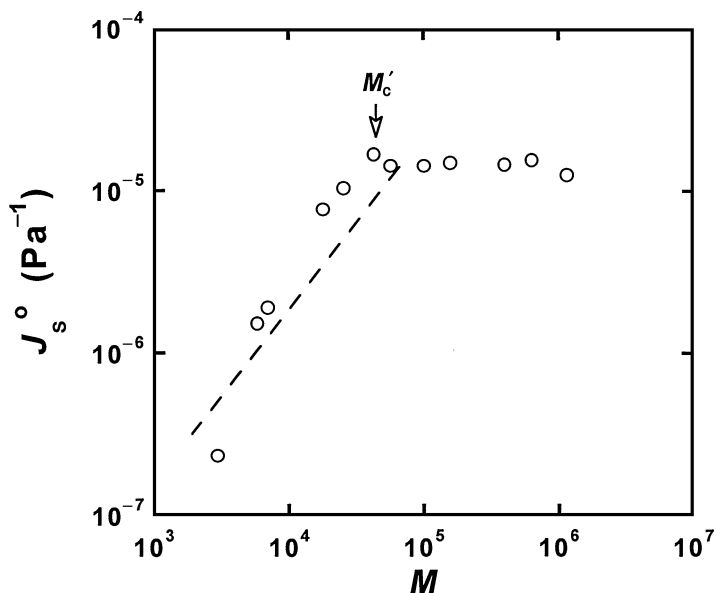


Fig. 3.36. The molecular weight dependence of the recoverable compliance for undiluted nearly monodisperse 1,4-polyisoprenes [41].

The exponent b is typically about 3.4; for 1,4-polyisoprene, $b \sim 3.7$ and $M_c \sim 10\,000$.

The pattern for recoverable compliance is similar. Below some crossover molecular weight, designated M'_c , the Rouse prediction – Eq. (3.41) as shown by the dashed line in Fig. 3.36 – is quite reasonable, especially considering that there are no adjustable parameters. Beyond M'_c , the behavior changes, J_s^0 becoming independent of molecular weight. Thus,

$$J_s^0 = \begin{cases} \frac{2}{5} \frac{M}{cRT} & M \lesssim M'_c \\ \frac{2}{5} \frac{M'_c}{cRT} & M \gtrsim M'_c \end{cases} \quad (3.43)$$

The value of M'_c may be several times M_c [11]. For 1,4-polyisoprene, $M'_c \sim 60\,000$.

A crossover is also found for self-diffusion coefficients in the melt state, from $\mathcal{D} \propto M^{-1}$ for short chains (after a chain-end correction) to $\mathcal{D} \propto M^{-d}$, where $d = 2$ or possibly more for long chains [43–45].

All these phenomena appear to be universal for linear polymers, and they also appear to apply to concentrated solutions as well as melts. Rouse-like behavior gives way to a new set of relationships for properties that are controlled by the slow dynamics of the chains. The characteristic molecular weights depend on species and concentration. The crossover regions are associated with the onset

Table 3.1. *Plateau moduli and entanglement molecular weights for various polymer species in the undiluted state [12, 13]*

Polymer	T (°C)	G_N^0 (10^6 Pa)	M_e^a
Polyethylene	150	2.20	1100
Polypropylene (atactic)	75	0.85	5000
Poly(1-butene) (atactic)	30	0.19	11 600
1,4-Polybutadiene	25	1.15	1900
1,2-Polybutadiene	50	0.42	5700
1,4-Polyisoprene	25	0.35	6400
Polyisobutylene	25	0.32	6900
Poly(dimethyl siloxane)	25	0.24	10 000
Polystyrene (atactic)	190	0.20	18 700

^a Calculated with Eq. (3.44).

of entanglement effects, and the new relationships reflect the influence of chain uncrossability on the slow dynamics.

In the earlier discussion of the plateau modulus, it was remarked that a liquid of long chains acts, at intermediate times or frequencies, like a network. The theory of rubber elasticity predicts a relationship between the shear modulus and the concentration of network strands (Chapter 1). This relationship is used to evaluate M_e , the equivalent molecular weight of a strand in the entanglement network, which is called the *entanglement molecular weight* [1]:

$$M_e = cRT/G_N^0 \quad (3.44)$$

Values of G_N^0 and M_e for several polymer species in the melt state are listed in Table 3.1 (for melts, c is the mass density ρ). Values of G_N^0 for many other species are available in recent reviews [12, 13, 46]. On the basis of a proposal first made by Lin [47], Fetters *et al.* [12] have shown that the plateau modulus in the melt state is related in a simple manner to the chain dimensions and mass density of the species though the *packing length*:

$$l_p = \frac{1}{N_A \rho K_o^2} \quad (3.45)$$

where K_o is defined in Eq. (3.36), and N_A is Avogadro's number. With the packing length defined by Eq. (3.45) (note that the authors employ a slightly different definition of l_p) the relationship is

$$G_N^0 = 0.48kT/l_p^3 \quad (3.46)$$

The values of M_c and M'_c are larger than M_e – for 1,4-polyisoprene $M_e = 6400$ – but the three are clearly related [11, 46]. All three characteristic molecular weights are insensitive to temperature, a fact indicating the occurrence of interactions of a geometric (topological) character, such as would be expected to occur for simple “uncrossability” constraints on the chain dynamics. The characteristic molecular weights are small compared with typical molecular weights for commercial polymers of the same species. Thus, entanglement effects dominate the flow behavior of most commercial polymers.

Small-molecule solvents such as plasticizers change G_N^0 and the characteristic molecular weights in simple and quite general ways. Thus, with ϕ as the volume fraction of polymer ($\phi = c/\rho$),

$$\begin{aligned} G_N^0(\phi) &= (G_N^0)_{\text{melt}} \phi^f \\ M_e(\phi) &= (M_e)_{\text{melt}} / \phi^{f-1} \end{aligned} \quad (3.47)$$

where $2.1 \lesssim f \lesssim 2.3$. The values of M_c and M'_c increase with dilution in the same manner and with the same power-law exponent as M_e . The specific nature of the diluent appears to play no role at all [48]. The exponent may depend slightly on the polymer species, hence the range given in Eq. (3.47), and is never much larger than 2, the value expected for interactions that are proportional to the concentration of pairwise contacts between chain units.

The zero-shear-rate viscosity and recoverable compliance also change with dilution. For $M > M'_c(\phi)$, the product $G_N^0 J_s^0$ is a dilution-independent property of the polymer sample. The product $G_N^0 J_s^0$ is in fact a measure of the polydispersity of relaxation times in the terminal zone [11]. It appears to be essentially universal for highly entangled linear polymers with narrow molecular weight distributions [49–51]:

$$G_N^0 J_s^0 = 2.0 \pm 0.4 \quad (3.48)$$

The invariance of $G_N^0 J_s^0$ means that the dilution dependence of J_s^0 is essentially universal, having the same power-law dependence and exponent, with sign reversed, as G_N^0 . Thus, for $M > M'_c(\phi)$,

$$J_s^0(\phi) = (J_s^0)_{\text{melt}} / \phi^f \quad (3.49)$$

The recoverable compliance, therefore, increases with dilution. The effect of dilution on J_s^0 is best understood physically from its definition in Eq. (3.9) in terms of the recovery phase after steady-state creep. Dilution reduces the concentration of strands in the entanglement network that support the stress. Thus, for a given stress, the coils are more deformed because the stress per strand is higher, so the recoverable strain and hence J_s^0 are larger in the diluted system.

Two factors, one universal and the other specific to the polymer–diluent system, influence the dilution dependence of viscosity [42]. Thus, for $M > M_c(\phi)$,

$$\eta_o(\phi) = (\eta_o)_{\text{melt}} \frac{(\mathcal{D}_o)_{\text{melt}}}{\mathcal{D}_o(\phi)} \phi^g \quad 3.4 \lesssim g \lesssim 3.9 \quad (3.50)$$

where $\mathcal{D}_o(\phi)$ is the unattached-mer diffusion coefficient for the solution. The ratio $\mathcal{D}_o(\phi)/(\mathcal{D}_o)_{\text{melt}}$ reflects how the glass temperature, and hence the local dynamics, is changed by dilution. The factor ϕ^g accounts for the decrease both in the concentration of chains, $c/M \propto \phi$, and in the number of entanglements per chain, $M/M_e(\phi) \propto \phi^{f-1}$. Methods for establishing $\mathcal{D}_o(\phi)/(\mathcal{D}_o)_{\text{melt}}$ are described elsewhere [42, 48, 52]. The entangled-chain formulas, Eqs. (3.47)–(3.50), are applicable to concentrated solutions, perhaps down to 20% polymer unless $(M/M_e)_{\text{melt}}$ is very large. In any case they must cease to apply if the dilution is carried far enough, since other interactions such as excluded volume effects eventually become important.

3.5.4 Theoretical interpretation

Molecular theories of entangled-chain dynamics, based on the *tube model* and *reptation*, have evolved rapidly in recent years. Figure 3.37 illustrates the problem of individual-chain motion in a liquid medium filled with long chains. The chains overlap extensively to provide a kind of mutually shared meshwork in which each chain lies along its own tunnel through the mesh. No chain can move sideways very far without crossing through other chains, which is forbidden. As pointed out by de Gennes [53], however, a linear chain can always move freely along its own tunnel and thereby, over time, change its conformation and its location in the liquid. Thus, this snake-like motion, called reptation, provides a mechanism for relaxation of stress and diffusion in highly entangled liquids, and it became the basis of a detailed molecular theory by Doi and Edwards [54].

The Doi–Edwards theory assumes that reptation is the dominant mechanism for conformational relaxation of highly entangled linear chains. Each molecule has the dynamics of a Rouse chain, but its motions are now restricted spatially by a “tube” of uncrossable constraints, illustrated by the sketch in Fig. 3.38. The tube has a diameter corresponding to the mesh size, and each chain diffuses along its own tube at a rate that is governed by the Rouse diffusion coefficient (Eq. (3.37)). If the liquid is deformed, the tubes are distorted as in Fig. 3.39, and the resulting distortion of chain conformations produces a stress. The subsequent relaxation of stress with time corresponds precisely to the progressive movement of chains out of the distorted tubes and into random conformations by reptation. The theory contains two experimental parameters, the unattached mer diffusion coefficient $\mathcal{D}_o$

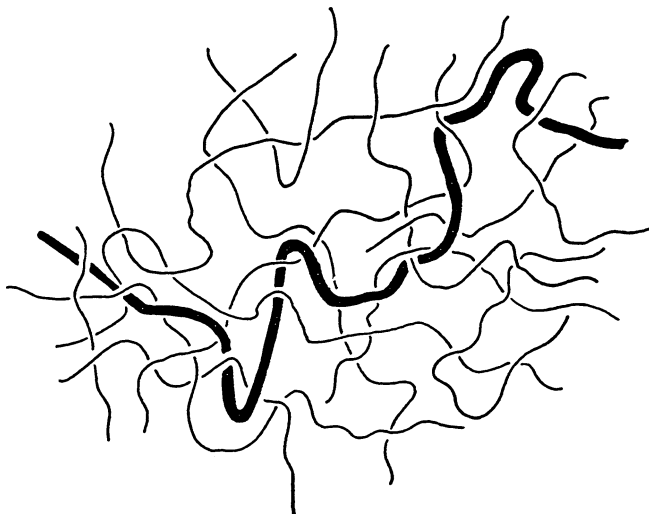


Fig. 3.37. One chain in an entangled melt of chains [56].

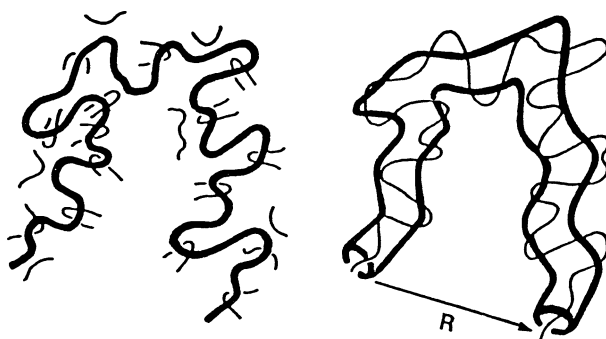


Fig. 3.38. A depiction of a chain with the uncrossability constraint represented by a tube [56].

and the tube diameter, a , but, once these parameters are established, predictions for all properties of the slow dynamics follow directly [55].

Despite the simplicity of its basic premises about entanglement interactions, which must be very complex in local detail, the Doi–Edwards theory has been remarkably successful. It encompasses a diverse range of dynamic phenomena within a single molecular framework, and its predictions for nearly monodisperse linear polymers are seldom in gross conflict with observations [56]. In many cases, its agreement with experiment is essentially quantitative. Thus, self-diffusion coefficients are predictable with some accuracy – $\mathcal{D}_0$ and a having been established by some independent means – and the predicted molecular weight independence and magnitude of the recoverable compliance are reasonably consistent with

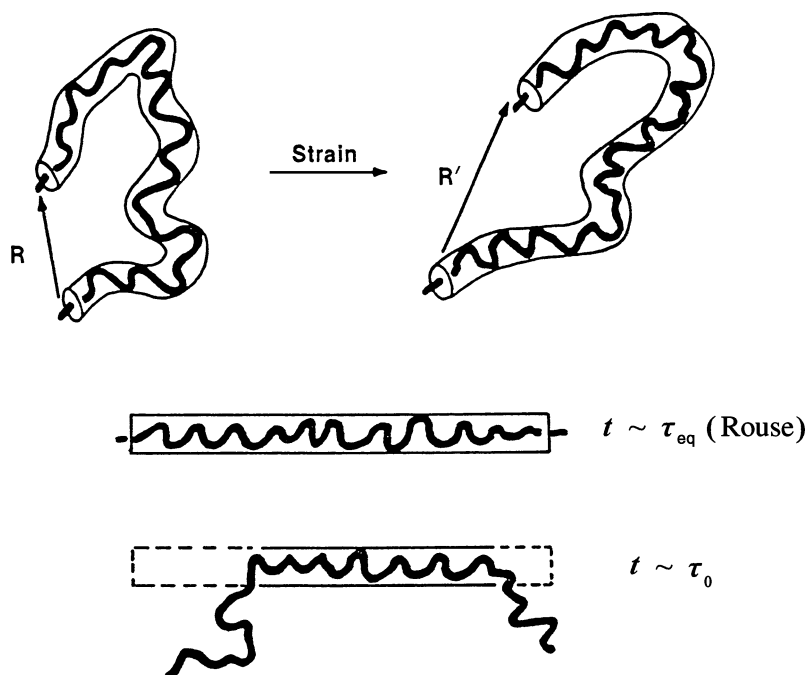


Fig. 3.39. Deformation of the tube and the subsequent progression of the chain it contains as it diffused from the distorted tube back to equilibrium [56].

the data (Eq. (3.48)):

$$J_s^0 = \frac{6}{5G_N^0} \quad (3.51)$$

The predicted molecular weight dependence of viscosity, $\eta_0 \propto M^3$, is slightly weaker than the observed $M^{3.4}$, however, and the magnitudes of viscosity in the experimental range are too large [55]. The predicted shear-rate dependence of viscosity appears to be too strong, but the theory gives a value for the normal-stress ratio, N_2/N_1 , of the correct sign and about the right magnitude.

Some deficiencies of the theory, such as its prediction for $\eta_0(M)$, have been attributed to competing mechanisms for relaxation that were not considered in the original theory [56]. One such feature is the time-dependent fluctuations in the length of tube occupied by the chain. Even if the chain did not reptate, the *fluctuations in tube length* over time would still relax the stress, albeit much more slowly than would reptation. Another omitted feature is the finite lifetime of the constraints that define the tube. Unlike reptation and fluctuations, which reflect only the individual-chain properties, the constraint lifetime is a matrix effect. The constraints for any of the chains are the strands of neighboring chains, all of which

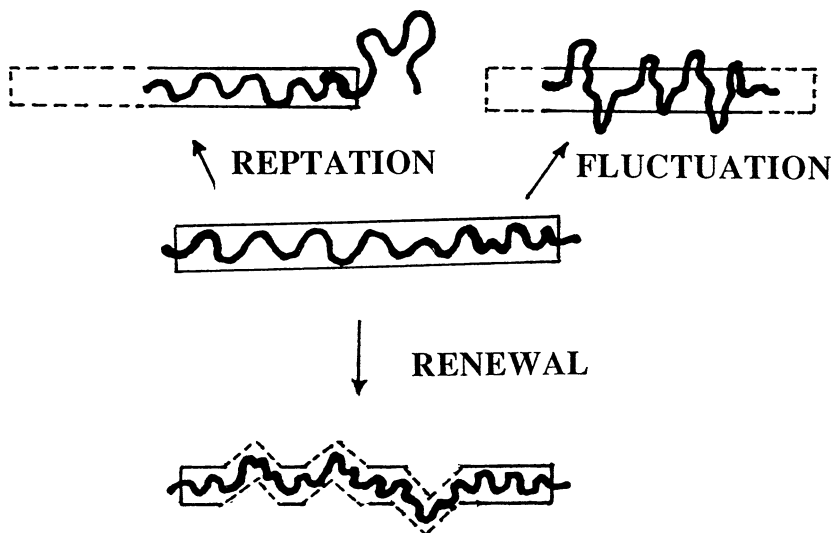


Fig. 3.40. An illustration of the reptation, fluctuation, and constraint-release mechanisms for relaxation of entangled chains [56].

are themselves diffusing through the liquid and releasing constraints as they go. Release of constraints permits the tubes themselves to undergo a random Rouse-like motion over time, thereby relaxing the stress. The basic elements of all three mechanisms are shown schematically in Fig. 3.40. Judged by the recent, essentially quantitative prediction of $\eta_o(M)$, it would appear that tube-length fluctuations and constraint release together are responsible for the discrepancy in the pure-reptation prediction of η_o [57]. Constraint release plays a dominant role in the relaxation of polydisperse linear polymers, and both effects are crucial when long branches suppress reptation, as discussed below.

3.5.4.1 Molecular weight distributions

How does polydispersity change the viscoelastic properties of linear polymers? The most remarkable effect is the enormous enhancement of the recoverable compliance with a broadening of the high molecular weight tail of the distribution. Though it is perhaps surprising at first, this increase in J_s^o for chain-length mixtures is readily understandable as a special kind of dilution effect (see Eq. (3.49) and the attendant discussion). Thus, the longest chains have larger and more easily deformable coils than the average. They also have more frictional sites and hence support a disproportionately large share of the steady-state stress, all of which lead to greater coil distortion, larger recoil in the recovery phase, and hence an increase in J_s^o .

For the Rouse model [1],

$$(\eta_o)_R \propto M_w \quad (3.52)$$

$$(J_s^o)_R = [J_s^o(M_w)]_R \frac{M_z M_{z+1}}{M_w^2} \quad (3.53)$$

in which $[J_s^o(M_w)]_R$ is the monodisperse value at $M = M_w$. These equations describe the behavior of short chains rather well, and some aspects of them carry over into the entangled region. Thus, Eq. (3.42) with M_w in place of M accounts approximately for the effect of polydispersity on η_o ; and Eq. (3.53), with the observed monodisperse value in place of $[J_s^o(M_w)]_R$, tracks roughly the rapid rise in J_s^o found experimentally when the distribution is broadened. Other combinations of molecular weight averages have been proposed to replace $M_z M_{z+1}/M_w^2$, but without significant improvement. A simple extension of the Doi–Edwards theory to mixtures is inadequate [55, 58].

Even accepting reptation as the primary motion, the constraint-release mechanism appears to hold the key to understanding effects of polydispersity in viscoelasticity. Double reptation, an approximate method for implementing constraint release without introducing new parameters, shows considerable promise [59–61]. The idea is most easily envisioned in terms of the stress relaxation experiment. In the Doi–Edwards model (single reptation), the fraction of stress remaining at any time t following a step strain is equal to the average fraction of chain length still occupying the strain-distorted tubes at that time. In double reptation, the remaining fraction of stress is equal to the fraction of surviving entanglements. The picture is that each entanglement involves two chains, both reptating, and that an entanglement survives until it is released when either end of either chain first reptates past it. The result is an expression for the stress relaxation modulus in a system with arbitrary molecular weight distribution:

$$G(t) = \left(\int_0^\infty W(M) G^{1/2}(M, t) dM \right)^2 \quad (3.54)$$

in which $G(M, t)$ is the stress-relaxation modulus for monodisperse samples of the species at the temperature of interest.

The first tests of Eq. (3.54) gave good agreement with data for η_o and J_s^o for binary mixtures of nearly monodisperse components [62]. Detailed studies of mixtures [58] and polydisperse commercial systems [58, 63] have now been published. Comparisons between experiment and prediction based on Eq. (3.54) for the dynamic moduli of various polyolefins ($T_0 = 190^\circ\text{C}$) are shown in Figs. 3.41–3.43. Figure 3.41 is the result for a commercial polypropylene ($M_w = 420\,000$, $M_w/M_n = 5.7$, $M_z/M_w = 3.8$) with distribution data from SEC

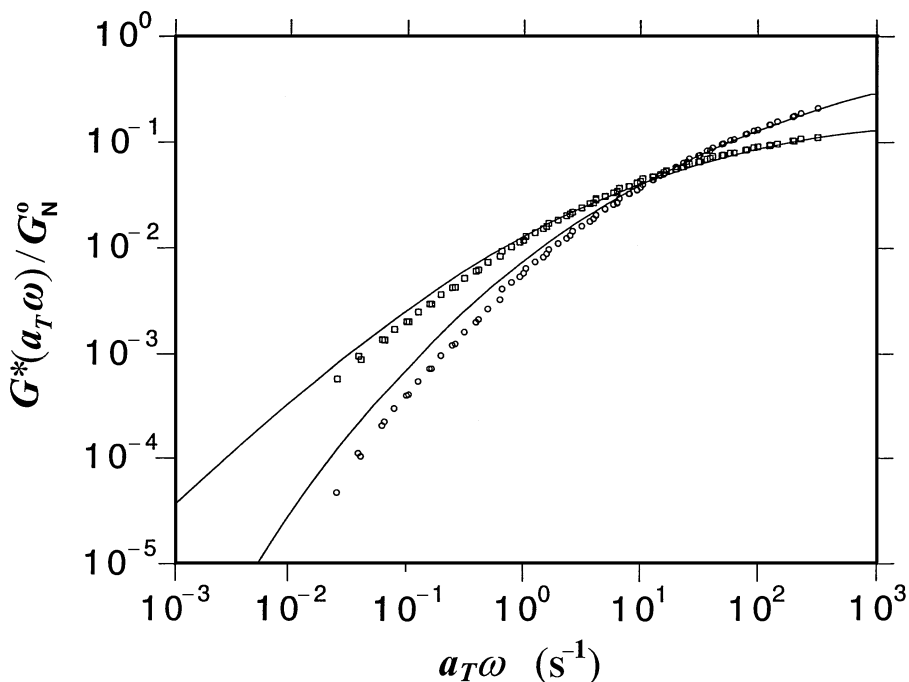


Fig. 3.41. The experimental master curve for a commercial polypropylene and the prediction from its molecular weight distribution obtained by consideration of double reptation [63].

alone. Figure 3.42 is the result for SRM-1475, a high-density polyethylene standard ($M_w = 58\,000$, $M_w/M_n = 3.2$, $M_z/M_w = 2.7$), with distribution data from SEC and in-line viscometry. Figure 3.43 is the result for SRM-1476, a low-density polyethylene standard containing long-chain branches ($M_w = 160\,000$, $M_w/M_n = 6.1$, $M_z/M_w \sim 70$), with distribution data from SEC and in-line light scattering. Considering that there are no adjustable parameters, the agreement for the first two samples is reasonable. The large difference between experiment and calculation for the low-density polyethylene is almost certainly caused by the extremely high viscosity of the melt owing to the presence of long branches.

Nonlinear flow properties and melt-processing behavior are also strongly dependent on polydispersity. As seen in Fig. 3.25(a), the steady-state viscosity data for nearly monodisperse polystyrenes of several molecular weights superpose when they are plotted in reduced form, $\eta(\dot{\gamma})/\eta_0$ versus $\dot{\gamma}\tau_0$. The same master curve describes results for entangled polymers of several species obtained at different temperatures and concentrations, with different diluent species and chain lengths. The effect of the molecular weight distribution is shown in Fig. 3.44. Viscosity–shear-rate data at 180 °C are given for two polystyrenes; a

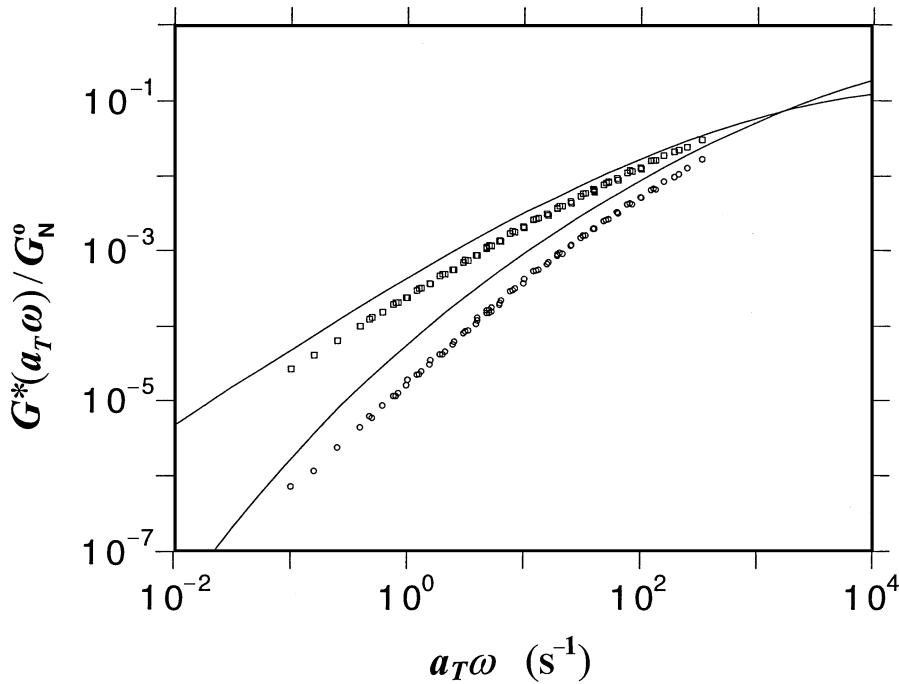


Fig. 3.42. The experimental master curve for SRM-1475, a high-density polyethylene reference material, and the prediction from its molecular weight distribution obtained by consideration of double reptation [63].

commercial sample ($M_w = 260\,000$, $M_w/M_n \sim 2.5$; $\eta_o = 32\,000$ Pa, $\tau_o = 1.9$ s) and a nearly monodisperse sample ($M_w = 160\,000$, $M_w/M_n \sim 1.1$; $\eta_o = 20\,000$ Pa, $\tau_o = 0.29$ s). Polydispersity broadens the transition from Newtonian to power-law behavior. In this example, M_w is larger for the polydisperse sample, and so it has a higher value of η_o . However, non-Newtonian behavior appears at a much lower shear rate for the broad-distribution sample: τ_o is much larger because η_o and J_s^o are both larger (Eq. (3.14)), the latter because of polydispersity alone. The two curves cross, and, at high shear rates, the polydisperse sample has a lower viscosity than does the nearly monodisperse sample. The combination of high viscosity at low shear rates and low viscosity at high shear rates is a desirable feature for certain melt-processing operations (blow molding, for example), and the effect of polydispersity can be advantageous in those cases.

Some success has been achieved in predicting the shape of viscosity–shear-rate curves from information on the molecular weight distribution. The curves drawn in Fig. 3.44 were calculated from SEC data by using a simplified model that attributes the progressive reduction in viscosity with increasing shear rate to a flow-induced disentanglement of the chains [64].

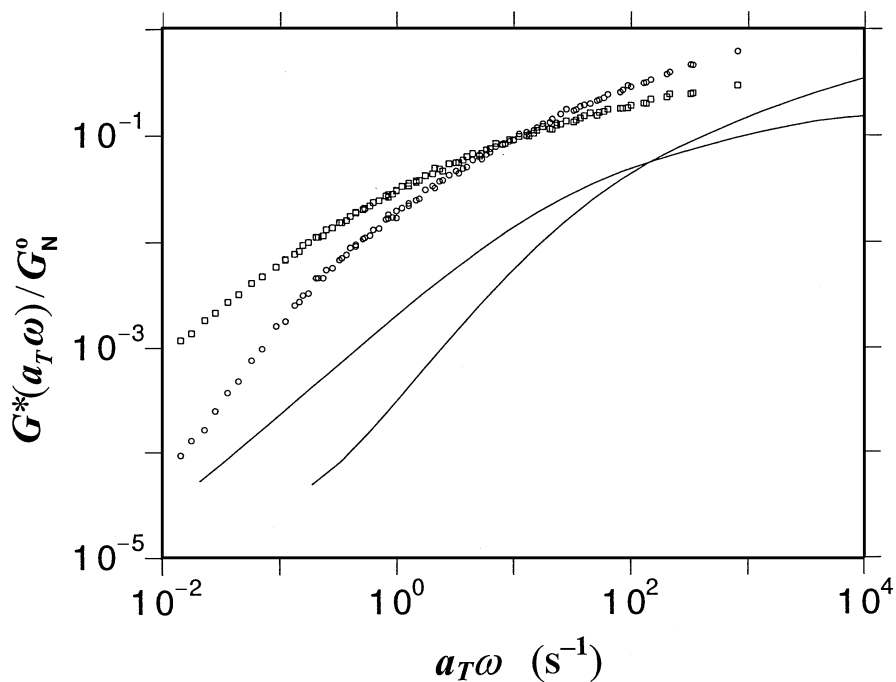


Fig. 3.43. The experimental master curve for SRM-1476, a low-density polyethylene reference material, and the prediction from its molecular weight distribution obtained by consideration of double reptation [63].

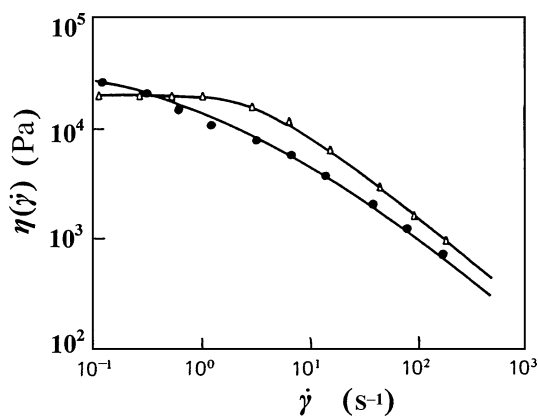


Fig. 3.44. Viscosity–shear-rate behavior for nearly monodisperse polystyrene (Δ) and polydisperse commercial polystyrene ($\bullet$) [32].

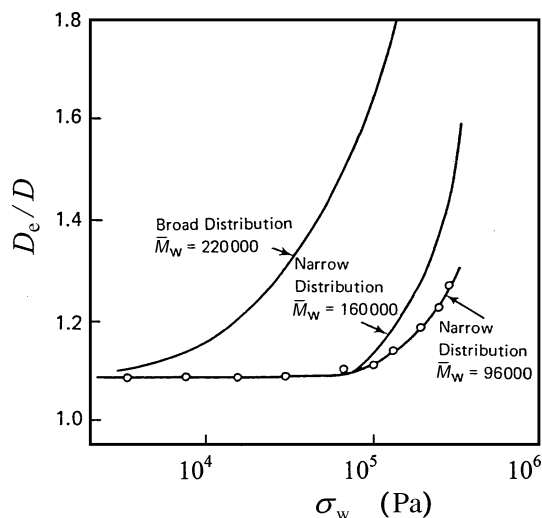


Fig. 3.45. Die swell versus wall shear stress for polystyrene samples of various molecular weights and distributions [32].

Figure 3.45 demonstrates the extreme importance of the distribution breadth in melt elasticity. Die swell D_e/D begins to increase at much lower capillary shear stress for the broad-distribution sample, and the change is more gradual than that for the narrow-distribution samples. The sensitivity of die swell to the distribution breadth follows naturally from the Tanner expression (Eq. (3.34)), according to which D_e/D is a function of the ratio N_1/σ alone. With the approximation $N_1 \sim 2J_s^0\sigma^2$ from Eq. (3.28), $N_1/\sigma \sim 2J_s^0\sigma$. Thus, since J_s^0 increases rapidly with the distribution breadth, die swell at constant shear stress should increase with the distribution breadth of the polymer.

3.5.4.2 Long-chain branching

Broadly speaking, viscoelastic behavior is only slightly modified if the branches are not too long. However, if the branches are long enough to be well entangled – if the molecular weight per branch M_b is much larger than M_e – then the effects of branching can be profound [65]. Nonlinear architectures in commercial polymers are typically generated by some random-branching chemistry, such as polymer transfer, end-group incorporation or cross-linking during polymerization. Low-density polyethylene is a prominent example of a randomly branched polymer (note Fig. 3.43). Random branching invariably introduces a broad distribution of structures, and it becomes extremely difficult to separate the effects due explicitly to branching from those due to the added polydispersity. Most of what is known about effects of branching has come from the study of model systems. Molecular

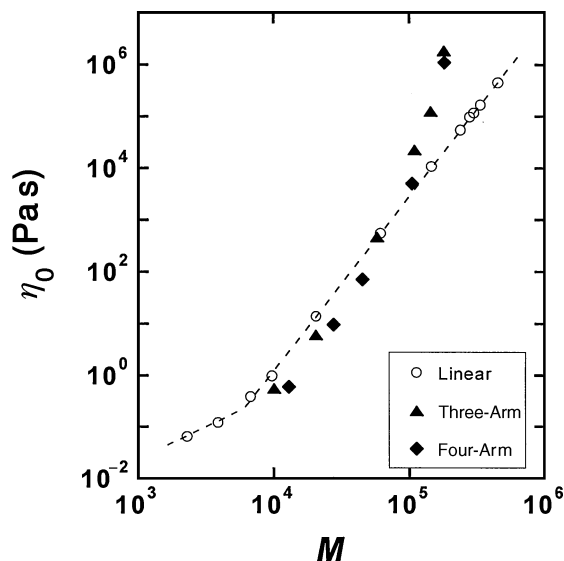


Fig. 3.46. Molecular weight dependence of viscosity at 107 °C for nearly monodisperse linear and star 1,4-polybutadiene [30].

stars, composed of three or more linear strands joined to a common junction, can be made with highly uniform structure by anionic polymerization followed by an appropriate linking reaction. The branch length and branch-point functionality can thus be varied, and their effects can be studied over wide ranges [24, 66, 67]. Each such molecule contains only one branch point, however, so that some effects of branching cannot be studied with stars. A limited amount of data is available for regular combs [68] and for randomly branched chains prepared by fractionation of polydisperse samples [69].

The Rouse theory applied to nonlinear polymers predicts both η_0 and J_s^0 to be smaller for branched chains than for linear chains of the same total molecular weight [70]. Qualitatively, the viscosity is smaller because the coil size is smaller, and the recoverable compliance is less because the coils are less easily deformable. Those predictions hold true experimentally, even in the entanglement region, until the branches themselves are long enough to become significantly entangled ($M_b > (2-4)M_e$, in which M_b is the molecular weight of a branch). For longer arms, as shown for three-arm and four-arm 1,4-polybutadiene stars in Fig. 3.46, the viscosity for branched polymers rises very rapidly relative to that for linear polymers and can easily exceed the latter by factors of 100 or more [30]. Viscosity no longer varies with molecular weight according to a power law. For long arms, the viscosity increases exponentially with branch length [52]:

$$\eta_0 \propto \exp\left(\beta \frac{M_b}{M_e}\right) \quad (3.55)$$

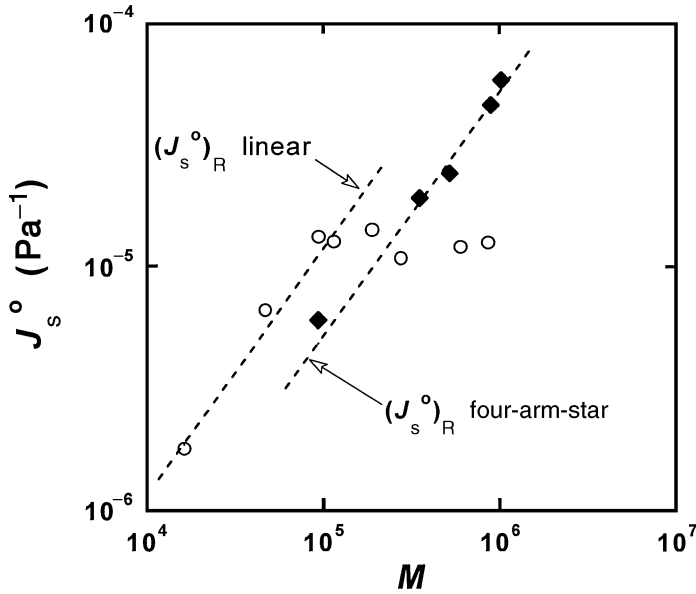


Fig. 3.47. Molecular weight dependence of the recoverable compliance for nearly monodisperse linear and star polystyrene [66, 71].

The exponential coefficient β is approximately 0.6 and insensitive to f , the number of arms per star. The viscosity decreases very rapidly with dilution [49] ($M_e \propto \phi^{1-f}$ from Eq. (3.47), so η_o varies approximately exponentially with ϕ), soon falling below the viscosity for a similarly diluted linear polymer of the same total molecular weight.

The variation of recoverable compliance with molecular weight also differs for linear and nonlinear polymers. In contrast to the behavior of nearly monodisperse linear polymers, for which J_s^o becomes a constant ($\sim 2/G_N^o$) beyond about $5M_e$, J_s^o for stars simply continues to increase in direct proportion to M_b , which is exemplified by the comparison of data for linear polystyrene [71] and four-arm polystyrene stars [66] in Fig. 3.47. Experimentally, the behavior of J_s^o for nearly monodisperse stars, irrespective of branch-point functionality, is described well by [52]

$$J_s^o = \beta' \frac{M_b}{\rho RT} \quad (3.56)$$

Experimentally, β' is approximately 0.6. Thus, for branched polymers in the entanglement region, both η_o and J_s^o may be quite large compared with the values for linear polymers of the same molecular weight. The terminal zone is inherently broader for well-entangled branched polymers than it is for linear polymers of comparable polydispersity [49]. The complex viscosities for a nearly monodisperse linear polybutadiene and three-arm polybutadiene star, shown in Fig. 3.24 for other purposes, exemplify the more gradual transition from Newtonian to power-law

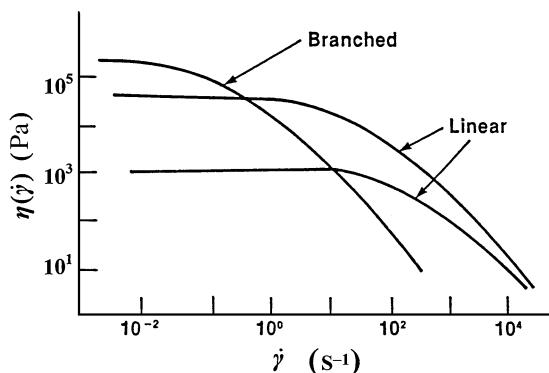


Fig. 3.48. Shifts of viscosity–shear-rate behavior due to the presence of long branches in the molecules.

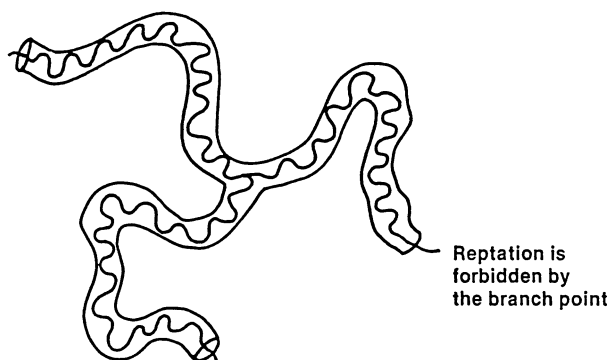


Fig. 3.49. A depiction of a branched polymer in its tube of entanglement constraints.

behavior for the star. The effect of branching on viscosity–shear-rate behavior is illustrated in Fig. 3.48. The larger values of J_s^0 for long-arm stars make τ_0 larger than would be obtained for a linear polymer with the same viscosity. The viscosity at high shear rates is lower for stars, and the viscosity–shear-rate curves for linear and branched polymers may cross. Branched systems in general can probably reach domains of viscosity–shear-rate behavior that are inaccessible to systems of linear chains. Unusual elastic effects would presumably occur too, but the entire subject of nonlinear responses of branched polymers is only now beginning to be investigated.

All these observed characteristics of viscoelasticity for star polymers are natural consequences of the tube model. As suggested by the sketch in Fig. 3.49, the presence of even one long branch would surely suppress reptation [53]. There is no longer any direction for the star to move freely into new positions and conformations, and accordingly relaxation and diffusion must occur by some other motion. The Pearson–Helfand theory for stars based on tube-length fluctuations alone [72]

leads directly to a broadened terminal region and expressions for η_0 and J_s^0 that in general agree well with the observed behavior for stars (Eqs. (3.55) and (3.56)). The main difference is in the coefficients: $\beta = \beta' = 15/8 = 1.875$ is predicted whereas $\beta \sim \beta' \sim 0.6$ is found.

The discrepancy in the coefficients is not trivial. Owing to the exponential form, the predicted η_0 and hence τ_0 are too large for star melts by several orders of magnitude. The predictions turned out to be in much better agreement with data for stars relaxing in a network environment [73], indicating that there is a large matrix effect and suggesting the need to consider constraint-release contributions in the melt. Ball and McLeish did this by applying the Marrucci idea of dynamic dilution [74] to the relaxation times associated with different locations along the arms of a star [75].

The physical picture is as follows. Fluctuations quickly relax the deformation-induced tube distortions – and hence distortions of the chain segments they contain – for segments located near the free end of the arm, but increasingly more slowly for locations nearer the center of the star. This is the qualitative essence of the Pearson–Helfand model. In their second role as potential suppliers of tubes, chain segments behave like permanent constraints toward faster-relaxing segments – the ones nearer a free end than they – but like a monomeric diluent toward slower-relaxing ones – those further from a free end. The effect is that of a tube diameter that increases with distance from the free end. Accordingly, the relaxation time is related to the distance from the free end as the product of two countervailing factors, the contribution from fluctuation increasing with distance and the dynamic contribution from dilution decreasing with distance. The result is essentially the Pearson–Helfand solution but with revised coefficients, $\beta = \frac{5}{8} = 0.625$ and $\beta' = 1.06$, in good agreement with experiment for η_0 although still a bit too high for J_s^0 . Recent refinements of the analysis [76, 77] yield $\beta = 0.48$ and $\beta' = 0.99$.

The entire subject of the viscoelasticity of branched polymers is an active area of research at present. The linear viscoelastic properties of nonsymmetric stars, H-shaped polymers, polymeric combs, and randomly branched species are being investigated both theoretically and experimentally [78–82], and new ideas about their nonlinear responses both during shear and during extension are being considered [83]. With these and other initiatives, the molecular understanding of flow behavior in entangled-polymer liquids will surely expand rapidly in the next few years.

3.6 Summary

The viscoelastic character and flow behavior of polymer melts and concentrated solutions have been considered both from the macroscopic and from the microscopic

point of view. The universal nature of the behavior, in particular its dependence on the large-scale molecular architecture for flexible-chain, non-associating polymers in the homogeneous liquid state, has been emphasized. Various experimental methods for characterizing viscoelastic responses have been described, and the main features of current molecular theories about the dynamics of polymer liquids have been outlined. Several important topics were omitted or touched upon only briefly. Introductions to some – polymer-melt processing [31], rheology of liquid-crystalline polymers [84, 85], rheo-optical techniques [86], and simulation methods [87] – are available in the literature.

References

- [1] J. D. Ferry, *Viscoelastic Properties of Polymers*, 3rd edition (John Wiley & Sons, New York, 1980).
- [2] B. D. Coleman, H. Markovitz, and W. Noll, *Viscometric Flows of Non-Newtonian Fluids* (Springer-Verlag, Berlin, 1966).
- [3] R. B. Bird, R. C. Armstrong, and O. Hassager, *Dynamics of Polymeric Liquids*, 2nd edition (John Wiley & Sons, New York, 1987), Vol. 1.
- [4] A. S. Lodge, *Body Tensor Fields in Continuum Mechanics, with Applications to Polymer Rheology* (Academic Press, New York, 1974).
- [5] G. Astarita and G. Marrucci, *Principles of Non-Newtonian Fluid Mechanics* (McGraw-Hill, Maidenhead, 1974).
- [6] C. W. Macosko, *Rheology: Principles, Measurements and Applications* (VCH, New York, 1994).
- [7] W. R. Schowalter, *Mechanics of Non-Newtonian Fluids* (Pergamon, Oxford, 1978).
- [8] R. I. Tanner, *Engineering Rheology*, 2nd edition (Oxford University Press, Oxford, 2000).
- [9] A. S. Lodge, *Elastic Liquids* (Academic Press, New York, 1964).
- [10] L. R. G. Treloar, *The Physics of Rubber Elasticity*, 3rd edition (Oxford University Press, Oxford, 1975).
- [11] W. W. Graessley, *Adv. Polym. Sci.*, **16** (1974), 1.
- [12] L. J. Fetters, D. J. Lohse, D. Richter, T. A. Witten, and A. Zirkel, *Macromolecules*, **27** (1994), 4639.
- [13] L. J. Fetters, D. J. Lohse, and W. W. Graessley, *J. Polym. Sci. Pt B: Polym. Phys.*, **37** (1999), 1023.
- [14] W. W. Graessley, *Macromolecules*, **15** (1982), 1164.
- [15] A. J. Levine and S. T. Milner, *Macromolecules*, **31** (1998), 8623.
- [16] H. Markovitz, *J. Polym. Sci. Symp.*, **50** (1975), 431.
- [17] S. H. Wasserman, private communication (1992).
- [18] S. Onogi, T. Masuda, and K. Kitagawa, *Macromolecules*, **3** (1970), 109.
- [19] T. Masuda, K. Kitagawa, T. Inoue, and S. Onogi, *Macromolecules*, **3** (1970), 116.
- [20] B. D. Coleman and H. Markovitz, *J. Appl. Phys.*, **35** (1966), 1.
- [21] C. S. Lee, J. J. Magda, K. L. DeVries, and J. W. Mays, *Macromolecules*, **25** (1992), 4744.
- [22] J. J. Magda and S. G. Baek, *Polymer*, **35** (1994), 1187.
- [23] K. Walters, *Rheometry* (Chapman & Hall, London, 1975).

- [24] W. W. Graessley, T. Masuda, J. E. L. Roovers, and N. Hadjichristidis, *Macromolecules*, **9** (1976), 127.
- [25] J. M. Dealy, *Rheometers for Molten Plastics* (Van Nostrand Reinhold, New York, 1982).
- [26] R. L. Crawley, Master's thesis, Northwestern University (1972).
- [27] W. P. Cox and E. H. Merz, *J. Polym. Sci.*, **28** (1958), 619.
- [28] M. J. Struglinski, Doctoral thesis, Northwestern University (1984).
- [29] R. A. Stratton, *J. Coll. Sci.*, **22** (1966), 517.
- [30] G. Kraus and J. T. Gruver, *J. Polym. Sci. Pt A*, **3** (1965), 105.
- [31] J. M. Dealy and K. F. Wissbrun, *Melt Rheology and its Role in Plastics Processing* (Van Nostrand Reinhold, New York, 1990).
- [32] W. W. Graessley, S. D. Glasscock, and R. L. Crawley, *Trans. Soc. Rheol.*, **14** (1970), 519.
- [33] R. I. Tanner, *Appl. Polym. Symp.*, **20** (1973), 201.
- [34] R. I. Tanner, *J. Polym. Sci. Pt A-2*, **8** (1970), 2067.
- [35] R. C. Penwell, W. W. Graessley, and A. Kovacs, *J. Polym. Sci.: Polym. Phys. Ed.*, **12** (1974), 1771.
- [36] S. Mori and H. G. Barth, *Size Exclusion Chromatography* (Springer-Verlag, New York, 1999).
- [37] H. Pasch, *Adv. Polym. Sci.*, **150** (2000), 1.
- [38] T. Sun, P. Brant, R. R. Chance, and W. W. Graessley, *Macromolecules*, **34** (2001), 6812.
- [39] J. E. Mark (ed.), *Physical Properties of Polymers Handbook* (AIP Press, Woodbury, New York, 1996).
- [40] R. B. Bird, O. Hassager, R. C. Armstrong, and C. F. Curtiss, *Dynamics of Polymeric Liquids*, 2nd edition (John Wiley & Sons, New York, 1987), Vol. 2.
- [41] H. Odani, N. Nemoto, and M. Kurata, *Macromolecules*, **5** (1972), 531.
- [42] G. C. Berry and T. G. Fox, *Adv. Polym. Sci.*, **5** (1968), 261.
- [43] P. F. Green and E. J. Kramer, *Macromolecules*, **19** (1986), 1108.
- [44] B. Crist, P. F. Green, R. A. L. Jones, and E. J. Kramer, *Macromolecules*, **22** (1989), 2857.
- [45] T. P. Lodge, *Phys. Rev. Lett.*, **83** (1999), 3218.
- [46] L. J. Fetters, D. J. Lohse, S. T. Milner, and W. W. Graessley, *Macromolecules*, **32** (1999), 6847.
- [47] Y. H. Lin, *Macromolecules*, **20** (1987), 3080.
- [48] R. H. Colby, L. J. Fetters, W. G. Funk, and W. W. Graessley, *Macromolecules*, **24** (1991), 3873.
- [49] V. R. Raju, E. V. Menezes, G. Marin, W. W. Graessley, and L. J. Fetters, *Macromolecules*, **14** (1981), 1668.
- [50] J. M. Carella, W. W. Graessley, and L. J. Fetters, *Macromolecules*, **17** (1984), 2775.
- [51] J. T. Gotro and W. W. Graessley, *Macromolecules*, **17** (1984), 2767.
- [52] D. S. Pearson, *Rubber Chem. Technol.*, **60** (1987), 439.
- [53] P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, New York, 1979).
- [54] M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Clarendon Press, Oxford, 1986).
- [55] W. W. Graessley, *J. Polym. Sci.: Polym. Phys. Ed.*, **18** (1980), 27.
- [56] W. W. Graessley, *Adv. Polym. Sci.*, **47** (1982), 67.
- [57] A. E. Likhtman and T. C. B. McLeish, *Macromolecules*, **35** (2002), 6332.
- [58] S. H. Wasserman and W. W. Graessley, *J. Rheol.*, **36** (1992), 543.

- [59] C. Tsenoglou, *Polym. Preprints*, **28** (1987), 185.
- [60] J. des Cloiseaux, *Europhys. Lett.*, **5** (1988), 437.
- [61] J. des Cloiseaux, *Macromolecules*, **23** (1990), 4678.
- [62] C. Tsenoglou, *Macromolecules*, **24** (1991), 1762.
- [63] S. H. Wasserman and W. W. Graessley, *Polym. Eng. Sci.*, **36** (1996), 852.
- [64] W. W. Graessley, *J. Chem. Phys.*, **47** (1967), 1942.
- [65] W. W. Graessley, *Acc. Chem. Res.*, **10** (1977), 332.
- [66] W. W. Graessley and J. Roovers, *Macromolecules*, **12** (1979), 959.
- [67] J. M. Carella, J. T. Gotro, and W. W. Graessley, *Macromolecules*, **19** (1986), 659.
- [68] J. Roovers and W. W. Graessley, *Macromolecules*, **14** (1981), 766.
- [69] R. A. Mendelson, W. A. Bowles, and F. L. Finger, *J. Polym. Sci. Pt A-2*, **8** (1970), 105.
- [70] D. S. Pearson and V. R. Raju, *Macromolecules*, **15** (1982), 294.
- [71] D. J. Plazek and V. M. O'Rourke, *J. Polym. Sci. Pt A-2*, **9** (1971), 209.
- [72] D. S. Pearson and E. Helfand, *Macromolecules*, **17** (1984), 888.
- [73] H.-C. Kan, J. D. Ferry, and L. J. Fetters, *Macromolecules*, **13** (1980), 1571.
- [74] G. Marrucci, *J. Polym. Sci.: Polym. Phys. Ed.*, **23** (1985), 159.
- [75] R. C. Ball and T. C. B. McLeish, *Macromolecules*, **22** (1989), 1911.
- [76] S. T. Milner and T. C. B. McLeish, *Macromolecules*, **30** (1997), 2159.
- [77] S. T. Milner and T. C. B. McLeish, *Macromolecules*, **31** (1998), 7479.
- [78] A. L. Frischknecht, S. T. Milner, A. Pryke, R. N. Young, R. Hawkins, and T. C. B. McLeish, *Macromolecules*, **35** (2002), 4801.
- [79] T. C. B. McLeish, J. Allgaier, D. K. Bick, G. Bishko, P. Biswas, R. Blackwell, B. Blottiere, N. Clarke, B. Gibbs, D. J. Groves, A. Hakiki, R. K. Heenan, J. M. Johnson, R. Kant, D. J. Read, and R. N. Young, *Macromolecules*, **32** (1999), 6734.
- [80] D. R. Daniels, T. C. B. McLeish, B. J. Crosby, R. N. Young, and C. M. Fernyhough, *Macromolecules*, **34** (2001), 7025.
- [81] D. J. Read and T. C. B. McLeish, *Macromolecules*, **34** (2001), 1928.
- [82] B. J. Crosby, M. Mangnus, W. de Groot, R. Daniels, and T. C. B. McLeish, *J. Rheol.*, **46** (2002), 401.
- [83] S. T. Milner, T. C. B. McLeish, and A. E. Likhtman, *J. Rheol.*, **45** (2001), 539.
- [84] G. C. Berry, *J. Rheol.*, **35** (1991), 943.
- [85] R. G. Larson, *The Structure and Rheology of Complex Fluids* (Oxford University Press, New York, 1999).
- [86] G. G. Fuller, *Optical Rheometry of Complex Fluids* (Oxford University Press, New York, 1995).
- [87] K. Binder (ed.), *Monte Carlo and Molecular Dynamics Simulations in Polymer Science* (Oxford University Press, New York, 1995).

4

The crystalline state

Leo Mandelkern

4.1 Introduction

In this chapter we shall be concerned with the basic principles that govern the crystallization behavior of flexible long-chain molecules. The more-rigid type of polymers will be discussed in Chapter 5. The subject matter divides itself naturally into several interrelated subdivisions. These include thermodynamics of crystallization, kinetics and mechanisms of crystallization, structure and morphology, and microscopic and macroscopic properties. We shall discuss each of these topics in terms of fundamental physical and chemical concepts. There is an interrelation among the various aspects of polymer crystallization as is indicated by the chart given in Fig. 4.1.

Essentially all properties are controlled by the molecular morphology. In turn the molecular morphology is determined by the crystallization mechanisms. Such mechanisms are deduced from detailed studies of crystallization kinetics. Knowledge of the equilibrium requirements, or the thermodynamics of crystallization, is necessary in order to analyze the kinetics properly. Although this information is important and can be obtained theoretically, the actual equilibrium state of a crystalline polymer is rarely, if ever, achieved. This well-known situation is due to kinetic factors involved in crystallization from the melt that lead to the formation of relatively small crystallites with accompanying high interfacial free energies. Crystallites involving extended chains are difficult to achieve. The difficulties in establishing the equilibrium state led early on to the recognition that one is dealing with a metastable state [1]. The various aspects of the problems are clearly interdependent upon one another. This interdependence will become apparent as we examine experimental results. Hence, very few, if any, of the problems concerned with crystallization behavior, or properties in the crystalline state, can be studied in isolation.

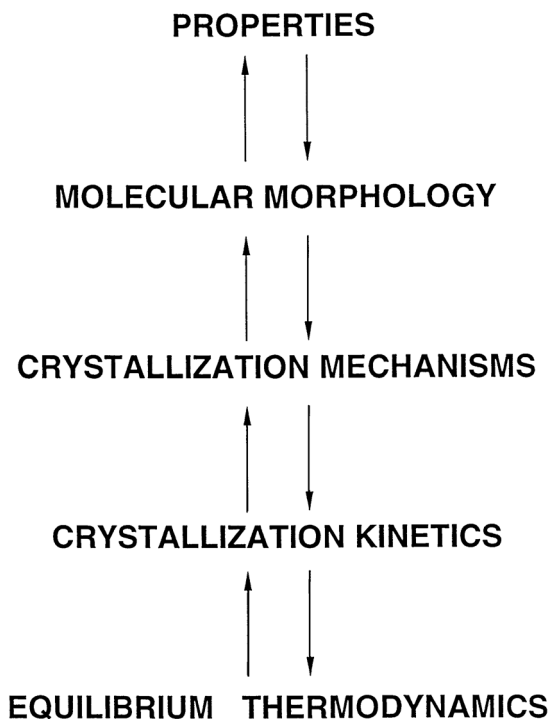


Fig. 4.1. A perspective on the crystalline state, representing problem areas in the study of crystalline polymers. (Reproduced with permission from [3], copyright 1979, *Faraday Discussions of the Chemical Society*.)

This chapter is not meant to be a review of current research activity in this field. Serious efforts have been made, however, to keep the subject matter timely. We shall be primarily concerned with developing the basic principles that are involved. In order to accomplish this objective, the reader must have a level of understanding equivalent to that gained from an introductory first course in polymer chemistry or physics. Knowledge of the basics of molecular constitution and chain structure is essential for understanding the discussion that follows. The level of the chapter is intended to be between that of an introductory polymer-science course and current research in the field.

The study of crystalline polymers closely parallels the development of polymer science itself [2]. In placing the subject in proper perspective, it needs to be understood that there are certain areas that are well developed and interpretations that have been accepted for a long time. There are other areas that have been under intensive study and controversy has existed regarding certain aspects of the problems [3]. However, difficulties in interpretation that existed in these cases have gradually been resolved and a set of unifying concepts is emerging. The guiding principles

needed to understand the thermodynamics of fusion and many aspects of the crystallization kinetics are firmly established both by theory and by experiment. Modern emphasis has, therefore, been directed toward the understanding of the structure and morphology of crystalline polymers and their influence on properties. Since the thermodynamics and kinetics of crystallization are extensively documented in the literature, we shall be content to review these areas briefly here and to establish their salient features and note the problems that still need to be resolved. A major emphasis will be on understanding the structure–property relations. The basic principles that evolve will then be demonstrated with selected sets of examples. Once the principles are understood, they can be applied to the resolution of a variety of problems. We begin by considering the structure of individual polymer molecules.

Long-chain molecules can exist in either one of two states. These are characterized by the conformation of the individual molecular chains and their organization relative to one another. The liquid state is the state of molecular disorder. In this state, the individual chains adopt a statistical conformation, commonly called the random coil. The centers of mass of the molecules are arranged randomly relative to one another in this situation. All the thermodynamic and structural properties observed in this state are those which are commonly associated with a liquid, although usually a very viscous one. This state exhibits the characteristic long-range elasticity. The liquid state in polymers is also commonly called the amorphous state.

The crystalline or ordered state is one that is characterized by three-dimensional order over at least a portion of the chains. The ordered conformation may be fully extended or may represent one of many known helical structures. Irrespective of the details of the unit cell and the ordered chain structure, the molecules are organized into a regular three-dimensional array. The chain axes are usually aligned parallel to one another and the substituent groups are brought into regular register. Such ordered systems diffract X-rays in the conventional manner and display all the properties characteristic of the crystalline state. It can be stated as a general principle that all chain molecules that have a reasonable structural regularity will crystallize, under suitable conditions. However, it is important to note that the crystallization is rarely, if ever, complete. Therefore, the crystalline state in polymers is more properly thought of as being semicrystalline, or partially crystalline.

In contrast to the liquid state, the crystalline state is relatively inelastic and rigid. For example, there is a difference of about five orders of magnitude between the moduli of elasticity in the two states. There are also major differences in other properties, including spectral and thermodynamic ones. Moreover, within the crystalline state it is possible to change properties by control of structure. This ability to control properties turns out to be of major concern in the application and end use of polymeric systems.

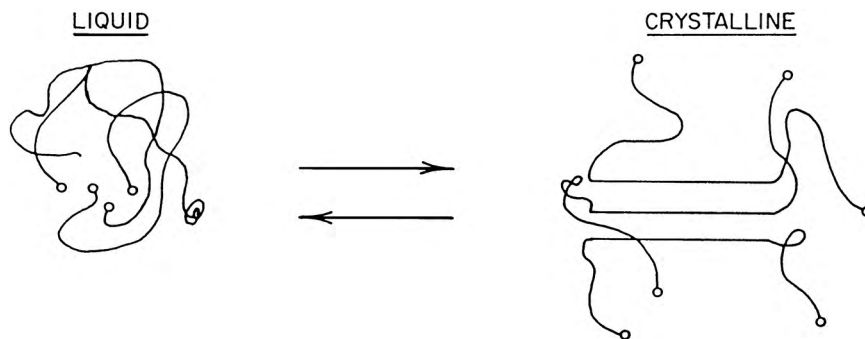


Fig. 4.2. A schematic diagram illustrating conformational differences of chain molecules in the liquid and crystalline states. A straight line represents an ordered conformation. Details of interfacial structure are not being considered at this point.

The conformational difference of the molecules in the two states is schematically illustrated in Fig. 4.2. In the crystalline state, the bonds adopt a set of successive preferred orientations; participation of the complete molecules in the ordering process is not required. In the liquid state the bond orientations are such that the chain adopts a statistical conformation.

Our primary interest is in learning how the properties of the crystalline state are influenced by the chemical nature of the repeating unit, the crystallite structure above the level of the unit cell, and the organization of crystallites. There are many properties of interest. These range from the thermodynamic ones to the physical ones and include spectroscopic characteristics, mechanical behavior, and problems of ultimate strength.

4.2 The thermodynamics of crystallization–melting of homopolymers

We initiate our discussion of the crystalline state by outlining the basic foundations of the subject. From the point of view of formal thermodynamics, it has been established that the transformation from one state to another can be properly treated as a first-order phase transition in the classical sense. The transformation is very similar to the fusion of low molecular weight substances. A typical example of the melting of homopolymers is given in Fig. 4.3, for fractionated and unfractionated samples of linear polyethylene. When melting is carried out carefully, the process is relatively sharp and a well-defined melting temperature is clearly discerned. It is easily seen in Fig. 4.3 that, for the molecular weight fraction, fusion takes place over a very narrow temperature interval. From the specific-volume–temperature plot the disappearance of the last traces of crystallinity, which defines the melting temperature, can be clearly observed in both examples. The transition,

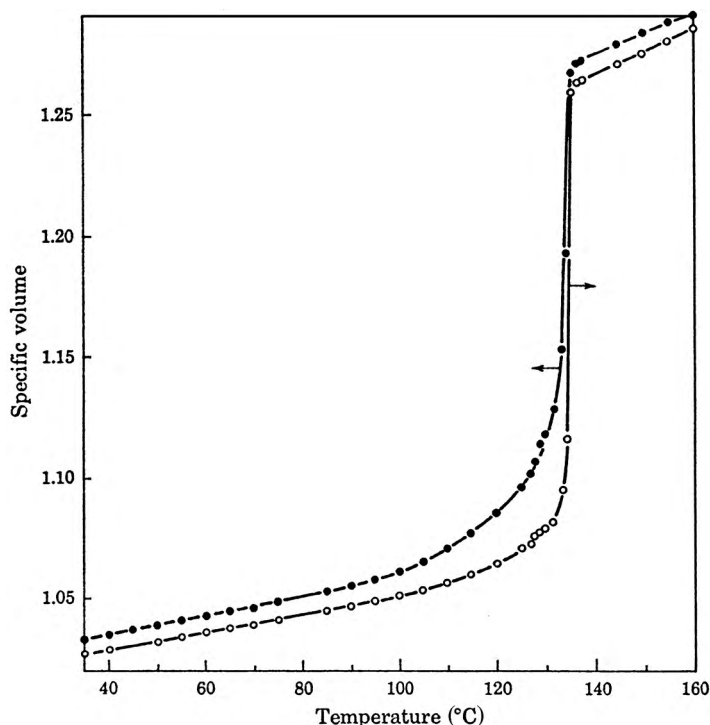


Fig. 4.3. Specific-volume–temperature relations for the melting of linear polyethylene. Key: ●, unfractionated polymer; ○, fraction $M = 32\,000$. (Reproduced from [4], copyright 1961, American Chemical Society.)

although it is a diffuse one, can still be classified as a first-order phase transition [5, 6].

Normal alkanes, as well as oligimers of repeating units of other types, can form molecular crystals at sufficiently low temperatures since all the molecules are of precisely the same length. In this case, as is illustrated in Fig. 4.4(a), the chain ends are paired one with the other, so that well-defined planes delineating the end groups are developed. In contrast, for polymers, no matter how well the system is fractionated, the individual molecules will not be of exactly the same length. Consequently, for polymers the necessary condition for the formation of molecular crystals cannot be fulfilled. The equilibrium state for this case has been established by statistical-mechanical analysis [6], as well as by experiment [7]. The equilibrium case is that in which the end portions of the molecules are disordered, or unpeeled, and can be schematically represented by the model given in Fig. 4.4(b). Thus, a chain of x repeating units is characterized by an equilibrium crystallite length ζ_c , with $x - \zeta_c$ end-repeating units being disordered. The melting temperature for such

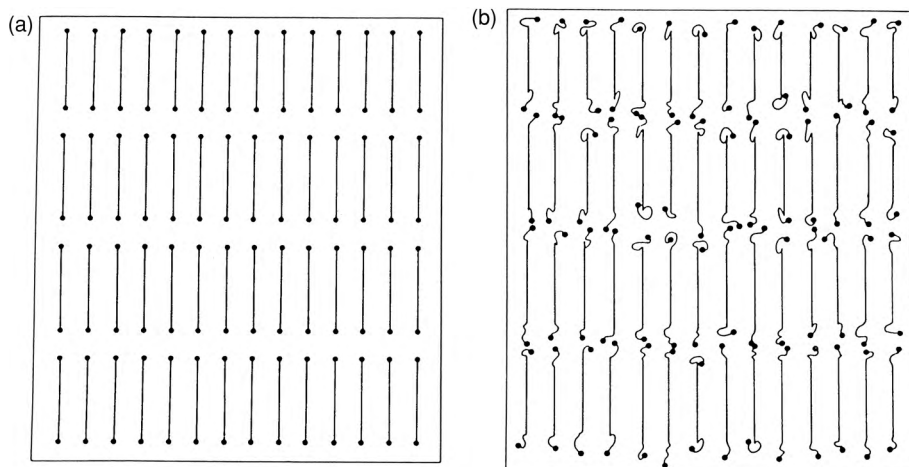


Fig. 4.4. A schematic representation of crystallites of extended chain crystals: (a) for n-alkanes with end groups paired; and (b) for polymer fractions with end sequences in disordered conformation.

a system, i.e its dependence on chain length, can be expressed as [6]

$$1/T_{\text{me}} - 1/T_{\text{m}}^0 = (R/\Delta H_{\text{u}})\{(1/x) + [1/(x - \zeta_{\text{e}} + 1)]\} \quad (4.1)$$

$$2\sigma_{\text{e}} = RT_{\text{me}}\{[\zeta_{\text{e}}/(x - \zeta_{\text{e}} + 1)] + \ln[(x - \zeta_{\text{e}} + 1)/x]\} \quad (4.2)$$

Here T_{m}^0 is the equilibrium melting temperature for an infinite molecular weight chain and T_{me} is the corresponding temperature for a fraction containing x repeating units. The effective interfacial free energy associated with the basal plane of an equilibrium crystallite of length ζ_{e} is σ_{e} and ΔH_{u} is the enthalpy of fusion per repeating unit. At this point it should be noted that, in the study of crystalline polymers, three different interfacial free energies, that are characteristic of the basal plane, are involved. One, σ_{e} , is for the equilibrium extended-chain crystallite of Eq. (4.2); σ_{ec} represents that for the mature, but non-equilibrium, crystallite, whereas σ_{en} is the interfacial free energy involved in forming a nucleus. There is no basis on which these quantities can be identified with one another.

For a polydisperse system that possesses a most probable chain-length distribution, the melting temperature molecular weight relation can be expressed as

$$1/T_{\text{m}}^* - 1/T_{\text{m}}^0 = (R/\Delta H_{\text{u}})(2/\bar{x}_{\text{n}}) \quad (4.3)$$

where $\bar{x}_{\text{n}}$ is the number-average degree of polymerization. For this molecular weight distribution, the quantity $2/\bar{x}_{\text{n}}$ represents the mole fraction of noncrystallizing units. Equation (4.3) results from the stipulation of the conditions for phase equilibrium. It is specific to, and valid only for, polymers that have a most

probable molecular weight distribution. The melting-temperature relation for each polydisperse system has to be treated individually.

The application of formal phase-equilibrium thermodynamics leads to an expression for the depression of the melting temperature by low molecular weight diluent, when it is excluded from the crystalline phase. This expression is given by [6]

$$1/T_m^* - 1/T_m^0 = (R/\Delta H_u)(V_u/V_1)(v_1 - \chi_1 v_1^2) \quad (4.4)$$

Here T_m^0 is the equilibrium melting temperature of the pure system, T_m^* is the melting temperature corresponding to a volume fraction of diluent v_1 , V_u/V_1 is the ratio of the molar volume of the chain repeating unit to that of the diluent, χ_1 is the polymer–diluent thermodynamic interaction parameter, and ΔH_u is the enthalpy of fusion per chain repeating unit of the completely crystalline polymer. ΔH_u is characteristic of the chain repeating unit and does not depend on the specific nature of the crystalline state (i.e. the level of crystallinity). Equation (4.4) is simply the adaptation to polymers of the classical freezing point depression expression when the crystalline phase remains pure. Strictly speaking, use of Eq. (4.4) requires that the crystallite thickness and interfacial free energy be independent of concentration. Results from comparable solubility studies of the same sample as a function of concentration have established the validity of Eq. (4.4) [8]. Results from melting point–composition studies with extended-chain crystallites have also confirmed Eq. (4.4) [9, 10]. Since χ_1 depends both on composition and on temperature, it is not advisable to utilize melting point depression to determine the value of this interaction parameter. In the few exceptions noted, in which the diluent enters the crystal lattice, Eq. (4.4) is obviously no longer valid. Equation (4.4) has received widespread experimental verification for many different polymers [11]. The same value of ΔH_u is obtained for a given polymer when it is studied with a series of different diluents. Thus, by use of Eq. (4.4) one can obtain ΔH_u for a given polymer. By combining this with the equilibrium melting temperature, ΔS_u , the entropy of fusion per repeating unit, is obtained. These thermodynamic parameters, for a selected set of polymers, are given in Table 4.1.

Table 4.1 is not meant to be exhaustive. More extensive tables can be found in [11, 12]. Values of ΔH_u can be found also from measurements of the dependence of the melting temperature on applied hydrostatic pressure and by applying the Clapeyron equation [11, 12]. Comparable results are obtained by using these two methods. However, the examples have been selected to illustrate typical key situations.

The data in Table 4.1 illustrate the guiding structural principles that determine the melting temperatures of polymers. These examples make clear that there is no correlation between the melting temperature and the enthalpy of fusion, as is found for many monomeric systems. The ΔH_u values of polymers generally fall into two

Table 4.1. Thermodynamic quantities (ΔH_u , the enthalpy of fusion per repeating unit; and ΔS_u , the entropy of fusion per repeating unit) characterizing the fusion of selected polymers

Polymer	T_m^0 (°C) ^a	ΔH_u (cal mol ⁻¹) ^b	ΔS_u (cal °C ⁻¹ mol ⁻¹)
Poly(ethylene)	145.5±1	990	2.36
Poly(propylene)	208	2100	4.37
Poly(<i>cis</i> -1,4-isoprene)	35.5	1050	3.46
Poly(<i>trans</i> -1,4-isoprene)	87	3040	8.75
Poly(<i>trans</i> -1,4-chloroprene)	107	2000	5.08
Poly(styrene), isotactic	243	2075	4.02
Poly(oxymethylene)	200	1676	3.55
Poly(oxyethylene)	80	2080	5.91
Poly(2,6-dimethoxy-1,4-phenylene oxide)	287	761	1.36
Poly(decamethylene adipate)	79.5	10 200	29
Poly(decamethylene sebacate)	80	12 000	34
Poly(ethylene terephthalate)	282	5600	10.2
Poly(decamethylene terephthalate)	138	11 000	27
Poly(tetramethylene terephthalate)	230	7600	15.1
Poly(hexamethylene adipamide)	269	10 365 ^c	45.8
Poly(decamethylene sebacamide)	216	8300	17
Poly(decamethylene azelamide)	214	8800	27
Poly(tetrafluoroethylene)	346	1220 ^c	24.4
Poly(dimethyl siloxane)	-38	650	2.76
Poly(tetramethyl- <i>p</i> -silphenylene siloxane)	160	2700	6.20
Poly(ether ether ketone)	338	11 319 ^c	18.5
Cellulose trinitrate	>700	900–1500	1.50
Cellulose tributyrate	207	8800	8.1

^a Best estimates of the equilibrium melting temperature.

^b ΔH_u determined from the depression of the melting temperature by monomeric diluents unless indicated otherwise.

^c ΔH_u determined by means of the Clapeyron equation.

classes. They are either of the order of just a few thousand calories per mole or about 10 000 cal mol⁻¹. For the examples given here, and as is also found more generally, many high melting point polymers possess low heats of fusion while conversely many low melting point polymers possess high values for the heat of fusion. Consequently, the entropy of fusion is a key factor in establishing the location of the melting temperature. A striking causal relation between the entropy of fusion and the chain conformation in the completely molten state can be developed. Hence, polymers commonly designated as elastomers, such as poly(dimethyl siloxane) and poly(*cis*-1,4-isoprene) have relatively low melting temperatures and high entropies of fusion, which reflect the compacted, highly flexible nature of the chain.

At the other extreme the so-called engineering plastics such as poly(aryl ether ether ketone), poly(tetrafluoroethylene), and poly(2,6-dimethoxy-1,4-phenylene oxide) have high melting temperatures and more extended chain structures with correspondingly lower entropies of fusion. Cellulose derivatives are another case in point. As a class of polymers, they are characterized by very high melting points and low heats of fusion. The low entropy of fusion must result from the highly extended nature of the chain.

The introduction of ring structures into a linear chain substantially raises the melting temperature relative to that of the aliphatic chain. This would be expected because of the decrease in conformational entropy of the melt that results. Striking examples of this phenomenon are found on comparing the melting temperatures of the aliphatic and aromatic polyesters and polyamides.

Another example of the influence of the entropy of fusion is found on comparing aliphatic polyesters and polyamides. For repeating units of corresponding type the melting temperatures of the polyamides are well known to be substantially higher than those of the corresponding polyesters. Despite the hydrogen-bonding capacity of the polyamides, there is no substantive difference between the enthalpies of fusion of the two types of chains. Hence, the difference of 150–200 °C in melting temperature must result from differences in the entropy of fusion.

From the few examples that have been described, it should be apparent that, as a general rule, the chain structure influences the melting temperature through its conformational properties and thus the entropy of fusion. In fact, by utilizing rotational isomeric state theory, a quantitative correlation between the entropies of fusion at constant volume and the chain conformations of the many polymers can be made [11, 13].

4.3 Melting of copolymers

By applying classical phase-equilibrium theory, the melting temperatures of copolymers relative to those of the parent homopolymers can be derived. It is crucial to understand that, from the point of view of crystallization behavior, in addition to different chemical repeating units, structural irregularities such as stereo-irregularity, branch points, head-to-head structures, and geometric irregularities all behave as copolymeric units when they are incorporated into the chain. In treating the melting-point–composition relations for copolymers, a problem similar to that with binary mixtures of monomers is encountered. It has to be decided *a priori* whether the crystalline state remains pure, i.e. whether the co-unit enters the lattice. If the co-unit enters the lattice, then it has to be further specified whether this situation represents the equilibrium state or non-equilibrium defects are involved. Moreover, the specific structure in the crystalline state has to be delineated. Detailed calculations have

been performed for the restrictive, but common, situation in which the co-units or structural irregularities do not participate in the crystallization, i.e. the crystalline phase remains pure. For this case, one obtains [6, 14]

$$1/T_m - 1/T_m^0 = (R/\Delta H_u) \ln p \quad (4.5)$$

In this equation, the quantity p represents the sequence-propagation probability, i.e. the probability that a crystallizable unit in the copolymer is succeeded by another such unit. T_m^0 and ΔH_u are as defined already while T_m is the equilibrium melting temperature of the copolymer. We thus have the interesting expectation that the melting temperature of a copolymer does not depend directly on its composition, but rather depends on the nature of its sequence distribution. This unique result is a consequence of the chain-like character of polymers. Emphasis must then be placed on the nature of the sequence distribution of the copolymer, rather than on its nominal composition. This requirement also applies to the case in which the co-units enter the lattice. In this case the sequence distribution needs to be specified for each phase. It has been shown that Eq. (4.5) represents the ideal case [15]. Only the number of ways in which the sequences can be arranged along the chain has been taken into account. Consequently, only an ideal entropy contribution is being considered. There is an analogy here to Raoult's law and ideal solution theory. The sequence distribution in the liquid, or molten, state can be obtained from the reactivity ratios.

Three major types of sequence distributions can be discussed in terms of X_A , the mole fraction of crystallizable units. For an ordered, or block, copolymer $p \gg X_A$ and in many cases p approaches unity. For such copolymers, there will at most be only a slight depression of the melting temperature from that of the corresponding homopolymer. On the other hand, for an alternating copolymer $p \ll X_A$ and there will be a rather drastic reduction in the melting temperature. For a random copolymer $p = X_A$, so Eq. (4.5) becomes

$$1/T_m - 1/T_m^0 = (R/\Delta H_u) \ln X_A \quad (4.6)$$

These relations between p and X_A are based on the assumptions that the same crystal structure of the homopolymer is involved, only one type of unit enters the crystalline phase, and the melt is homogeneous. These conditions are not always fulfilled. Moreover, it must be emphasized that Eqs. (4.5) and (4.6) represent the ideal situation. If they are not fulfilled, it does not necessarily mean that the crystalline phase is not pure. Rather, there is the strong possibility of non-ideal terms contributing to the melting-point depression.

From a theoretical point of view, therefore, copolymers that have exactly the same composition could have drastically different melting temperatures, depending on the sequence distribution of the co-units. This expectation is indeed fulfilled. An

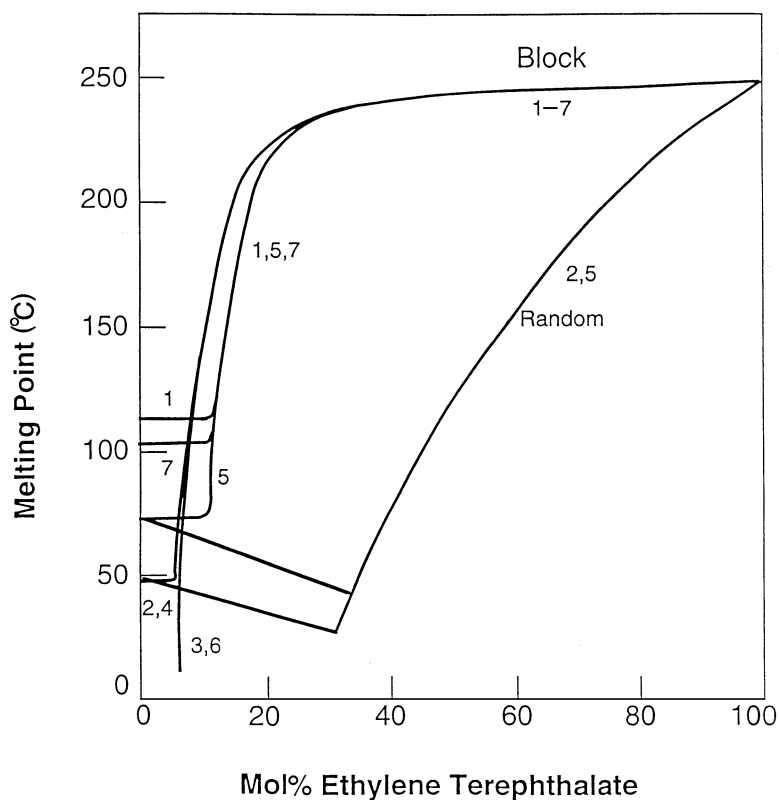


Fig. 4.5. Melting-temperature-composition relations for block copolymers of poly(ethylene terephthalate) with (1) ethylene succinate, (2) ethylene adipate, (3) diethylene adipate, (4) ethylene azelate, (5) ethylene sebacate, (6) ethylene phthalate, and (7) ethylene isophthalate. For comparative purposes data for random copolymers with ethylene adipate and with ethylene sebacate are also given. (Reproduced with permission from [16], copyright 1968, *Polymer Engineering and Science*.)

example is given in Fig. 4.5, where the melting-temperature-composition relations for block and random copolymers of poly(ethylene terephthalate), with various co-units, are given [16].

The differences between the melting-temperature relations for the two types of copolymers are quite marked and are in agreement with theoretical expectation. As would be expected for the block copolymers, the melting points remain constant over a large range of co-unit content and are also independent of the chemical nature of the co-unit. Only when the co-unit contents become extremely large does the melting point decrease, which is consistent with the crystallization of the added species. The results that are shown in Fig. 4.5 are typical of all types of block copolymers irrespective of their chemical constitution. Taking the data in Fig. 4.5

as an example, melting-point differences as great as 200 °C can be observed for the same nominal composition, depending on whether the two types of units are arranged randomly or in blocks.

The melting temperatures of random copolymers, when the crystalline phase remain pure, should depend only on the composition, not on the chemical nature of the second component. These conditions are also fulfilled experimentally, as illustrated in Fig. 4.6. Here some typical examples of melting temperature–composition relations for a set of random copolyesters and copolyamides are given. As is predicted by theory, there is a monotonic decrease in the melting temperature with

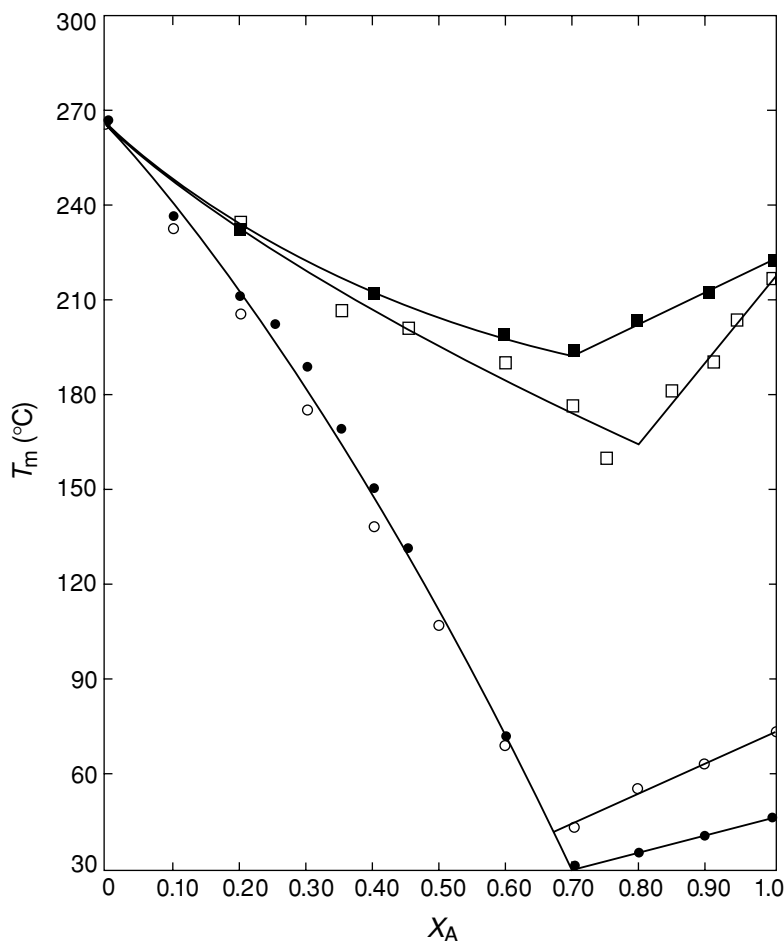


Fig. 4.6. A compilation of melting temperature–composition relations for typical random copolyesters and copolyamides. Key: ●, poly(ethylene terephthalate/adipate); ○, poly(ethylene terephthalate/sebacate); ■, poly(hexamethylene adipamide/sebacamide); and □, poly(hexamethylene adipamide/caproamide).

increasing concentration of the co-unit, independently of its chemical nature. The equivalence of a eutectic temperature is reached at a composition commensurate with the melting temperature of each component.

On focusing attention on the quantitative aspects of the melting temperature relation for random copolymers, it is found that, although the functional form of Eq. (4.6) is usually followed, the value obtained for ΔH_u is significantly less than that determined by other methods. The reason is that, even if the condition of ideality is fulfilled, the melting of very long sequences is required. Such sequences exist in low concentrations and their melting temperatures are extremely difficult to detect. Hence, the melting temperatures that are recorded will be lower than required. There are only very few examples in which the melting point depression of random-type copolymers yields the correct value of ΔH_u [11].

Although homopolymers and block copolymers melt relatively sharply, the fusion of random copolymers is broad. There is a theoretical basis for this behavior [6, 14]. The diffuse melting is a consequence of a greatly exaggerated impurity effect caused by sequence-length requirements. As fusion progresses, the shorter crystalline sequences melt at lower temperatures, shifting the equilibrium and thus broadening the melting range. Thus, both the crystallite size in the chain direction and the sequence distribution and free energy in the residual melt vary with the temperature. This phenomenon is illustrated in Figs. 4.7–4.9 for various types of random copolymers. Typical examples of the fusion of random type copolymers, in which the crystalline phase is pure and the co-units are chemically different, are found in ethylene-1-alkene copolymers. In Fig. 4.7 the fusion of such copolymers is given in terms of a plot of the specific volume against temperature [17]. These particular copolymers were prepared by the copolymerization of mixtures of diazomethane and the corresponding higher diazoalkane. Special measures were adopted to assure that a random distribution of the comonomers occurred. Crystallization was allowed to occur while the temperature of the molten sample was reduced gradually over many days. Very slow heating rates were utilized following the crystallization. The copolymer composition indicated for each curve is presented as the ratio CHR/100 CH₂. Typically sigmoidal-shaped fusion curves are observed, as is expected on a theoretical basis for this type of copolymer. The transformation occurs over a wide temperature interval compared with that for homopolymers. The melting range becomes broader as the concentration of noncrystallizable units is increased. Small amounts of crystallinity persist at temperatures just below T_m . Examination of the data in the vicinity of the melting temperature gives no direct evidence of a discontinuity. Although a discontinuity is predicted, its magnitude is beyond the reach of the usual experimental observation. The temperature at which a measurable departure from the liquid vanishes is taken to be the melting temperature.

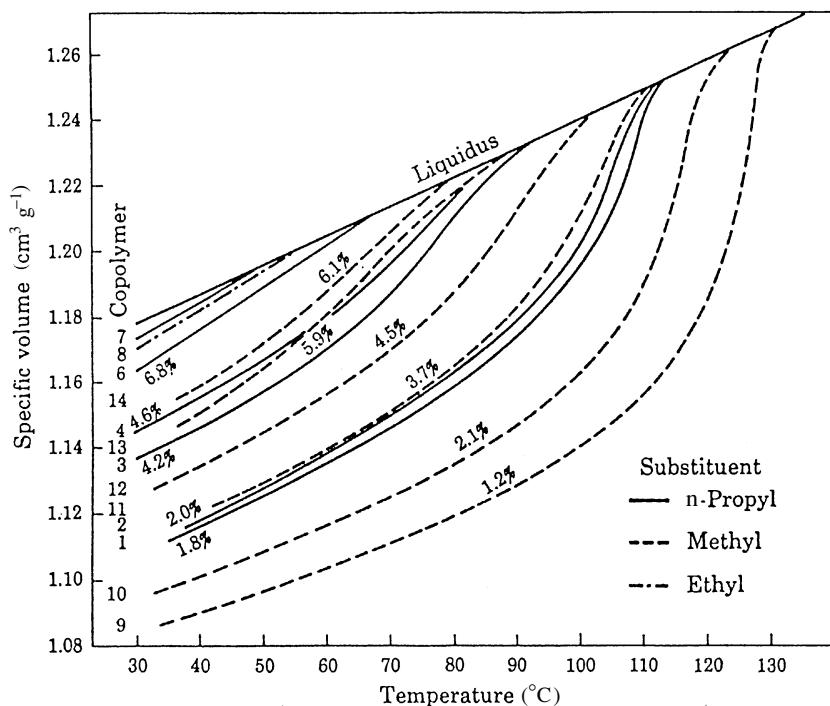


Fig. 4.7. Melting curves for polymethylene copolymers containing the indicated substituents as co-ingredients. Compositions of copolymers are indicated as percentages of co-ingredient present. Reproduced from [17], copyright 1963 with permission from Elsevier.

It is not necessary to have chemically different co-units incorporated into the chain in order to observe copolymeric behavior, in terms of crystallization. Any type of structural irregularity in the chain would serve the same purpose as long as it does not co-crystallize. Typical examples of such behavior are stereo-irregularities, regional defects, geometric isomers, branch points, and intermolecular cross-links. This type of copolymer melting is illustrated in Figs. 4.8 [18] and 4.9 [19] for sets of poly(butadienes) and isotactic poly(propylenes), respectively. The poly(butadienes) contain various amounts of the 1,4-*trans* crystallizing unit. As the content of the crystallization component decreases, the fusion occurs over a broader temperature range (Fig. 4.8).

The process of fusion eventually becomes very difficult to detect, as is evidenced by curve C. However, it is important to establish the existence of even small amounts of crystallinity because of its influence on mechanical and physical properties. This type of melting behavior typifies the fusion of random copolymers. An interesting question is that of whether there is any limit on the concentration of the crystallizing unit that would prevent the development of crystallinity in a random copolymer.

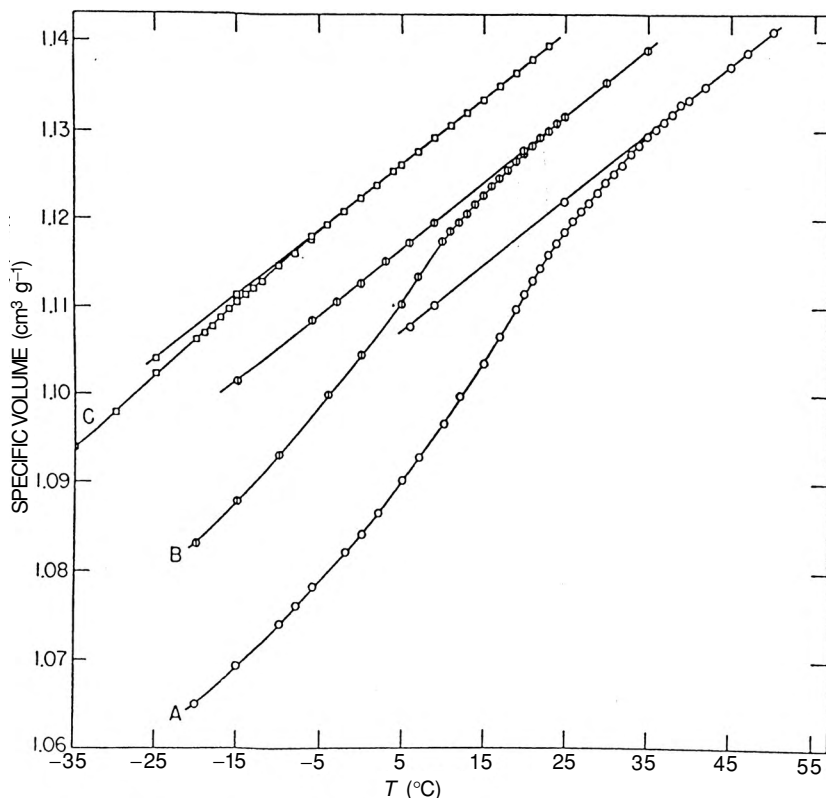


Fig. 4.8. Fusion of random copolymers. A plot of specific volume against temperature for polybutadienes of various mole fractions, X_A , of crystallizing 1,4-*trans* units. Curve A, $X_A = 0.81$; curve B, $X_A = 0.73$; and curve C, $X_A = 0.64$. Curves B and C are arbitrarily displaced along the ordinate. (Reproduced with permission from [18], copyright 1956, *Journal of Polymer Science*.)

Graessley and co-workers [20] were able to crystallize a poly(butadiene) sample that contained only 56 mol % of the 1,4-*trans* crystallizing unit, whose level of crystallinity ranged from 2% to 5%, depending on the molecular weight.

The melting of stereo-irregular poly(propylenes), illustrated in Fig. 4.9, follows a similar pattern. The melting temperature and level of crystallinity decrease as the crystallizing isotactic content decreases. Concomitantly, the fusion process becomes very much broader. It is often difficult to recognize the crystallinity and the fusion of copolymers that have high contents of structural irregularities.

Another important type of chain irregularity is branching, since the branch points are structurally different from the other repeating units in the chain. Long-chain branches are not usually of uniform length but are most often sufficiently long that they also can participate in the crystallization. Long-chain branched polyethylene,

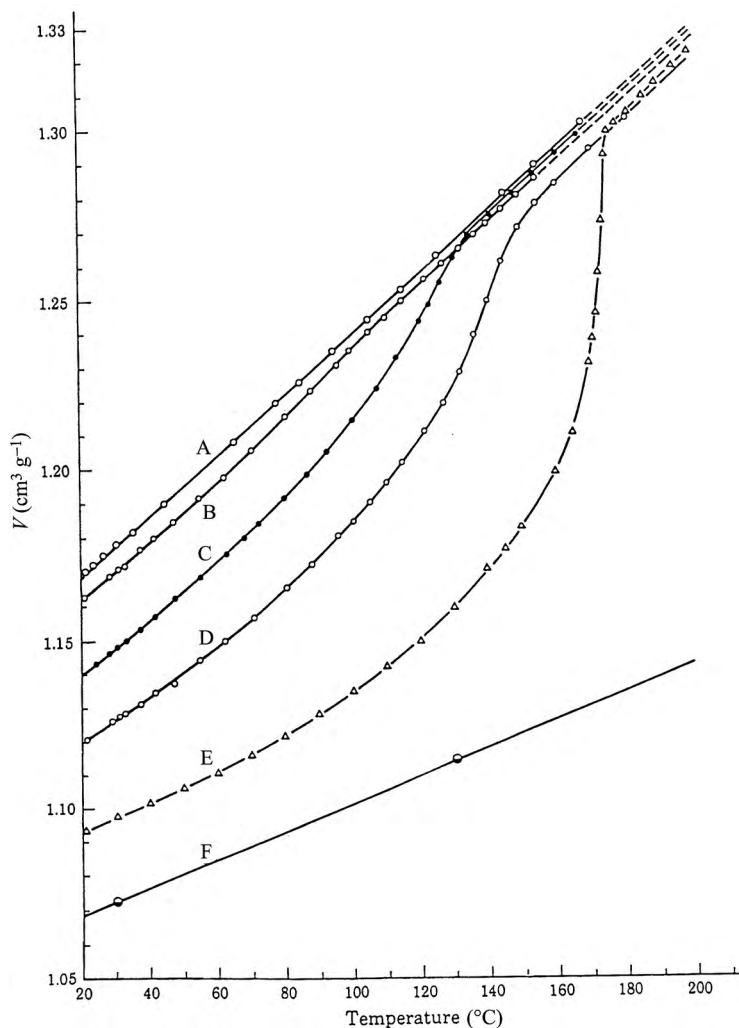


Fig. 4.9. Fusion of random copolymers. The melting of polypropylenes of various stereoregularities. A plot of specific volume as a function of temperature. Curve A, ether extract, quenched; curve B, pentane extract, annealed; curve C, hexane fraction annealed; curve D, trimethylpentane fraction annealed; curve E, experimental whole polymer annealed; and curve F, calculated for pure crystalline polymer. (Reproduced with permission from [19], copyright 1960, *Journal of Polymer Science*.)

commonly termed low-density polyethylene, typifies this class of polymer. An example of the effect of branching on the crystallization behavior is shown in Fig. 4.10 for two polyethylene polymers. Curve A is for the linear polymer; curve B is for the branched polymer. The melting temperature of the branched polymer is significantly less, by about 20 °C, than that of its linear counterpart. In addition, as

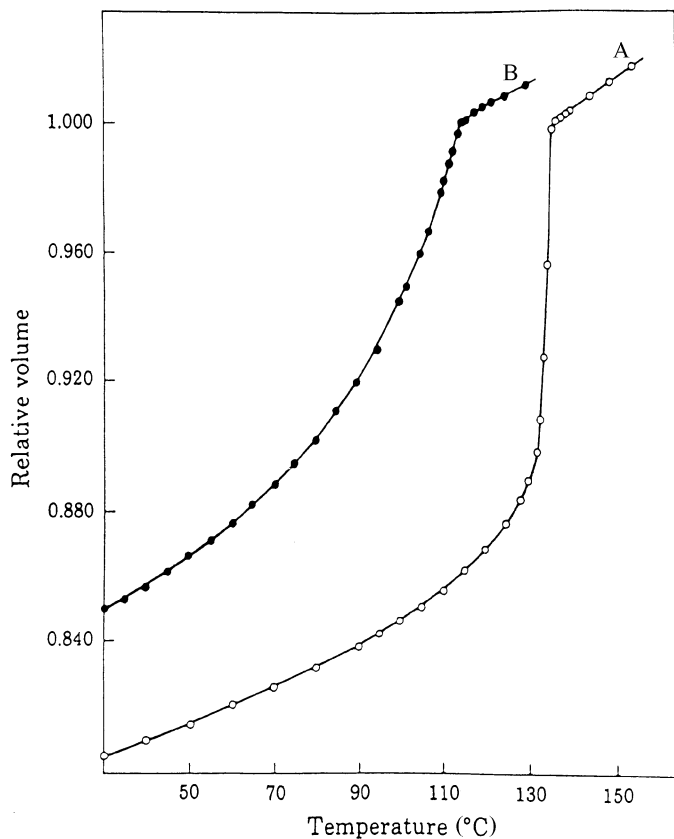


Fig. 4.10. The effect of long-chain branching on the melting process. Plots of relative volume against temperature for linear polyethylene (curve A) and branched polyethylene (curve B). (Reproduced from [21], copyright 1953, American Chemical Society.)

would be expected, its melting range is very much broader. For the linear polymer 70% of the melting takes place over an interval of only 3–4 °C. In contrast, the fusion of the branched polymer takes place over the whole of the temperature range studied. Thus, we have a striking example of two almost essentially chemically identical polymers that have markedly different crystallization behaviors. Qualitatively similar fusion behavior has also been observed for long-chain-branched poly(ethylene terephthalate) [22] and poly(phenylene sulfide) [23].

With the establishment of some of the unique features of the fusion of random copolymers, their melting temperature–composition relations can now be examined. Copolymers formed by condensation polymerization are usually characterized by a sequence-propagation probability p that is independent of copolymer composition and the extent of conversion. For such systems the quantity p can be

equated to the mole fraction of crystallizable units, and is independent of the nature of the co-unit.

The composition used in Fig. 4.6 is based on the liquidus. Therefore, the shapes of the curves do not give any direct information about the composition of the crystalline phase. In the example shown in Fig. 4.6, the fact that the same melting temperature–composition relation is obtained with different comonomers gives strong evidence that the crystalline phase remains pure. However, this conclusion is not necessarily correct without independent confirmation. Other polymers, such as poly(tetrafluoroethylene) and poly(methylene oxide), behave in a similar manner with the addition of various species [24, 25]. Although some copolymers give the same melting temperature–composition relation for a given set of comonomers, the addition of a particular co-unit can alter this relation [26–29]. Usually in this case the melting temperatures for comparable compositions are greater. The conclusion usually drawn is that such comonomers enter the crystal lattice as the parameter p increases. However, the possibility of there being a contribution by non-ideality to Eq. (4.6) cannot be ignored.

Some of the principles involved, as well as the problems encountered, are found in the melting of random-type olefin copolymers. Figure 4.11 is a compilation of melting temperature relations for rapidly crystallized copolymers with a set of 1-alkenes and norbornene as comonomers [30]. The plot clearly indicates that the melting temperature is independent of co-unit type under the rapid crystallization conditions that were employed. The observed melting temperatures of copolymers are known to depend on chain length [31], so the results shown have been limited to molecular weights of about 90 000. The melting temperatures of ethylene copolymer with bulkier side-group comonomers such as 1-decene, 4-methyl-1-pentene, cyclopentadiene, and dicyclopentadiene follow the curve of Fig. 4.11 [32]. Results from studies with ethylene–octene copolymers indicate that the curve in Fig. 4.11 will continue to lower melting temperatures with higher comonomer content.

The melting temperatures are sensitive to the quantity p , particularly at low comonomer composition. For example, the melting temperatures of two ethylene–butene random-type copolymers prepared by using similar catalysts differ by about 5 °C for 0.5 mol % of side groups and the difference increases to 10 °C with about 3 mol % of side groups [31]. These differences in melting temperature for chemically identical copolymers at the same composition can be attributed to differences in their respective sequence-propagation probabilities.

According to equilibrium theory the melting temperature–composition relations of ideal random-type copolymers should obey Eq. (4.6). The functional form of Eq. (4.6) is usually obeyed even when directly observed non-equilibrium melting temperatures are used. However, the ΔH_u values that are deduced are usually much

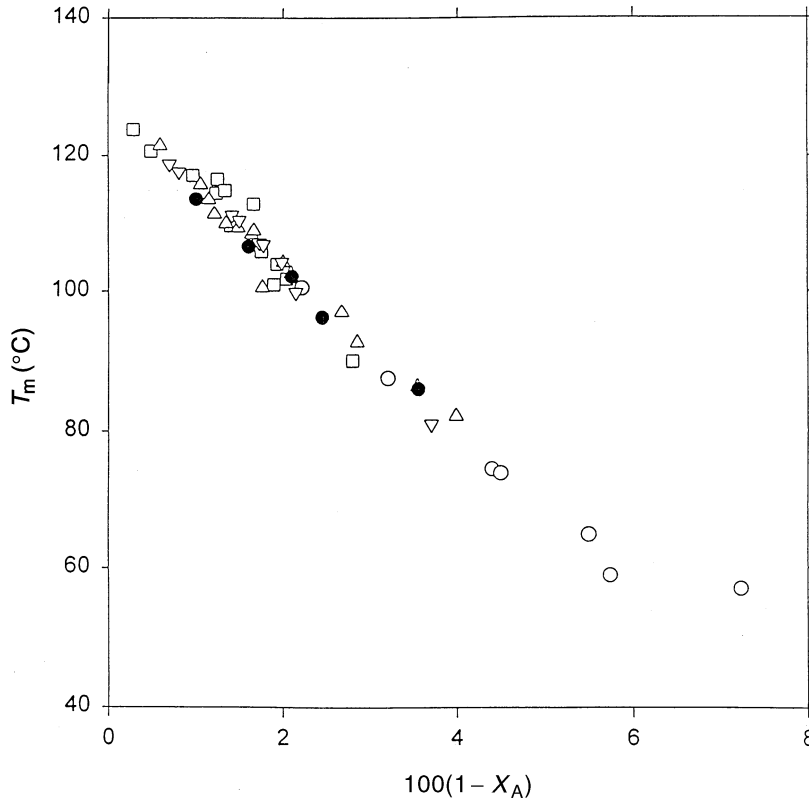


Fig. 4.11. A plot of observed melting temperature, T_m , against the mole percentage of structural irregularities in the polyethylene chain. ○, HPBD; □, ethylene-butene; ▽, ethylene-octene; Δ, ethylene-hexene; ●, ethylene-norbornene. $M \simeq 90\,000$. HPBD stands for hydrogenated poly(butadiene). Reproduced from [30], copyright 2000 with permission from Elsevier.

less than those found by other methods [11]. The reason for this discrepancy is the extreme difficulty of approaching equilibrium conditions with random copolymers. Furthermore, as was pointed out earlier, Eq. (4.6) represents an ideal system. It also should be noted when one is applying Eq. (4.6) to stereo-irregular polymers that the concentration of chain defects is appropriate, rather than that of pentads.

When there is a strong tendency for the comonomeric units to alternate, $p \ll X_A$, a large depression of the melting temperature is predicted by Eq. (4.5). However, this expectation is based on the assumption that only the A units crystallize and the crystal structure that corresponds to that of the homopolymer is formed over the complete composition range. As we shall learn, this condition is difficult to fulfill. Usually a new crystal structure, involving both the A and the B units, forms.

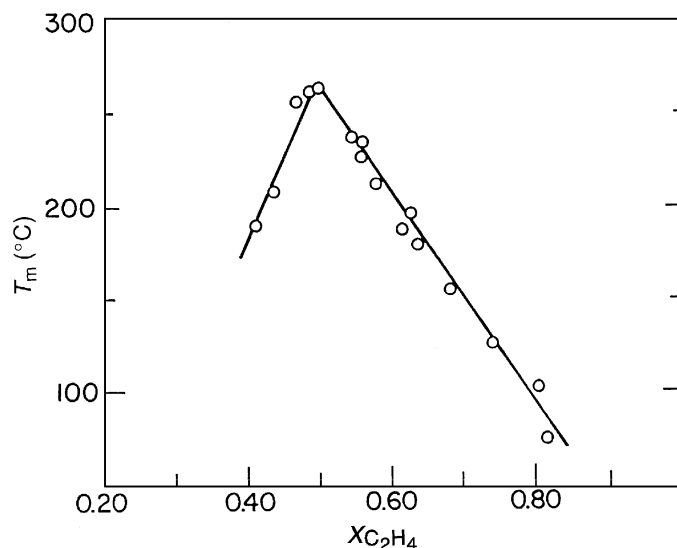


Fig. 4.12. A plot of melting temperature against mole fraction of ethylene units for alternating copolymers of ethylene/chlorotrifluoroethylene. Reproduced from [33], copyright 1967 with permission from Elsevier.

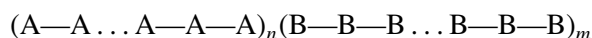
An example of the melting-temperature–composition relation for the alternating copolymer of ethylene and chlorotrifluoroethylene is given in Fig. 4.12 [33]. A maximum in the melting temperature is observed for an equimolar ratio of the two components. This temperature, 264 °C, corresponds to the melting of a sequence of $C_2H_4C_3F_3Cl$ repeating units and is much higher than that for the corresponding homopolymers. The melting temperature being above or below that for the equimolar concentration represents incomplete alternation. A new crystal structure is formed with thermodynamic parameters that differ from those of either of the pure species. The plot in Fig. 4.12 is obviously quite different from that expected for a random copolymer.

A classic example of an alternating-type copolymer is found in the ethylene–carbon monoxide copolymer [34–39]. This copolymer is polymorphic. The α form is stable at low temperature and transforms to the β form at 140 °C. The melting temperature of this form is about 255 °C. This temperature is much greater than that for linear polyethylene or any of its random copolymers. This again is the result of a crystal structure different from that of polyethylene that accompanies the high extent of alternation.

Alternating copolymers can be formed with many pairs, some quite diverse in nature. These include carbon monoxide with propylene, 1-butene, 1-hexene, norbornene, and styrene [38], tetrafluoroethylene with ethylene, propylene, and isobutylene [40–42], and ethylene with propylene [43] and 1-octene [44, 45].

Some general features have emerged from the study of the crystallization and melting of alternating copolymers. Almost invariably a new crystal structure that is different from that of the corresponding pure homopolymers is formed. Structural similarity of the two comonomers is, therefore, not a requirement for alternating copolymers to crystallize or be crystallizable. This is one of the unique properties of alternating copolymers. Consequently, crystallization can occur with unlikely or unexpected pairs of comonomers. Melting temperatures of alternating copolymers can be either higher or lower than those of their respective homopolymers. In some cases the melting temperature can be in between the two. A more detailed analysis of the melting point relations, in terms of the structure of the alternating sequence, is hampered by the paucity of data on the thermodynamic quantities that govern fusion for this class of copolymers.

Block or ordered copolymers, which are also known in special situations as multiblock or segmented copolymers, have the chain units organized into relatively long sequences. The sequence-propagation-probability parameter p is, therefore, much greater than X_A and approaches unity in the ideal case. Consequently the equilibrium melting temperature should be close to that of the pure homopolymer, provided that the melt is homogeneous and the crystalline phase is pure and devoid of any permanent built-in morphological constraints. The long sequence of the A and B units can be arranged in several different ways, or molecular architectures. A diblock copolymer, schematically represented as AB, is characterized by the number of repeating units in each of the sequences. A triblock copolymer, ABA or BAB, has two junction points of dissimilar units and is characterized by the molecular weight of each block. A multiblock copolymer can be represented in general as



The length of each type of block can be constant or variable.

It is particularly important in studying the crystallization behavior of block copolymers that the nature of the melt be defined. The reason for this concern is that the melt of a block copolymer is not necessarily homogenous, even under equilibrium conditions. The melt can be heterogeneous with a definite supermolecular or domain structure. Such a structure will affect the crystallization kinetics and thermodynamic properties relative to those of a homogeneous melt.

The basis for understanding the melt structure of block copolymers is related to the problem of mixing two chemically dissimilar polymers [46]. Two chemically dissimilar homopolymers will form a homogeneous mixture when the free energy of mixing is negative. The entropy to be gained by mixing two such homopolymers is very small owing to the small number of molecules involved. Therefore, only a small positive interaction free energy is sufficient to overcome this inherent mixing entropy. Immiscibility thus results. It can be expected, in general, that two

chemically dissimilar polymers will be incompatible with one another and hence that phase separation will occur. There are exceptions for pairs of comonomers that display favorable interactions.

Consider now a block copolymer composed of two chemically dissimilar blocks, each of which is noncrystalline. The same factors as those that are involved in homopolymer mixing will still be operative, so phase separation would be expected *a priori*. However, since the sequences in the block copolymer are covalently linked, the macrophase separation which is characteristic of binary blends is prevented. Instead, microphase separation and the formation of separate domains occurs. The linkages at the A–B junction points further reduce the mixing entropy. There has to be a boundary between the two species and the junction point has to be placed in this interphase. The interphase itself will not be sharp and will be composed both of A units and of B units. Mixing of the sequences, and homogeneity of the melt, will be favored as the temperature is increased. There is then a transition temperature between the heterogeneous and homogeneous melts, corresponding to what is known as the order–disorder transition.

The details of phase separation in the melt of block copolymers depend on the chain lengths of the respective blocks, their interaction, and the temperature and pressure. Depending on the compositions and molecular weights of the blocks, phase separation is favored by specific domain shapes. The simplest shapes calculated, as well as observed, are alternating lamellae of the two species, cylinders (or rods), and spheres of one species embedded in a continuous matrix of the other. Phase diagrams in the melt, involving the various possible microphases, have been calculated [47–49].

The examples cited previously have emphasized the important role of the sequence distribution in determining the melting temperatures of copolymers. However, in order to understand in more detail the dependence of the melting temperatures of block copolymers on the chain length of the crystallizing sequence and on the composition, it is necessary to take into account the special structural features that are inherent to such systems. The crystallization of block copolymers can be complicated since the process can be initiated either from a homogeneous melt or from various microdomain structures. Thus, depending on the initial state or pathway taken, differences in structure and morphology can be expected for polymers with the same, or similar, constitutions. Also important for the crystallization process is the influence of the second component on the crystallization. It can be crystallizable, rubber-like, or a glass. The fusion process, as well as the observed and equilibrium melting temperatures, will be influenced by the resulting structural features.

Microdomain structures are said to be either weakly or strongly segregated, depending on the value of $\chi_1 N_t$, where χ_1 is the Flory–Huggins interaction parameter

and N_t is the total number of segments in the block copolymer. When the microdomains in the melt are weakly segregated, crystallization in effect destroys the structure and a conventional lamellar-type morphology results. When the molecular weight of the copolymer increases, then, according to theory, the stability of the microdomain in the melt is enhanced and the structure is maintained during subsequent crystallization. As a result the block crystallizes without any morphological change, i.e. the domain structure is reflected in the crystalline state that results.

A schematic illustration of the major domain structures that are found in pure amorphous copolymers is illustrated in Fig. 4.13 [48]. Here the diblock copolymer poly(styrene)–poly(butadiene) is taken as an example. In (a) poly(styrene) spheres are clearly seen in a poly(butadiene) matrix; the spheres change into cylinders with an increase in the poly(styrene) content, as shown in (b). With a further increase in the concentration of poly(styrene), alternating lamellae of the two species are observed, (c). At the higher poly(styrene) contents, (d) and (e), the situation is reversed. Poly(butadiene) cylinders, and then spheres, now form in a poly(styrene) matrix. More quantitative descriptions of the domain structures have been given [49–51]. Crystallization and melting often occur on going to or from heterogenous melts with specific microphase structures.

The properties of block copolymers are often studied in the form of solvent-cast films. Preferential interaction of this solvent with each of the blocks prior to microphase separation can exert a profound influence on the size and shape of the domain.

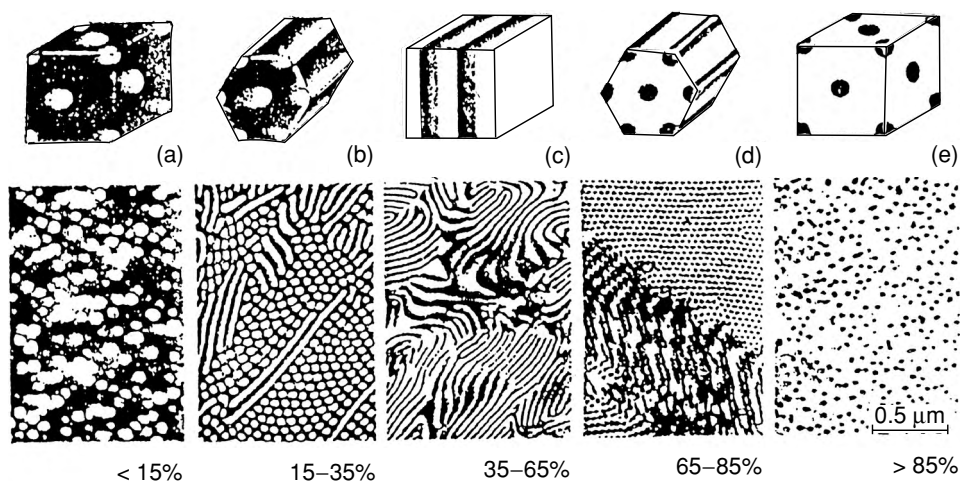


Fig. 4.13. A schematic representation of domain structure in amorphous diblock styrene–butadiene copolymers. Percentages indicate the poly(styrene) content. From [48].

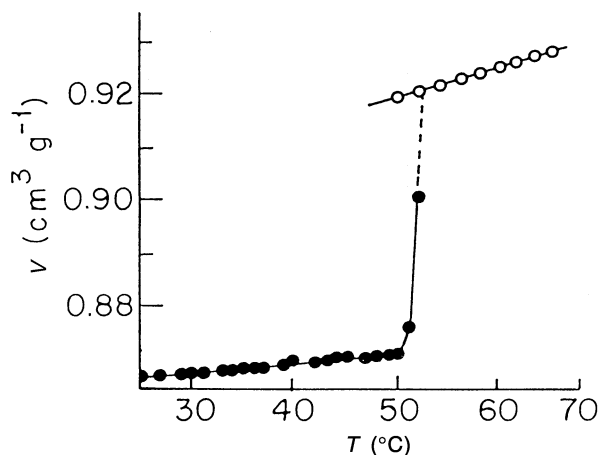


Fig. 4.14. A plot of specific volume against temperature for a diblock copolymer of styrene and ethylene oxide. Reproduced from [52] with permission. Copyright 1976, Wiley VCH.

It is of interest at this point to analyze the fusion properties of some typical ordered copolymers. On the basis of the previous discussion it is important that the structure of the melt and the pathway for crystallization be specified. Although the primary concern is the equilibrium condition, it can be expected that there could very well be complications in achieving this state. For an ideal, ordered copolymer of sufficient block length the parameter p will approach unity. Therefore, T_m should be invariant with composition. This expectation is drastically different from what is predicted for and observed with other types of copolymer. This expectation is unique to chain molecules and has been demonstrated in Fig. 4.5, which emphasizes the importance of this sequence distribution in determining melting temperatures. The fusion of block copolymers is sharp and comparable to that of a homopolymer. This point is illustrated in Fig. 4.14, where the specific volume is plotted against the temperature for a poly(styrene)–poly(ethylene oxide) diblock polymer [52]. The M_n of the crystallizing block of ethylene oxide is 9900 and its weight percentage in the sample is 67%. The melting range is clearly very narrow. All of the fusion characteristics are reminiscent of a well-fractionated linear homopolymer. This behavior is theoretically expected for a block copolymer with long crystallizable sequences, when there is no intervention of any morphological complications.

The role of the initial domain structure in the melt and hence the crystallization pathway is illustrated by the properties of a series of diblock copolymers composed of hydrogenated poly(butadiene) and poly(3-methyl-1-butene) with varying molecular weights [53]. The change in molecular weights allows differing degrees of

incompatibility, and thus melt structures. In this set of copolymers, the melt structures range from being homogeneous at low molecular weights to a strongly segregated hexagonally packed cylindrical morphology at the higher ones. Crystallization from the strongly segregated melts was confined to the cylindrical domain and was essentially independent of thermal history. In contrast, the morphology that results from either weakly segregated or homogeneous melts is dependent on the thermal history. In weakly segregated systems fast cooling from the melt confines the crystallization to the cylindrical domain; slow cooling leads to complete disruption of the cylindrical melt. Concomitantly, thermodynamic properties are altered. The samples of lowest molecular weight, for which crystallization proceeds from a homogeneous melt, develop the highest level of crystallinity and melting temperatures. Crystallization from the strongly segregated melt results in a lower level of crystallinity, about 10%, and the melting temperature is about 4 °C lower. Although these differences might be small on a global scale, they are important and emphasize the influence of the melt structure. Other examples of the influence of the initial domain structure of the melt on the crystallization are found in diblock copolymers of poly(styrene) and poly(ϵ -caprolactone), for which the molecular weights were varied [54], and in triblock copolymers of hydrogenated poly(butadiene–isoprene–butadiene) [55].

Studies of the thermal behaviors of diblock and triblock copolymers of hydrogenated butadiene (HB) and vinylcyclohexane (VC) further illustrate the influence of the initial melt structure [56]. In these copolymers the 145 °C glass-transition temperature of the poly(vinylcyclohexane) block is much higher than the crystallization range of the hydrogenated poly(butadiene) component. A wide range of domain structures was developed in the melt by varying the molecular weight of each block. The structures included hexagonally packed cylinders, lamellae, gyroids, and spheres. The order–disorder transition of each of the copolymers was more than 60 °C greater than T_g of the poly(vinylcyclohexane) block. Therefore, the domains in the melt are well established, or segregated, prior to the vitrification of the poly(vinylcyclohexane) block. Crystallization in these copolymers is thus restricted by the glassy VC block. Small-angle-X-ray-scattering measurements showed that the domain structure of the melt was preserved upon crystallization.

The melting temperature–composition relations for the diblock and triblock, VCHB and VCHBVC, are shown in Fig. 4.15 [56]. The melting temperatures of the diblock copolymers are essentially constant for W_E values equal to, or greater than, 0.5. They are only 1–2 °C lower than that of pure hydrogenated poly(butadiene). There is just a very small continuous decrease in T_m as the poly(butadiene) content decreases. Thus, the constraints placed on the crystallization by the vitrification of the VC blocks are limited for the diblock copolymers. More striking is the observation that the melting temperatures of the triblock copolymers are lower than those

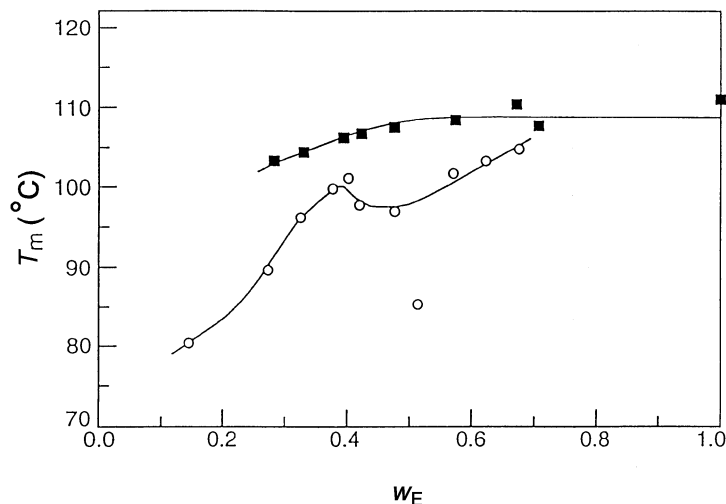


Fig. 4.15. Plots of the melting temperature T_m for HBVC diblocks (■) and VCH-BVC triblocks (○) as functions of the weight fraction W_E of the HB component. Reproduced from [56] with permission. Copyright 1999, John Wiley & Sons, Inc.

of the diblocks of the same composition. For the high butadiene concentrations the melting temperatures are relatively close to one another. However, there is a significant difference in melting temperatures for the lower butadiene compositions. The glassy nature of the end blocks places a major constraint on the crystallization of the central block. The levels of crystallinity that are observed follow a similar pattern.

Booth and co-workers have performed an extensive set of studies on the melting of fractions of block copolymers based on ethylene oxide (E) as the crystallizing sequence and propylene oxide (P) as the noncrystallizing sequence [57–61]. All of the crystallizing blocks had narrow molecular weight distributions. Results from studies of the mixing behavior of low molecular weight fractions of poly(ethylene oxide) and poly(propylene oxide) indicate that the two components are compatible in the melt. This observation leads to the conclusion that the corresponding block copolymers do not exhibit microphase separation in the melt. This set of copolymers then provides a good reference point for melting-temperature studies. Various copolymer architectures were studied. A comparison of the thermodynamic behaviors of the diblock, PE, the two triblocks, PEP and EPE, and the multiblock copolymers $P(EP)_n$ can be made.

Diblock copolymers with the length of E fixed at 40 units and that of P increasing from zero to 11 units were studied [57]. The thickness of the crystalline portion of the lamellar structures that formed was about 25 ethylene oxide units. The crystallites are, therefore, of close to extended form, but not completely so. A small, but

significant, portion of the ethylene oxide units was found to be noncrystalline. These units are intermixed with those of propylene oxide, which is typical of block copolymers. The level of crystallinity of the homopolymer with 40 repeating units is about 70%. This level of crystallinity was maintained by all of the diblock copolymers studied. The observed melting temperature of the corresponding homopolymer was 50–51 °C, depending on the crystallization temperature. There was a decrease of about 3.5 °C on going from the melting temperature of the homopolymer to that of the copolymer with 11 propylene oxide units. This small melting-point depression can be attributed to interfacial effects caused by the increasing length of the non-crystallizing sequences. The basic equilibrium requirements appear to be applicable to this series of diblock copolymers.

An interesting comparison between the triblock copolymers PEP and EPE can be made. In the PEP copolymer the length of the E block ranged from 48 to 98 repeating units and that of the P blocks from 0 to 30 units [59]. When E was 48 units long, either extended or folded crystallites were formed, depending on the length of the P block. For E blocks whose lengths were greater than 48 units only folded-type crystals formed, irrespective of the lengths of the P blocks. For the extended crystallite (E being 48 units long) there is a depression by 1 °C in T_m , relative to that of the pure homopolymer (P being one unit long). However, when P is of length two units, there is a depression by 6 °C of the melting temperature. When the length of P is increased to five units or more, only folded-chain crystallites are formed and the melting temperatures are depressed by about 15 °C relative to that of the homopolymer. The levels of crystallinity remain constant at about 70% for the extended-chain conformation, but increase slightly for the folded chains. The fact that extended-chain crystallites can form in block copolymers having this type of architecture is a verification of equilibrium theory. It also indicates that the folded structures that form at the large block lengths are a result of kinetic factors. Only folded-chain crystallites are observed when the length of the central E block is increased. Concomitantly, there is a decrease in the observed melting temperature relative to that of the corresponding homopolymer. This melting-point depression becomes accentuated as the length of the P end blocks increases.

In the EPE copolymers the lengths of the P blocks ranged from 43 to 182 units while the crystallizing E blocks contained from 18 to 69 units [60]. The chain structures and melting temperatures of the crystallites are quite different from those of the PEP copolymer. If any chain folding occurs at all in this system, it does so only at the higher lengths of the E blocks. The melting temperatures of the EPE block copolymers and the corresponding homopolymers are essentially identical, except for the highest chain lengths. Even here, the differences are small. These results stand in sharp contrast to the melting temperatures of the PEP blocks, even for the extended-chain structures. The position of the crystallizing block in a

symmetric triblock copolymer makes an important difference in the observed melting temperature.

The melting temperature of multiblock copolymers of ethylene oxide with propylene oxide, $P(EP)_m$, can be compared with that of the triblock polymer PEP [59, 61]. The ethylene oxide and propylene oxide sequences have discrete lengths that range from 45 to 136 units for E and from four to 12 units for P. The value of m varies from 1 to 7. The level of crystallinity in these multiblock copolymers is only about 60% of that observed for comparable PEP copolymers. The melting temperatures of the $P(EP)_m$ and PEP copolymers with the same sequence length for E are, however, comparable to one another, the differences in melting temperature being only about 1–3 °C. Similar results are found when multiblock copolymers of poly(styrene) and poly(ethylene oxide) are compared with diblock and triblock ones.

Studies of block copolymers of hydrogenated poly(isoprene) and hydrogenated poly(butadiene) have also addressed the role of the molecular weight, the character of the noncrystallizing block, and the molecular architecture [55]. In these copolymers hydrogenated poly(butadiene) (B) is the crystallizing block while hydrogenated poly(isoprene) (I) is rubber-like. Diblock and triblock BIB and IBI were studied. The molecular weights of all the copolymers were about 200 000. The melting temperatures of these copolymers were all the same, 102 °C, independently of the molecular architecture and the concentration of butadiene. This is the same melting temperature as that observed for the random copolymer of hydrogenated poly(butadiene) by itself. Thus, in accord with theory, the melting temperature of the crystallizing component is independent of its arrangement within the copolymer.

An example of constrained crystallization occurs when the two blocks crystallize independently of one another. The block that crystallizes first does so to a high level of crystallinity and restricts the space available for the crystallization of the other block. Thus, the morphology and kinetics are affected [62]. An example of such behavior is found in diblock and triblock copolymers of poly(ϵ -caprolactone) and poly(ethylene oxide) [63–67].

The crystallization of multiblock copolymers has been studied extensively, particularly with copolyesters [68–71] and the poly(urethanes) [72–73]. The block that is amorphous, or liquid-like, with a relatively low glass-transition temperature is often referred to as the soft segment since it imparts rubber-like behavior to the copolymer. The other component can be either glass-like or crystalline, and is termed the hard block. Thus, soft and hard segments alternate along the chain. The interest here is in those copolymers in which the hard segment is crystalline. The melting-temperature relations follow a pattern that is typified by a segmented block copolyester based on poly(tetramethylene terephthalate) as the crystallizable block and various low molecular weight poly(ethylene glycols), that do not

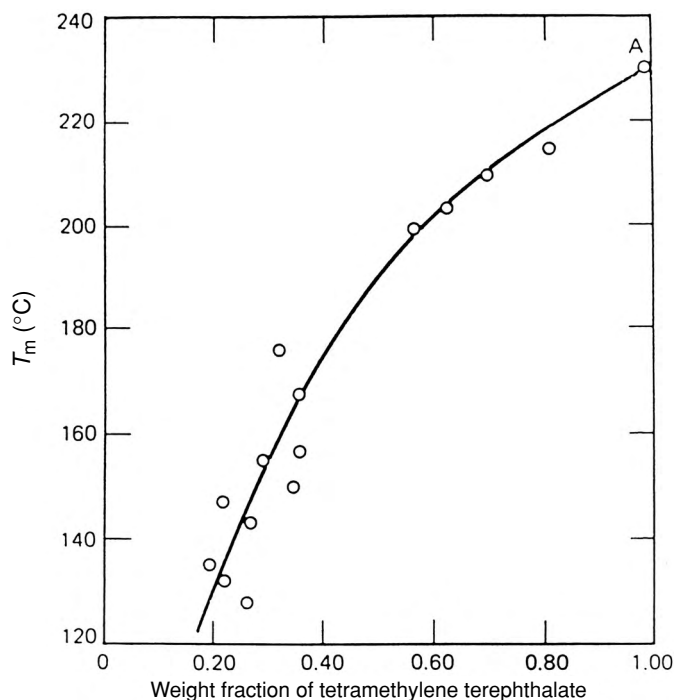


Fig. 4.16. The dependence of the melting temperature on the average block length of tetramethylene terephthalate in its copolymer with poly(oxytetramethylene glycol). From [74].

crystallize, as the other block [73–77]. The melting temperature–composition relation for the segmented block copolymer of poly(tetramethylene terephthalate) and poly(oxytetramethylene glycol) is given in Fig. 4.16 [74]. Here the observed melting temperatures are plotted against the average length of the tetramethylene terephthalate block. The melting temperatures of these copolymers increase with increasing block length and approach 230 °C, the melting temperature of the pure homopolymers. Following theoretical expectations, the melting temperature at a given block length is independent of the chemical nature of the poly(glycol) [75]. In general, the melting temperature–composition relations of multiblock copolymers are similar to one another, irrespective of the chemical nature of the co-units. When the sequence length of the crystallizing block is sufficiently long, the melting temperature is independent of composition. In accord with theory, it is either identical or very close to that of the corresponding homopolymer. This expectation is found to apply to many examples [78–82]. The level of crystallinity that is attained is in most cases the same as that for the pure homopolymer of the crystallizing units. Put another way, crystallization is far from complete and the level of crystallization is comparable to that of the corresponding homopolymer. Consequently, there is a

mixing in the amorphous phase of an appreciable portion of the crystallizable units with those which are not.

To summarize copolymers in general, and block copolymers of various architectures in particular, one can hope for control of both microscopic and macroscopic properties [11, 83]. A wide range in properties can be achieved by varying the sequence distribution and spatial arrangement. It is important to note that the structural principles that have been discussed for the ordered synthetic copolymers have applicability to naturally occurring macromolecules, in particular the fibrous proteins [11].

The discussion of the crystallization of copolymers so far has been limited to the case in which the crystalline phase remains pure. This restraint greatly simplifies the analysis. However, as a result the crystallization of many copolymers has not received adequate attention. It will be found in the following that, when the co-unit enters the crystal lattice, the analysis is more complex and has not been as successful as would be desired. However, because of the importance and occurrence of such systems, a discussion of this problem will be given.

The failure of the Flory theory, Eq. (4.5), even when extrapolated equilibrium melting temperatures are used, does not necessarily mean that the co-unit is entering the lattice. It has been pointed out that Eq. (4.5) is applicable only to an ideal melt. Specific factors such as interactions between co-units and volume effects, among others, can cause deviations from ideality. To complicate the problem further, a decision regarding whether the co-unit enters the lattice cannot in general be made solely on the basis of the liquidus. Values for the liquidus of a few cases can be very similar to one another. An example is given in Fig. 4.17, showing the melting temperatures of bacterially synthesized random copolyesters of 3-hydroxybutyrate (3HB) and 3-hydroxyvalerate (3HV) [84]. Here, the melting-temperature–composition relation, which is based on the liquidus, is reminiscent of similar curves for the copolyesters and copolyamides, for which it has been demonstrated that the crystalline phase is pure. In the example illustrated the level of crystallinity is greater than 50% over the complete composition range [84, 85]. This indicates that some type of co-crystallization has occurred. Wide-angle X-ray diffraction patterns [84, 85], as well as data from solid-state carbon-13 NMR studies [86–88], demonstrate that isodimorphism occurs over the complete composition range [89]. Isodimorphism would not be suspected solely on the basis of the liquidus. A very similar situation has been observed for the random copolymers of ethylene terephthalate and ethylene naphthalene 2,6-decarboxylate [90].

Indirect methods are sometimes successful at determining whether the crystalline phase remains pure. For example, when a variety of comonomers with different sizes and shapes is found to yield the same melting temperature–composition relation it is reasonable to assume that the crystalline phase is pure for these specific

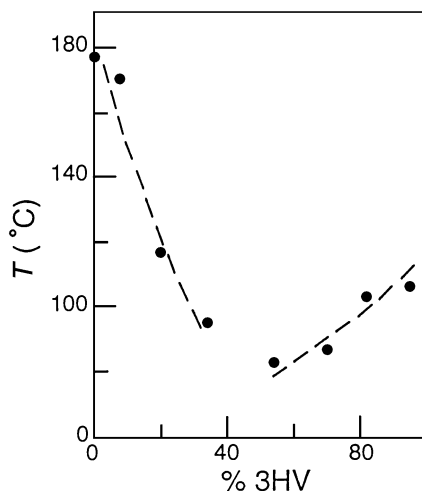


Fig. 4.17. A plot of melting temperature against the melt composition for random copolymers of 3-hydroxybutyrate and 3-hydroxyvalerate. Reproduced from [84]. Copyright 1992, American Chemical Society.

co-units. Such examples are found among copolyesters [91] and copolymers of poly(tetrafluoroethylene) [24]. In contrast, when the melting temperature depends specifically on the comonomer incorporated it is not unreasonable to assume that the co-unit is entering the lattice.

In the discussion of the melting temperature–composition relation of the ethylene–1-alkene random copolymers (Fig. 4.11) ethylene–propylene copolymers, with directly bonded methyl groups, were not considered. The reason is that they have significantly higher melting temperatures than do those with either large alkyl branches or bulkier side groups [15, 17]. Results of detailed studies indicate that there is a maximum, at low branch-point content, in the melting-temperature–composition relation for this copolymer [15, 17]. The maximum in the liquidus suggests the occurrence of compound formation, as is observed in many binary mixtures of metals and other monomeric substances. It reflects the fact that the methyl group enters the lattice on an equilibrium basis. Results of solid-state carbon-13 NMR studies have now supported this conclusion [92, 93].

The melting temperature–composition relations for ethylene–vinyl chloride copolymers are virtually identical to those for ethylene–propylene copolymers [94]. Hence we can also surmise that the Cl atom enters the lattice on an equilibrium basis. Results of similar studies have shown that smaller side groups such as CH₃, Cl, OH, and O can enter the lattice of ethylene copolymers [95].

Natta [96] has described two types of isomorphism. In isomorphism itself, both units participate in the same crystal structure over the complete composition range.

In the other type, termed isodimorphism, the system consists of two different crystalline structures. The formation of one or the other depends on the sequence distribution (composition) of the crystalline phase. Examples of these types of replacements are found in virtually all types of copolymer, including copolyamides [97–103], synthetic and natural copolyesters [89, 90, 104–107], vinyl copolymers [29, 94, 108, 109], diene polymers [110], poly(olefins) [111–114], poly(aryl ether ether ketones) [115], and poly(phenyls) [116]. A detailed summary of other copolymers in which co-crystallization occurs can be found in [117]. There appear to be two underlying principles that govern isomorphic replacement [117]. These are that the two repeating units should have the same shape and volume and that the new ordered chain conformation be compatible with both types. In many of these examples the melting temperatures are essentially a linear function of the composition, whereas in others there is a smooth monotonic change.

Ideally, the crystalline state should be probed by appropriate physical methods in order to ascertain whether it is pure. If it is not pure, then the distribution of sequences within the crystalline phase needs to be established from first principles. This is an extraordinarily difficult task. Up to now one has had to be satisfied with determining the composition of the co-unit within the crystalline phase and thus establishing the solidus, in the more conventional sense. A rare example of determination both of the liquidus and of the solidus, and thus of the complete phase diagram, can be found in the work of Hachiboshi *et al.* [104], who crystallized random copolymers of ethylene terephthalate with ethylene isophthalate over the complete composition range. The wide-angle X-ray patterns of these copolymers change systematically with co-unit content. It was concluded that the two units can co-crystallize and form a new unit cell. The complete phase diagram is shown in Fig. 4.18 [92]. The solidus was determined by assuming the additivity of the lattice spacings. The phase diagram is a classical one. It even contains an azeotropic point. Crystallization of polymers, therefore, is not atypical. For low molecular weight systems the liquid and solidus must have the same composition, or activity, at the azeotropic point. For random copolymers, the comparable requirement would be that the sequence-propagation probability be the same in both phases. With the utilization of advanced techniques to probe the structure and composition in the solid state, the presentation of complete phase diagrams can be expected in the future.

For an analysis of the melting temperature–composition relation when both comonomers are in the lattice one has to make a distinction between whether they are present on an equilibrium basis or as non-equilibrium defects. At present we focus attention on the equilibrium case. When both comonomers are present in the crystalline and liquid phases the analysis of the equilibrium condition is more complex than it is when the equilibrium phase remains pure. The necessary requirements can, however, be stated in a strictly formal manner.

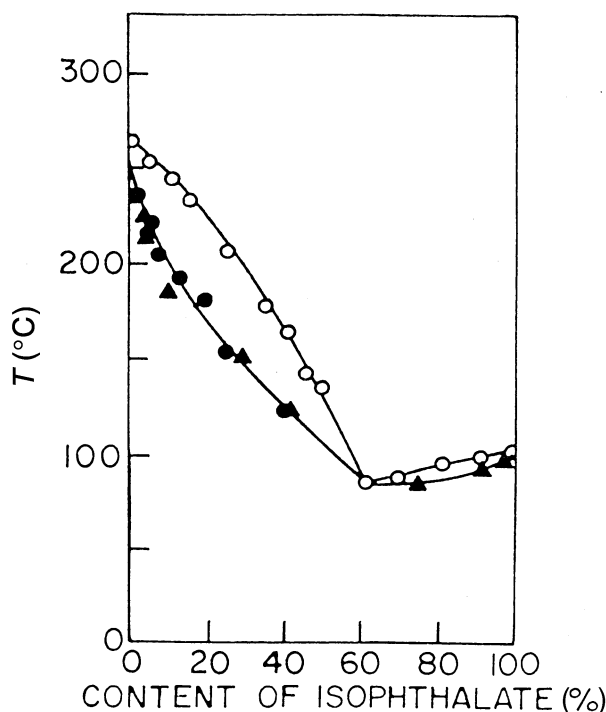


Fig. 4.18. The complete phase diagram for ethylene terephthalate–isophthalate copolymers. Reproduced from [104], copyright 1960 with permission Marcel Dekker Inc.

In addition to the uniformity of the temperature and pressure, two further conditions need to be satisfied. The chemical potentials of each of the species, A and B, must be invariant in each of the phases. Thus

$$\mu_{A1} = \mu_{Ac} \quad \mu_{B1} = \mu_{Bc} \quad (4.7)$$

For monomeric systems the chemical potentials of the species in each of the phases are specified in terms either of composition or of activity. The melting-temperature relations are then derived in a straightforward manner [118]. For an ideal mixture of low molecular weight species the free energy of mixing in each phase is determined by a Raoult's law-type calculation, i.e. only the combinatorial entropy is considered. The composition is then expressed in terms of mole fractions. The equilibrium melting temperature in terms of the composition of each phase is then specified.

For copolymers one can in principle proceed, in analogy with the pure system [15], to calculate the number of distinguishable ways in which the different sequences in the crystalline phase can be arranged. The sequence distributions in the

pure melt will be unaltered and determined by the copolymerization mechanism. The sequence distribution in the crystalline phase will depend on the concentration of the B units and the specifics of the crystal structure containing the B units. Specifically, the stoichiometric relation between the A and B units in the crystallite is required. With this information the ideal chemical potential of the A and B units in the crystalline phase can be obtained. The melting temperature of the ideal system will be obtained by invoking Eq. (4.7) for both units in both phases. However, to accomplish this task requires the *a priori* specification of the number and lengths of the different sequences involved and the crystallite composition. In general, these requirements are extremely difficult to fulfill, so the melting-temperature-composition relation is not yet available for the ideal case.

Efforts have been made, however, to develop an equilibrium theory without consideration of the ideal contributions [119–124]. Thus, the underlying foundation has been neglected. The importance of the sequence distribution in the crystalline state has not been taken into account in these works. In some cases, an arbitrary distribution has been assumed for ease of calculation. It is still appropriate, however, to consider the approaches that have been taken, since the results have been applied to experimental data.

In one approach to the problem it has been assumed that there is a binomial (most probable) distribution of B units in the melt, i.e. $p = X_A$ [122]. All that is considered is the excess free energy that is involved for a B unit replacing an A unit within the crystalline lattice. This free energy is designated by ε . With these assumptions, and applying equilibrium conditions, the free energy of fusion of such a crystal, G , is given by

$$\Delta G = \Delta G^0 + RT \ln\{1 - X_B + X_B \exp[-\varepsilon/(RT)]\} \quad (4.8)$$

Here X_B is the overall, or nominal, mole fraction of B units and ΔG^0 is the free energy of fusion of the pure crystallite. In deriving Eq. (4.8) the sequence distribution within the crystalline phase is not taken into account. Under these conditions the equilibrium melting temperature, T_m , can be expressed as

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{R}{\Delta H_u} \ln \left[1 - X_B + X_B \exp \left(\frac{\varepsilon}{RT_m} \right) \right] \quad (4.9)$$

Equation (4.9) is just a perturbation of the melting-point equation pertinent to a pure crystalline phase. When ε is very large the change in free energy that is involved becomes excessive. The B units will then not enter the lattice and the Flory equation is regenerated.

Since ε is an arbitrary parameter, Eq. (4.9) has an advantage in explaining experimental results. However, the basic assumptions that have been made in deriving Eq. (4.9) need to be borne in mind. Only a non-ideal term appropriate to the

crystalline phase has been added to the ideal expression for the case of the crystalline phase being pure. The role of the sequence distribution within the crystalline phase, which is crucial to resolving the problem, has not been considered.

This type of analysis was extended by Wendling and Suter [124], who incorporated proposals made by Kilian [125, 126] and by Baur [127]. In this case only sequences of length ζ are included in lamellar crystallites whose thicknesses correspond to that length. This assumption describes a particular non-equilibrium situation. On following this procedure, it is found that

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{R}{\Delta H_u} \left\{ \ln \left[1 - X_B + X_B \exp\left(-\frac{\varepsilon}{RT_m}\right) \right] - \langle \zeta \rangle^{-1} \right\} \quad (4.10)$$

where $\langle \zeta \rangle$ is given by

$$\langle \zeta \rangle^{-1} = 2 \left[X_B - X_B \exp\left(-\frac{\varepsilon}{RT_m}\right) \right] \left[1 - X_B + X_B \exp\left(-\frac{\varepsilon}{RT_m}\right) \right] \quad (4.11)$$

The introduction of an additional parameter gives better agreement with experimental results.

4.3.1 Non-equilibrium considerations

It is appropriate at this point to consider also the non-equilibrium aspects of the fusion of copolymers. The reason is that, for melting of copolymers, even the approach to equilibrium is extremely difficult, if not impossible, to attain.

A variety of real non-equilibrium features can be addressed. These include, among others, the formation of crystallites of small size, folded-chain crystallites, the role of the interfacial free energy, σ_{ec} , characteristic of the surface normal to the chain axis, and its dependence on the composition of the copolymer. For convenience the discussion that follows is divided into two categories. In one, the B units are excluded from the lattice; in the other, they are allowed to enter.

For kinetic reasons crystallites smaller than those predicted from equilibrium theory will usually develop. The appropriate melting-temperature relation can be formulated in a straightforward manner by invoking the Gibbs–Thomson equation. For an ideal random copolymer [128]

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{R}{\Delta H_u} \ln X_A + \frac{2\sigma_{ec}}{T_m \Delta H_u \rho_c L_c} \quad (4.12)$$

Here T_m is the observed temperature, and ρ_c and L_c are the density and thickness, respectively, of the crystallite. Equation (4.12) merely states how the equilibrium melting temperature is reduced by the presence of crystallites of finite size. Both L_c and σ_{ec} will be expected to depend on the composition of the copolymer. The

enthalpy of fusion, ΔH_u , results from the expansion of the free energy of fusion about the melting temperature. The variation with temperature of this free energy is more sensitive than that of a homopolymer because of the changing sequence distribution in the melt. Thus, using only the conventional temperature expansion of ΔG_u is not sufficient.

The equilibrium requirement that the largest sequence of A units crystallize, and do so in extended form, is extremely difficult to attain experimentally. To account for the size of the crystallites that actually form, attention is focused on the mean sequence length $\langle \zeta \rangle$, and the melting of crystallites of the same thickness. For random copolymers [127, 129]

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{R}{\Delta H_u} [\ln(1 - X_B) - \langle \zeta \rangle^{-1}] \quad (4.13)$$

Here $\langle \zeta \rangle = [2X_B(1 - X_B)]^{-1}$ is the average length of an A-unit sequence in the pure melt. This quantity is also taken to represent the thickness of an average crystallite.

A kinetic approach, based on “rough surface growth” [130], that also focuses on the finite thickness of the lamellae leads to a modification of Eq. (4.12). With a set of approximations, the melting temperature can be expressed as [131]

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{R}{\Delta H_u} \left(\frac{L_c - 1}{2} \right) \ln p + \frac{2\sigma_{ec}}{\Delta H_u \rho_c L_c} \quad (4.14)$$

Equations (4.12–4.14) represent non-equilibrium situations in which the crystalline phase remains pure. Primary attention has been paid to the finite size of the crystallites through use of the Gibbs–Thomson equations and consideration of the influence of the sequence selected. The alternative situation in which the B units enter the crystal lattice as defects must also be considered.

Following the previous analysis, the melting temperature when the B units enter the lattice on a non-equilibrium basis is given by [121–123]

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{R}{\Delta H_u} \left[\frac{\varepsilon X_{CB}}{RT_m} + (1 - X_{CB}) \ln \left(\frac{1 - X_{CB}}{1 - X_B} \right) + X_{CB} \ln \left(\frac{X_{CB}}{X_B} \right) \right] \quad (4.15)$$

Here X_{CB} is the mole fraction of B units in the lattice, and X_B is their mole fraction in the overall composition. The occurrence of a random sequence distribution of B units in the crystalline phase has been assumed [123].

When $X_{CB} = X_B$ what is termed the uniform-exclusion model results. Equation (4.15) can be written as [123]

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{R}{\Delta H_u} \frac{\varepsilon X_{CB}}{RT_m} \quad (4.16)$$

On combining these results with those of Baur [127, 129], it is found that [124]

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{R}{\Delta H_u} \left[\frac{\varepsilon X_{CB}}{RT_m} + (1 - X_{CB}) \ln \left(\frac{1 - X_{CB}}{1 - X_B} \right) + X_{CB} \ln \left(\frac{X_{CB}}{X_B} \right) + \langle \zeta \rangle^{-1} \right] \quad (4.17)$$

This portion of the chapter can be summarized by noting that there is a substantial body of evidence demonstrating that formal phase-equilibrium thermodynamics can be successfully applied to the fusion of homopolymers, copolymers, and polymer–diluent mixtures. This conclusion has many far-reaching consequences. It has also been found that the same principles of phase equilibrium can be applied to the analysis of the influence of hydrostatic pressure and various types of deformation on the process of fusion [11]. However, equilibrium conditions are rarely obtained in crystalline polymer systems. Usually, one is dealing with a metastable state, in which the crystallization is not complete and the crystallite sizes are restricted. Consequently, the actual molecular structure and related morphology that is involved determines properties. Information that leads to an understanding of the structure in the crystalline state comes from studying the kinetics and mechanism of crystallization. This is the subject matter of the next section.

4.4 Crystallization kinetics

There are several methods by which the kinetics of crystallization of polymers from the pure melt, or from polymer–diluent mixtures, can be investigated. One procedure is to study the overall rate of crystallization using methods such as dilatometry, calorimetry, and various spectroscopies, for example. Another popular method by which to study the process of crystallization is to measure the rate of growth of spherulites by direct light microscopic examination. These two methods complement one another. Measurements of the rates of growth of specific crystal faces have also been employed in favorable cases for studying the kinetics of crystallization from dilute solution.

The formal basis for analyzing the kinetics of crystallization from the pure melt has been developed substantially. With appropriate modifications, crystallization of polymers has been shown to follow the general mathematical theory that was developed many years ago for the crystallization of metals and other low molecular weight substances. The most elementary form, developed by von Göler and Sachs [132] postulated a process of nucleation and growth. However, in the original formulation there was no termination step, or demarcation for the end of the transformation. To remedy this problem, it was proposed independently by several different investigators that, when two crystallites collided, or made contact,

their growth ceased [133–136]. In this way there was introduced a mechanism for the termination of the process that has been successful in explaining the complete transformation of low molecular weight substances. Since this approach has been modified and adapted for dealing with polymers [137], it is important that the basis of the theory be examined in detail. To accomplish this, the formalism and specifics of Avrami's approach will be used.

Avrami found that the fraction transformed at a time t , namely $1 - \lambda(t)$, can be expressed as

$$1 - \lambda(t) = 1 - \exp\left(-\frac{\rho_c}{\rho_l} \int_0^t V(t, \tau) N(\tau) d\tau\right) \quad (4.18)$$

Here, $N(\tau)$ is the nucleation frequency per unit of untransformed volume, $V(t, \tau)$ is the corresponding volume of the growing center, and ρ_c and ρ_l are the densities of the crystalline and liquid phases, respectively. Equation (4.18) describes the kinetics of phase transformation for a one-component monomeric system. This is the basic Avrami equation and only an integral has to be evaluated. The integral can be evaluated by specifying the laws of nucleation and growth that are operative. This procedure leads to the specific, derived Avrami expression that describes the fraction transformed as a function of time. There is obviously a very large number of possibilities. One set of conditions, among many, that has been popular is that the steady-state nucleation rate is achieved at $t = 0$ and remains invariant with the fraction of material transformed. Then $N(\tau)$ can be treated as a constant. In a similar manner, the rate of crystal growth is assumed to be linear and constant. With these simplifying assumptions the analytic solution of Eq. (4.18) is obtained and can be written as

$$1 - \lambda(t) = 1 - \exp(-kt^n) \quad (4.19)$$

where k is the rate constant. Although Eq. (4.19) is commonly termed the Avrami equation, it is in effect a derived expression that is based on a specific set of assumptions. The exponent n is usually termed the Avrami exponent. The value of n that is appropriate to invariant rates of nucleation and growth is dependent on the geometry of crystal growth. The values of n specific geometries, either for interface- or for diffusion-controlled growth, are summarized in Table 4.2. Also included in Table 4.2 are values of n for a specific type of heterogeneous nucleation [138]. It is clear from this summary that, even using the derived expression, the exponent does not define a unique process of nucleation and growth. At a low extent of the transformation Eq. (4.19) reduces to

$$1 - \lambda(t) = kt^n \quad (4.20)$$

Table 4.2. Values of the exponent n for various types of nucleation and growth

Growth habit	Homogeneous nucleation		Heterogeneous nucleation		
	Linear growth		Diffusion-controlled growth		Linear growth
	Steady state	$t = 0^a$	Steady state	$t = 0$	
Sheaf-like	6	5	$\frac{7}{2}$	$\frac{5}{2}$	$5 \leq n \leq 6$
Three-dimensional	4	3	$\frac{5}{2}$	$\frac{3}{2}$	$3 \leq n \leq 4$
Two-dimensional	3	2	2	1	$2 \leq n \leq 3$
One-dimensional	2	1	$\frac{3}{2}$	$\frac{1}{2}$	$1 \leq n \leq 2$

^a All nuclei are activated at $t = 0$.

Equation (4.20) also corresponds to the reduced form of the free-growth expression. A comparison of the complete (von Göler–Sachs) free-growth expression and the derived Avrami expression for $n = 4$ is given in Fig. 4.19. It turns out that the two isotherms are very similar to one another for all values of n . However, as the transformation progresses, the precise agreement depends on the value of n . In Fig. 4.19, for $n = 4$, the isotherms are virtually identical for up to about 30% of the transformation. The difference between the two isotherms remains very small for up to about 70% of the transformation. At higher levels of the transformation there is a significant divergence between the two isotherms. It is important to note that, in general, except toward the end of the transformation, the isotherms for the two theories are not far apart from one another. It remains to be seen how the derived Avrami expression fits the experimental data.

A typical set of crystallization-kinetic isotherms for a pure polymer crystallizing from the melt is given in Fig. 4.20 [139]. This example is for a molecular weight fraction, $M = 284\,000$, of linear polyethylene. In Fig. 4.20, the extent of the transformation, or degree of crystallinity, is plotted against the logarithm of time elapsed for various crystallization temperatures in the vicinity of the equilibrium melting temperature. Some important features of the crystallization process are illustrated here. The isotherms have a very characteristic sigmoidal shape that is typical for all homopolymers. There is an initial induction time, that is more apparent than real. It is essentially a measure of the sensitivity of the detector. It is followed by a period of accelerated crystallization. A retardation of the crystallization process then occurs and a pseudo-equilibrium level of crystallinity is reached. After sufficient time has elapsed the same limiting value is attained at each crystallization temperature for this homopolymer. The rate of change with time of the level of crystallinity is extremely small in this region. It is important to note that complete

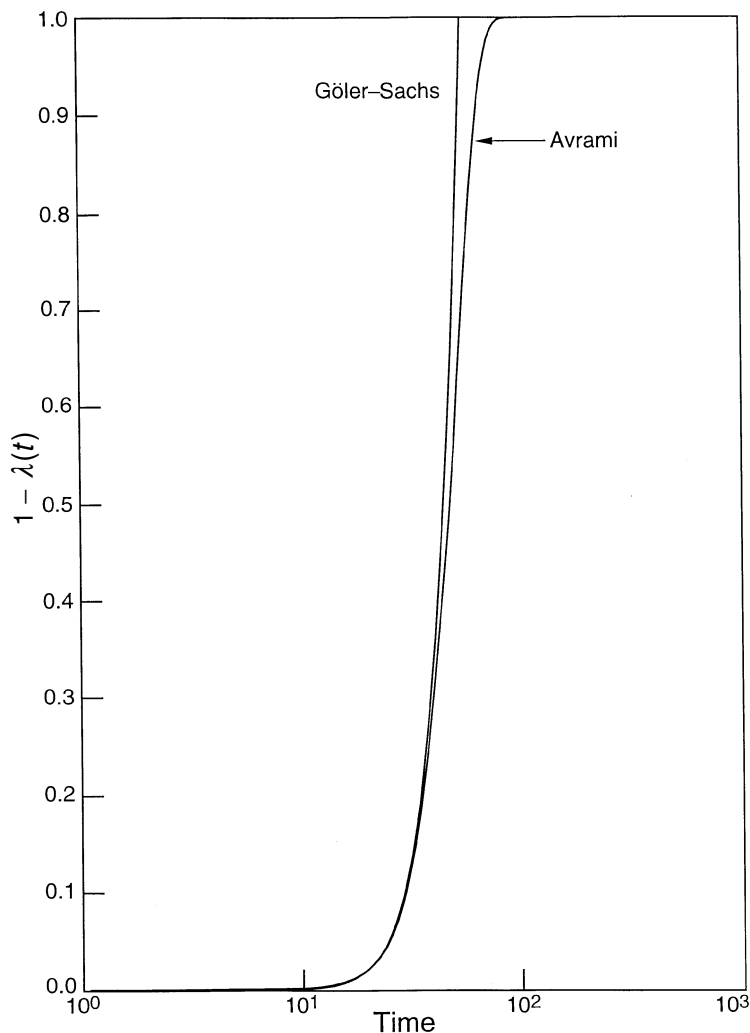


Fig. 4.19. A comparison of theoretical isotherms for von Göler-Sachs and derived Avrami expressions for exponent $n = 4$.

crystallinity is rarely, if ever, attained for polymers. The level of crystallinity that is attained depends on the molecular weight (see later) and the structural regularity of the chain. It can be realized from the results of these kinetic studies that polymers are best typified as being semicrystalline.

The shapes of the isotherms in Fig. 4.20 are typical of crystallization processes that involve nucleation and growth. Moreover, the isotherms at the various temperatures appear to be similar to one another. They are in fact identical in shape and can be superposed upon one another merely by shifting them along the horizontal

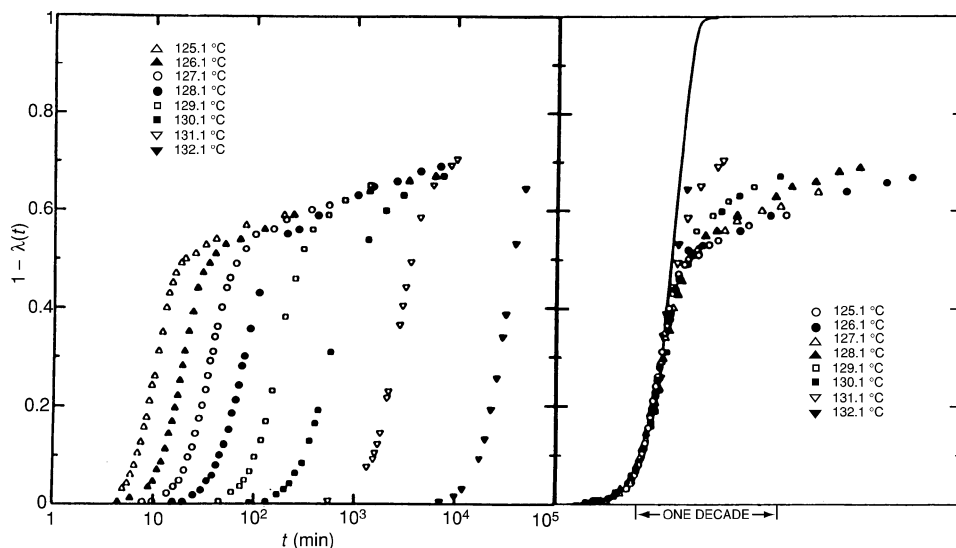


Fig. 4.20. An example of the kinetics of crystallization from the pure melt. Left: a plot of the degree of crystallinity against log time for a molecular weight fraction of linear polyethylene, $M = 2.84 \times 10^5$, at the temperatures indicated. Right: the master isotherm after superposition, with exponent $n = 3$. Reproduced from [139]. Copyright 1972, American Chemical Society.

axis. Thus, one master isotherm results, as is illustrated in the right-hand portion of Fig. 4.20. This procedure shows that there is a single reduced time variable, which is dependent on temperature, that describes the crystallization process. The solid line in Fig. 4.20 represents the derived Avrami equation, Eq. (4.19), with $n = 3$. In this example, the experimental data adhere to this theory for up to about 50% of the transformation. Beyond this point significant deviations from theory occur. The rate of crystallization is significantly retarded as the pseudo-equilibrium level of crystallinity is approached. It should be noted in passing that corresponding isotherms for random copolymers and long-chain branched polymers do not superpose [138, 140]. The reason is that the concentration of crystallizing units and sequence distribution change during the course of isothermal crystallization [141]. Thus in these situations the undercooling changes at constant crystallization temperature.

Returning to the discussion of homopolymers, it is found that deviations from the derived Avrami expression and the final level of crystallinity that can be attained are dependent on the molecular weight. Figure 4.21 shows a set of isotherms, superposed to 127 °C for the indicated molecular weight fraction of linear polyethylene [139]. Here, the absolute level of crystallinity is plotted against the logarithm of time. The solid curve represents the derived Avrami expression for $n = 3$. The level of crystallinity at which deviations from the theoretical curves occur decreases as

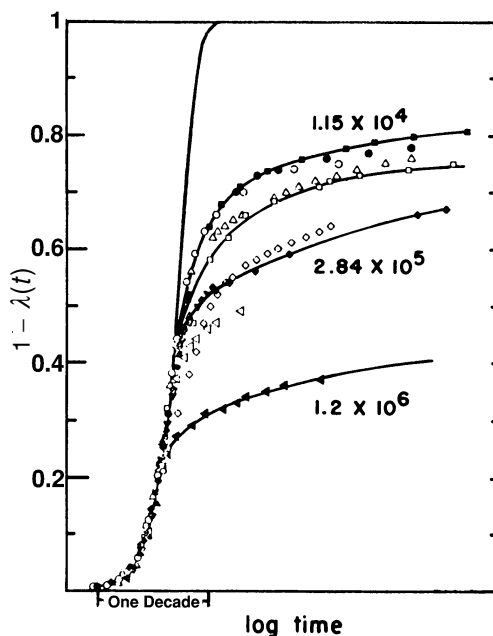


Fig. 4.21. A plot of the degree of crystallinity $1 - \lambda(t)$ against log time for the indicated molecular weight fractions of linear polyethylene. Isotherms for each molecular weight are superposed to 127°C . From [139].

the molecular weight increases. For example, deviations occur at a level of crystallinity of about 0.25 for $M = 1.2 \times 10^6$ and the level at which deviations occur increases to about 0.55 for $M = 1.15 \times 10^4$ at the fixed isothermal crystallization temperature. Other polymers exhibit similar dependences of the level of crystallinity on the molecular weight [142, 143].

The level of crystallinity attained by linear polyethylene is plotted against the molecular weight in Fig. 4.22 for several different situations [139]. The influence of the molecular weight is quite evident in this figure. The level of crystallinity remains constant up to $M = 10^5$, after which there is a precipitous drop with increasing chain length. Most important, and quite striking, is the fact that, within experimental error, both the derived Avrami expression and the free-growth expression give the same results. Put another way, insofar as quantitative agreement between theory and experiment is concerned, the free-growth approximation does just as well as the derived Avrami relation for fitting this set of experimental results. Studies with poly(ethylene oxide) gave similar results.

The similarity in ability of the two theories to explain the experimental results, prior to deviation, has been observed for many other polymers, as is indicated in Table 4.3, in which the final level of crystallinity that is attained, namely $(1 - \lambda)_\infty$,

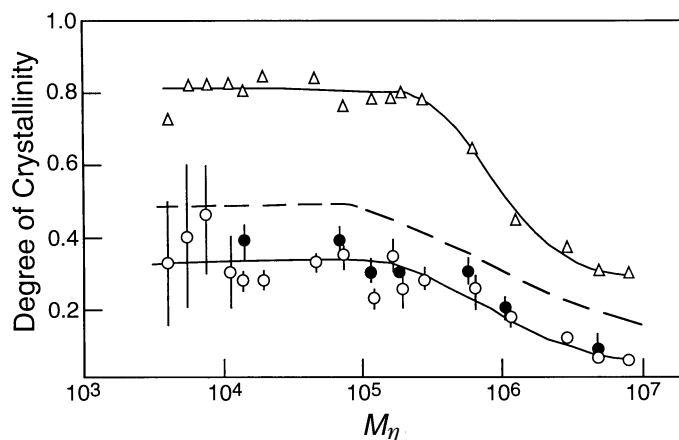


Fig. 4.22. A plot of the level of crystallinity as a function of the molecular weight for linear polyethylene fractions, showing the pseudo-equilibrium level of crystallinity that is attained (Δ) and the levels of crystallinity at which deviations from theory occur (von Göler-Sachs, $\bullet$; Avrami, $\circ$). The dashed curve represents the ratio of the level of crystallinity at which deviation occurs and that actually attained. From [139].

the levels of crystallinity at which the predictions of the two theories deviate, and the ratio of the Avrami deviation $(1 - \lambda)$ to $(1 - \lambda)_{\infty}$ are tabulated. It is clear from this extensive set of data that the von Göler-Sachs expression and the Avrami expression produce similar results up to the point of deviation. Each satisfactorily explains the experimental results. Neither theory fits the experimental data at higher levels of the transformation. It can be concluded that this agreement is a general phenomenon. Other factors, besides the Avrami-type termination mechanism, must be involved as crystallization of a polymer progresses.

The strong influence of the molecular weight on the crystallization kinetics gives a clue regarding the reason why the free-growth and derived Avrami expressions adequately explain the early stages of the transformation, but both fail as the transformation progresses. Attention needs to be focused on the initial and residual melt as the transformation progresses. Initially, prior to the onset of crystallization, the polymer melt is composed of entangled chains, loops, and knots as well as other structures that can be considered to be topological defects. Although they are chemically pure, these structures cannot participate in the crystallization. The concentrations of such units are dependent on the molecular weight and they will be relegated to the noncrystalline regions. Moreover, there will be a region around such defects where the chain units are also uncrystallizable. Therefore, as the crystallization progresses, the availability of crystallizable units decreases relative to the total number of noncrystalline units. Under these conditions neither the

Table 4.3. Deviations of results from crystallization-kinetic theories from experiment for selected polymers

Polymer	$(1 - \lambda)_{\infty}$	von Göler-Sachs	Avrami	Avrami/ $(1 - \lambda)_{\infty}$	Reference
Poly(ether ether ketone)					
Low temperature	0.18	0.13	0.17	0.94	a
High temperature	0.35	0.23	0.22	0.63	
New poly(imide)					
Low temperature	0.24	0.15	0.23	0.96	b
High temperature	0.25	0.17	0.22	0.88	
Poly(1,3-dioxolane)	0.50	0.30	0.32	0.64	c
Poly(chlorotrifluoroethylene)	0.60	0.50	0.48	0.72	d
Poly(3,3-dimethyl oxetane)	0.63	0.30	0.48	0.76	e
Poly(oxetane)	0.53	0.28	0.25	0.47	f
Poly(<i>cis</i> -1,4-butadiene)					
Low temperature	0.50	0.50	0.50	1.00	g
High temperature	0.55	0.50	0.45	0.82	

^a P. Cebe and S. D. Hong, *Polymer*, **27** (1986), 1183.

^b B. S. Hsiao, B. B. Sauer, and A. Biswas, *J. Polym. Sci. Pt B: Polym. Phys.*, **32** (1994), 737.

^c R. Alamo, J. G. Fatou, and J. Guzman, *Polymer*, **32** (1982), 274.

^d J. D. Hoffman and J. J. Weeks, *J. Chem. Phys.*, **37** (1962), 1723.

^e E. Perez, J. G. Fatou, and A. Bello, *Coll. Polym. Sci.*, **262** (1984), 913.

^f E. Perez, A. Bello, and J. G. Fatou, *Coll. Polym. Sci.*, **262** (1984), 605.

^g G. Feio and J. P. Cohen-Addad, *J. Polym. Sci. Pt B: Polym. Phys.*, **26** (1988), 389.

rate of nucleation nor the rate of growth will be invariant with respect to the extent of the transformation. The result will be a retardation of the progression of crystallization.

The introduction of the concept of impingement made a substantial improvement in terms of fitting the observed crystallization kinetics of metal and other monomeric systems to theory. However, the analysis of experimental data indicates that no significant gain is achieved over the free-growth approximation for the crystallization kinetics of polymers. Cessation of crystalline growth due to the impingement of growing centers is, thus, not a major reason for the observed reduction in the rate of crystallization with the extent of the transformation. This is true even when the incomplete transformation is taken into account by normalization procedures [137]. Other factors, that are unique to polymers, must be the source of the deviations. Chain entanglement and other topological defects seem to be very likely candidates. When the total of the fractions transformed and untransformable approaches unity

there will be an effective termination of the crystallization. There is, therefore, a cessation mechanism that is unique to long-chain molecules. This effect will be minimal during the early stages of the transformation but will manifest itself more as the crystallization progresses. Thus, in crystallization of polymers other factors can intervene, before impingement becomes important. In this connection, when crystallization from dilute solution is carried out, the derived Avrami expression is followed over the complete extent of the transformation [144]. In dilute solution, with coil separation, chain entanglement in the disordered state is no longer an important consideration.

The isotherms in Fig. 4.20 illustrate another important feature that is inherent to crystallization of polymers. A strong and dramatically negative temperature coefficient is apparent from these plots. As the temperature is decreased, the rate of crystallization becomes much more rapid. This behavior is quite the opposite of the usual case for chemical reactions. The negative temperature coefficient is rather severe. In the example given, the rate of crystallization changes by five orders of magnitude over a temperature interval of only 7 °C. This type of behavior is clearly indicative of a nucleation-controlled crystallization process [138]. It illustrates an extremely important principle that underlies and controls many aspects of the crystallization of polymers. The central role played by nucleation in crystallization of polymers will be presented in more detail when rates of growth of spherulites are discussed.

The molecular weight influences not only the level of crystallinity that can be achieved but also the timescale, or rate of crystallization. A summary of the crystallization times for fractions of linear polyethylene covering an extensive range of molecular weights and isothermal crystallization temperatures is given in Fig. 4.23 [139]. Here, on a logarithmic scale, the time for 1% of the absolute amount of crystallinity to develop, $\tau_{0.01}$, is plotted against the molecular weight. Several important features are illustrated in this figure. In the lower molecular weight range, the crystallization times decrease by several decades as the molecular weight increases. However, a minimum in the timescale, namely a maximum in the rate of crystallization, is reached. The molecular weight at the extremal depends on the crystallization temperature. For the highest crystallization temperatures the maximum in the rate occurs in the range $M = (1-2) \times 10^5$. The locus defining the maximum decreases with decreasing temperature. It is in the range $M = (1-2) \times 10^4$ for the lowest isothermal crystallization temperatures. Concomitantly, $\tau_{0.01}$ at the maximum rate decreases from about 10^4 min at 132 °C to 1 min at 123 °C. On the left-hand side of the maximum the relation between $\tau_{0.01}$ and the molecular weight is qualitatively independent of the crystallization temperature. However, for molecular weights greater than that for which the maximum rate is found, this relation is dependent on the crystallization temperature. It is important to note

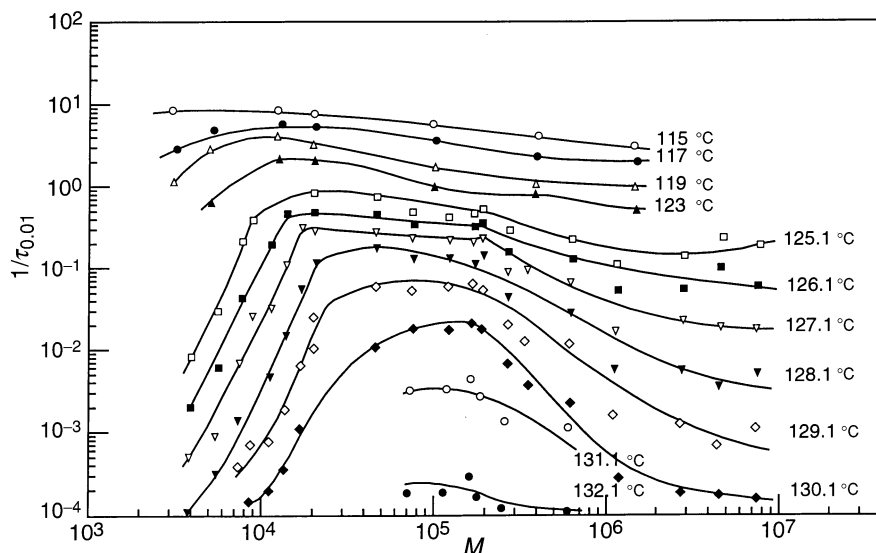


Fig. 4.23. A double-logarithmic plot of $\tau_{0.01}$ (the time taken for 1% of the transformation to occur) against the molecular weight for the crystallization temperatures indicated. From [139].

that, for the very high molecular weights, $\gtrsim 10^6$, and the high crystallization temperatures, the overall rate of crystallization is invariant with respect to the chain length. Results such as those illustrated in Fig. 4.23 are not limited either to linear polyethylene or to overall rates of crystallization. They are observed also for a variety of other polymers, in terms both of overall rates of crystallization and of rates of growth of spherulites, when an extensive range of molecular weights is studied [142, 145–151].

The discussion of the overall crystallization up to this point has been limited to temperatures in the vicinity of the equilibrium melting temperature. When the crystallization process is extended over a larger temperature range, well removed from the melting temperature, a well-defined maximum is observed in the rate. This phenomenon is illustrated in Fig. 4.24 by results from the classical crystallization studies of Wood and Bekkedahl with natural rubber, poly(*cis*-1,4-isoprene) [152]. As the crystallization temperature is lowered, the rate of growth of crystallites becomes more dominant relative to the nucleation rate. Segmental motion and transport, which are essential to growth, are reduced as the glass temperature of the polymer is approached. Consequently, there is a competition between the two mechanisms involved in the process of crystallization. The nucleation rate increases rapidly as the temperature is lowered while the rate of transport of chain segments to growing crystallites is reduced. Because of this competition, there

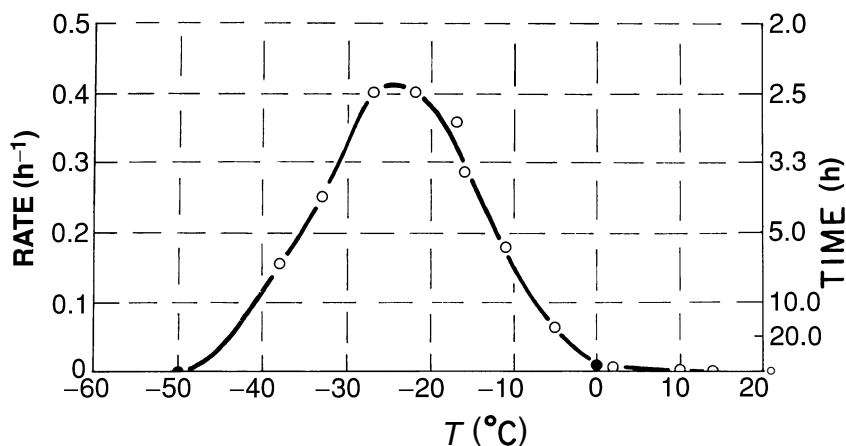


Fig. 4.24. A plot of the rate of crystallization of natural rubber, poly(1,4-*cis*-isoprene), over an extended temperature range. The rate plotted is the reciprocal of the time required for half the total change in volume. From [152].

results a maximum in the rate of crystallization. Such maxima are observed for all homopolymers as long as the rate of crystallization does not become so rapid that it cannot be recorded. Despite the extensive temperature range studied, the isotherms are still superposable.

We noted earlier that the measurement of the rate of growth of spherulites is another convenient method by which to study crystallization kinetics. Spherulites are morphological forms that are very common, but not universal, modes involved in crystallization of polymers (see later). There have been many studies of the growth of spherulites from the melt, for virtually all crystalline polymers. There are far too many of these even to attempt to enumerate. The salient features of spherulite growth are found to be common to all polymers. As an example, a plot of the radius of a growing spherulite as a function of time, for isotactic poly(styrene), is given in Fig. 4.25 [153]. For all homopolymers the radius increases linearly with time. Thus, the rate of growth $G = dr/dt$ is constant. G has a strong negative temperature coefficient in the vicinity of the melting temperature. In the data for poly(styrene) illustrated here, as well as for many other polymers, a maximum in G with the crystallization temperature is observed.

At this point it is appropriate to consider the temperature coefficient of overall crystallization and in particular that of spherulite growth. Given the observation of maxima in either type of rate study, two main factors need to be considered. One is the application of the general concepts of nucleation theory to polymers. The other involves the description of the transport of chain units across the liquid-crystal interface, the transport term.

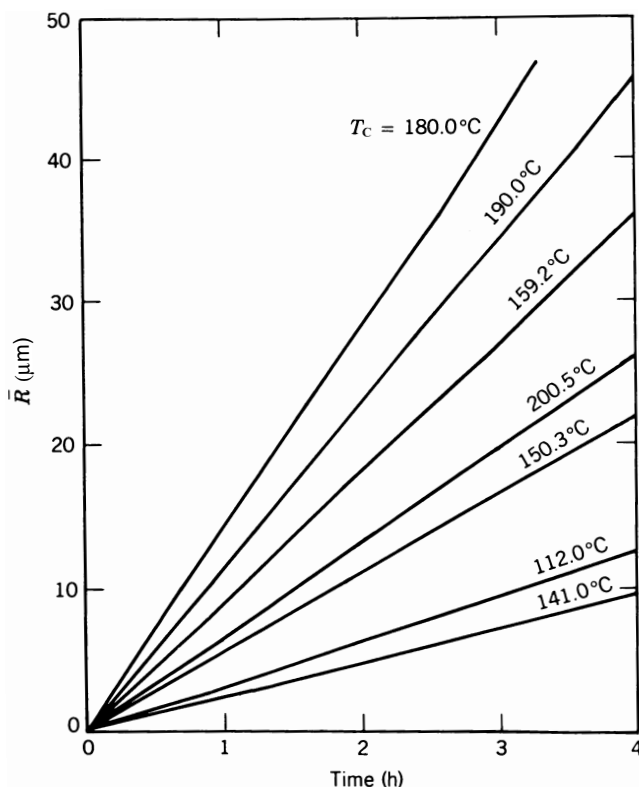


Fig. 4.25. A plot of the radius of spherulites of isotactic poly(styrene) as a function of time. From [153].

Consider first nucleation theory. Nucleation dominates in the vicinity of the equilibrium melting temperature. In principle two different types of nucleation can be operative [154, 155]. The initiation of crystallization involves primary nucleation. Crystallite growth could also be nucleation-controlled. Such nucleation is termed secondary, or growth, nucleation. Although the basic theory of nucleation is common to all classes of substances, polymers bring some unique features to the problem. These involve the dimensions of a critical nucleus relative to the length of the molecular chain and the arrangement, or conformation, of the repeating units within the nucleus. Quantitative descriptions of a variety of types of nucleation are given elsewhere [155].

Nucleation is the process by which a new phase is initiated within a parent phase. A nucleus is a small structural entity, or embryo, of the new phase. If two phases A and B of a single component are in equilibrium at T_m and if phase B has the lower free energy at temperatures below T_m , it does not necessarily follow that phase B will spontaneously form when the temperature is lowered. For a macroscopic phase

to develop, it must first pass through a stage at which it consists of relatively small particles. It is, therefore, possible for small structural entities of phase B to be in equilibrium with phase A at temperatures below T_m . This can occur because the decrease in the Gibbs free energy that normally characterizes the development of a large macroscopic phase is offset by contributions from the surfaces of the small embryo. Hence, the relative contributions of the surface area and volume, that are of opposite sign, to the Gibbs free energy of the particle, the embryo, determine its stability. Initially, there will be an increase in the free energy as the embryo grows due to the dominance of the surface contribution. However, as the growth proceeds a maximum in the free energy ΔG^* that is determined by the dimensions of the geometry of the embryo is reached. The dimensions of the nucleus corresponding to ΔG^* are those of a nucleus of critical size. As the embryo grows beyond the critical size there is a decrease in the free energy, that eventually becomes negative. Various shapes of nuclei are possible. Since the polymer molecule is asymmetric, the shape of the nucleus could be a cylinder or parallelepiped, among others. At least two surfaces will be involved. One will be parallel to the chain axis, the other normal to it. ΔG^* represents the barrier in free energy that must be overcome in order to form stable nuclei that allow crystallization to proceed.

Nuclei can be formed homogeneously in the parent phase by means of statistical fluctuation of molecular, or segmental, clusters. The formation of nuclei can be catalyzed by the action of appropriate heterogenetics. Nuclei can also form preferentially on foreign particles, walls, or cavities, as well as on the surfaces of already existing crystals. Our primary interest here, in terms of kinetics, is in the rate at which stable nuclei are formed.

The steady-state nucleation rate, N , can be expressed in its most general form as [156]

$$N = N_0 \exp\left(-\frac{E_D(T)}{RT} - \frac{\Delta G^*}{RT}\right) \quad (4.21)$$

This simple statement is applicable to all classes of substance, including polymers. In Eq. (4.21), N_0 is a constant that is only slightly temperature-dependent. E_D represents the energy of activation for the transport of chain units across the crystal-liquid interface. The Arrhenius form used in Eq. (4.21) turns out to be valid for temperatures greater than 70°C above the glass-transition temperature. This expression can then be used for studying kinetics in the vicinity of the equilibrium melting temperature. Appropriate modifications need to be made when one is analyzing kinetics over an extended temperature range (see later). As mentioned previously, ΔG^* is the change in free energy that is required in order to form a nucleus of critical size. The magnitude of ΔG^* will depend on the shape assumed

and whether a substrate is involved. There are obviously many possibilities. We consider two extreme examples to illustrate the principles that are involved.

The value of ΔG^* for a cylindrical nucleus formed homogeneously is expressed as [138]

$$\Delta G^* = \frac{8\pi\sigma_{\text{un}}^2\sigma_{\text{en}}}{\Delta G_{\text{u}}^2} \quad (4.22)$$

where Eq. (4.22) represents the high molecular weight approximation [157]. Here, σ_{un} is the interfacial free energy associated with the lateral surface and σ_{en} is that associated with the surface normal to the chain direction. A nucleus formed in this manner is termed a three-dimensional nucleus. The other type of nucleus to be considered here is due to Gibbs [158]. In this case chain units are deposited unimolecularly and coherently on an already existing crystal surface. The critical barrier height for this type of nucleus, in the high molecular weight approximation, can be expressed as [138].

$$\Delta G^* = \frac{4\sigma_{\text{en}}\sigma_{\text{un}}}{\Delta G_{\text{u}}^2} \quad (4.23)$$

The respective interfacial free energies, σ_{un} and σ_{en} , are those appropriate to forming a nucleus. They should not be identified either with the quantities σ_{uc} and σ_{ec} characteristic of the actual mature crystallite that develops or with σ_{ee} , which is appropriate to the equilibrium crystallite. It should be noted that, in either case, no assumption has been made with regard to the chain conformation within the nucleus. The formal expression for ΔG^* does not depend on the chain structure within the nucleus.

For the three-dimensional nucleus $\Delta G^* \sim 1/\Delta G_{\text{u}}^2$, whereas for the two-dimensional one $\Delta G^* \sim 1/\Delta G_{\text{u}}$. Expanding ΔG_{u} to first order about T_{m}^0 gives

$$\Delta G_{\text{u}} \simeq \Delta S_{\text{u}} \Delta T \simeq \frac{\Delta H_{\text{u}} \Delta T}{T_{\text{m}}} \quad (4.24)$$

where $\Delta T = T_{\text{m}}^0 - T_{\text{c}}$, the undercooling. The steady-state nucleation rate can then be written as

$$N = N_0 \exp\left(-\frac{E_{\text{D}}}{RT} - \frac{K_3 T_{\text{m}}^{02}}{T(\Delta T)^2}\right) \quad (4.25)$$

for three-dimensional nucleation, and

$$N = N_0 \exp\left(-\frac{E_{\text{D}}}{RT} - \frac{K_2 T_{\text{m}}^0}{T \Delta T}\right) \quad (4.26)$$

for the two-dimensional case. The change in ΔT in the vicinity of the melting temperature is the cause of the large negative temperature coefficient that is observed.

The constant K_3 in Eq. (4.25) specifies several quantities. These are the geometry of the nucleus, whether it is formed homogeneously or heterogeneously, and the enthalpy of fusion per repeating unit. The constant K_2 plays a similar defining role for two-dimensional nucleation.

Assuming that the linear rate of growth of spherulites G is nucleation-controlled in the vicinity of T_m , it can be written as

$$G = G_0 \exp\left(-\frac{E_D}{RT} - \frac{g_3 T_m^{02}}{T(\Delta T)^2}\right) \quad (4.27)$$

$$G = G_0 \exp\left(-\frac{E_D}{RT} - \frac{g_2 T_m^0}{T \Delta T}\right) \quad (4.28)$$

for three- and two-dimensional nucleations, respectively. Utilizing the Arrhenius form for the transport term limits the range to temperatures 70 °C and more above the glass-transition temperature. Attention is focused on the rate of growth of spherulites when only one nucleation process is involved. The analysis of the temperature coefficient for overall crystallization is more complex since both nucleation and growth are involved in this case and they can in general be different from one another.

Before applying the above analysis to experimental results, there are several important factors than need to be kept in mind. As was pointed out above, except for constant factors the value of ΔG^* is independent of the chain conformation. Thus, any type of chain structure that is used to analyze the temperature coefficient of growth is merely an assumption. This is true, irrespective of whether the chains in the nucleus are bundle-like, regularly folded, or, in fact, of any other type. Put another way, a definitive chain structure, or chain conformation, within the nuclei cannot be deduced safely from an analysis of the temperature coefficient of growth.

It has also been shown quite definitively that, within the precision of the kinetic data that are available, no decision can be made regarding whether a two- or three-dimensional nucleation process is operative [138]. This conclusion is true for virtually all polymers that have been studied. This is admittedly a rather frustrating situation, since nucleation plays such an important role in crystallization of polymers. In analyzing the kinetic data we shall for convenience utilize the Gibbs two-dimensional-nucleation model. The same general conclusions are reached if instead three-dimensional nucleation is assumed. In what follows, no assumptions are made with respect to the chain structure within the nucleus.

In analyzing experimental data as many different types of polymer will be used as is practical. Accordingly, the growth rate G is plotted against the temperature function for nucleation, $T_m/(T \Delta T)$ for poly(ethylene oxide) [159] and poly(chlorotrifluoroethylene) [160] in Figs. 4.26 and 4.27, respectively. The

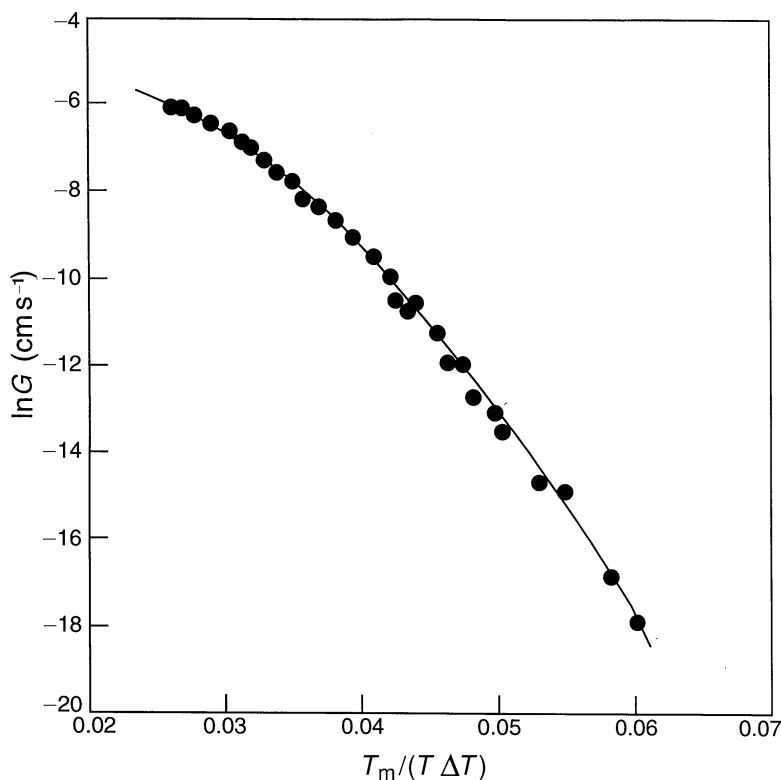


Fig. 4.26. A plot of $\ln G$ against $(T_m/T)(1/\Delta T)$ for a molecular weight fraction of poly(ethylene oxide), $M = 152\,000$. From [159].

accepted values of T_m^0 were used in preparing these two figures [161]. On examining these representative plots it is found that, contrary to expectation from the theory developed so far, the data in each case cannot be represented by a single straight line. The data for each polymer are represented well by a continuous curve. Similar results are obtained if the overall rates of crystallization, in terms of $\ln(1/\tau)$, are analyzed. The range of crystallization temperatures that has been studied up to this point is important. None of the polymers at present under discussion exhibits a maximum in the rate of crystallization. The temperature range that can be studied with some polymers is severely restricted. For example, the rates of growth of spherulites of linear polyethylene are limited to a range of 6–8 °C in crystallization temperature.

The representative plots in Figs. 4.26 and 4.27 present a serious dilemma that needs to be resolved before any progress in understanding crystallization kinetics can be made. This is a fundamental concern that lies well beyond how best to represent the data. In the temperature range of present interest, attention will be

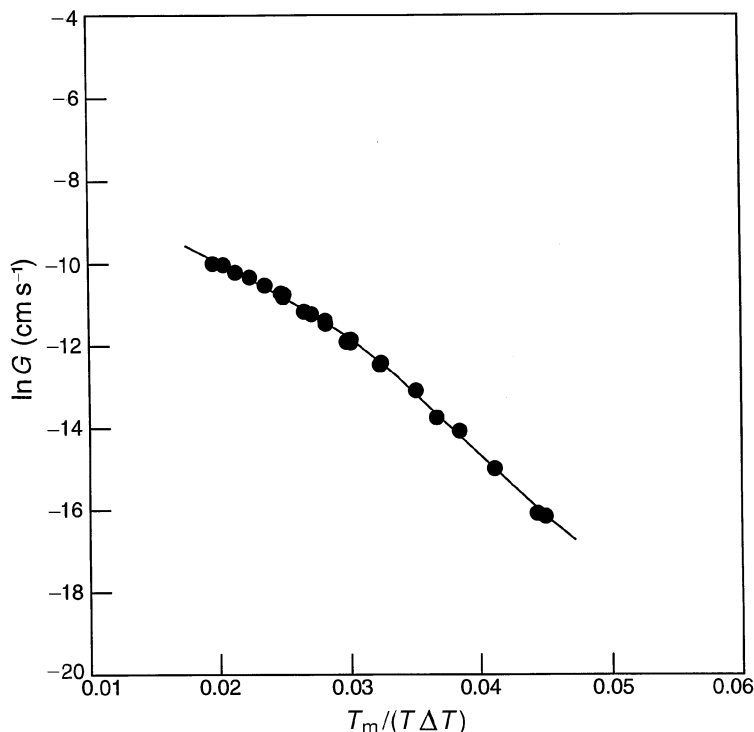


Fig. 4.27. A plot of $\ln G$ against $(T_m/T)(1/\Delta T)$ for a molecular weight fraction of poly(chlorotrifluoroethylene). From [160].

focused on any shortcomings in the nucleation term. The role of the transport term is best considered when crystallization over the entire accessible temperature range has been examined.

A key factor in considering growth by successive acts of nucleation on a crystal surface is the relation between the rates of nucleation and of the spreading of the chain in directions normal to its axis. This problem was addressed by several investigators treating the similar problem for monomeric systems [148, 162, 163]. The magnitudes of the rates of nucleation and spreading will be different and they will have different temperature coefficients. The rate of spreading will be designated g . The relationship between these two rates with undercooling leads to some interesting situations. In one case, at low undercoolings, the rate of spreading is much greater than the nucleation rate. Hence, under these conditions, a given growth layer will be completed before a new one is initiated. This temperature region corresponds to unimolecular nucleation, which was discussed above. This region is termed regime I in the literature [164]. As the temperature is lowered the rates of nucleation and spreading will become comparable to one another. Therefore, several acts of nucleation will take place on the same crystallite surface before a

given layer is filled and growth can proceed. This situation is termed regime II. In another case, which is limited to very large undercoolings, both ΔG^* and the sizes of nuclei are extremely small and essentially constant with the crystallization temperature. Thus there is only a limited small area, or niche, into which a nucleus can grow. The rate of spreading will, therefore, be retarded in the direction normal to the chain axes. This low-temperature region has been termed regime III [165]. There are, therefore, several possible reasons for the nonlinearity of the data in Figs. 4.26 and 4.27. The possible influence of regimes I and II at low to moderate undercooling will be discussed first. Since regime III is postulated to occur at larger undercoolings, it will be examined when rates of growth of spherulites over an extended temperature range are discussed.

The physical situations that describe regimes I and II appear to be quite reasonable. The issue involved is not their existence but the nature of the transition between the two regimes. In particular, is the transition sharp or diffuse? If it is diffuse, how broad is the transition? In adapting the results obtained for monomeric substances, one can make the assumption that the rate of spreading in the chain direction is severely retarded relative to that in the lateral direction. This is a reasonable assumption for chain molecules, irrespective of the chain conformation within the nucleus. With this assumption, the results for small molecules can be adapted to polymers, resulting in a two-dimensional problem [166–168]. It is found that the rate of growth in regime I, $G(I)$, can be expressed as

$$G(I) = bLN \quad (4.29)$$

The rate of growth in regime II, $G(II)$, can be expressed as

$$G(II) = b(Ng)^{1/2} \quad (4.30)$$

In the above L is the lateral dimension of the substrate, or crystal face, and b is the chain width.

Equations (4.29) and (4.30) represent the two extreme situations that have been treated. They should be considered as asymptotes for the physical situations described by regimes I and II. The nucleation term should dominate in the vicinity of T_m . Therefore,

$$\frac{d \ln G(II)}{d(T\Delta T)^{-1}} \bigg/ \frac{d \ln G(I)}{d(T\Delta T)^{-1}} = \frac{1}{2} \quad (4.31)$$

and the temperature coefficients of the rates of growth in the two regimes will differ by a factor of two for these extremes. Thus, it is not surprising that typical growth-rate data, such as those illustrated in Figs. 4.26 and 4.27, do not adhere to the simple formulation given by Eq. (4.28). The physical situations described by Eqs. (4.29) and (4.30) merely represent extreme, or asymptotic, situations. However,

the transition from one regime to the other has tacitly been assumed to be sharp. Experimental data have been analyzed from this point of view. A slope ratio of two (within experimental error) is required in order to satisfy the criteria for a sharp transition [164, 169]. However, there has been concern that the transition is so diffuse that in fact the two regimes as such might not exist [170–172]. This problem has been resolved by adapting Frank's theory [173] to experimental data.

The analysis according to Frank's theory indicates that Eqs. (4.29) and (4.30) are appropriate asymptotes for regimes I and II, respectively, and have the proper slope ratio. The transition from regime I to regime II is in fact diffuse, with the diffuse interval depending on the polymer. For example, the diffuse range is 4 °C for poly(ethylene oxide), 6 °C for poly(trichlorofluoroethylenes), 8 °C for poly(dioxolane), and 1–2 °C for linear polyethylene. Other polymers give very similar results. It is possible in several cases to draw two intersecting straight lines through the data. However, the slopes do not have the ratio of two required for a regime transition. The diffuse nature of the I–II transition, as predicted by the Frank theory, is well established for many polymers. Linear polyethylene, a polymer that has been studied extensively in this regard, is atypical since it exhibits a relatively sharp transition.

With the introduction of the concept of these regimes the spherulite-growth-rate data can be given a straightforward explanation in terms of nucleation theory. It is important to bear in mind that the principle governing the I–II regime transition is not limited to polymers. It is equally applicable to low molecular weight substances. For long-chain molecules a regularly folded chain conformation within the nucleus is not required in order to observe this regime transition.

When crystallization is conducted over an extended temperature range, most, but not all, homopolymers display maxima in rates both of spherulite growth and of overall crystallization. The rate maximum was illustrated in Fig. 4.24 for the crystallization kinetics of natural rubber. The main points that need to be addressed here are the reality of a transition from regime II to regime III and the basis for the maximum in the rate. The analysis proceeds in the same way as for the case of low undercooling, except that the Arrhenius expression for the transport terms fails about 70 °C above the glass-transition temperature. In its stead, the Vogel expression that has been useful in explaining the bulk viscosities of glasses can be used [174]. With this assumption the rate of growth of spherulites over an extended temperature range can be expressed as [164]

$$G = G_0 \exp\left(-\frac{U^*}{T - T_\infty}\right) \exp\left(-\frac{KT_m^0}{T_c \Delta G_u(T)}\right) \quad (4.32)$$

The particular regime involved remains undefined at the moment. Since crystallization over a large temperature interval is involved, the temperature dependences

of the interfacial free energies, embodied in K , and of ΔG_u need to be taken into account. The latter can formally be expressed by the further expansion of $\Delta G_u(T)$ about T_m^0 utilizing the appropriate derivatives of the specific heats. An empirical relation based on several assumptions has also been proposed [175]. In the analysis of experimental results that follows, these corrections, although proper, do not greatly affect the interpretation of results.

In the above equation T_∞ is the temperature at which molecular and segmental motion ceases. It can be defined in terms of the glass-transition temperature T_g as

$$T_\infty = T_g - C \quad (4.33)$$

Hence, U^* and C are constants unique to a given polymer and cannot be specified *a priori* [176]. Equation (4.32) can then be conveniently written as

$$G = G_0 \exp\left(-\frac{U^*}{T - T_g + C}\right) \exp\left(-\frac{KT_m^0}{T \Delta T}\right) \quad (4.34)$$

Several points need to be kept in mind when one is applying Eq. (4.34) to experimental results. The Vogel equation represents viscous flow and is global in character. On the other hand, the transport involved in crystallization of polymers takes place across a boundary and is thus localized. The form of the Vogel expression is what is important in the present context. It is not necessary that the parameters be the same as those involved in viscous flow. It should also be recognized that Eqs. (4.33) and (4.34) do not represent any basic theory. These equations represent the result of introducing a set of assumptions into the well-established Turnbull–Fisher theoretical expression for the steady-state nucleation rate. The assumptions inherent in the formulation of Eqs. (4.33) and (4.34) are the Gibbs-type nucleus and the Vogel expression for segmental motion. With this understanding of the basis of Eqs. (4.33) and (4.34) one can examine appropriate experimental data.

We take as an example the rate of growth of spherulites of isotactic poly(styrene), which has been studied extensively over a wide temperature range by many investigators. The results of Miyamoto *et al.* [177] serve as a good example since the data encompass a large temperature range, extending to 13 K above T_g and 22.4 K below T_m . The analysis of these results according to Eq. (4.34) is given in Fig. 4.28. Here the points represent the experimental data and the curve is drawn according to Eq. (4.34) with $U^* = 1499$ and $C = 39$, which are arbitrary, but reasonable, parameters. Figure 4.28 reveals that good agreement between theory and experiment was achieved. There is no evidence in this plot of a transition from one regime to another. Similarly good agreement with Eq. (4.34) is found with many other polymers that exhibit a maximum rate of crystallization. However, the values of U^* and C vary from polymer to polymer.

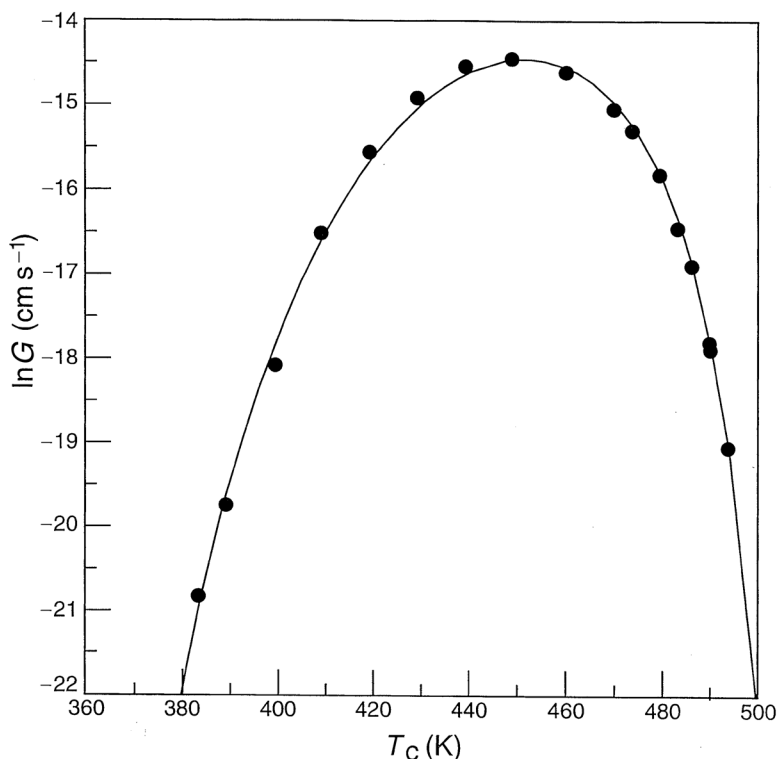


Fig. 4.28. A plot of $\ln G$ against the crystallization temperature, T_c , for isotactic poly(styrene). The solid curve is according to Eq. (4.34) with $U^* = 1499$ and $C = 39$. The solid circles show experimental results from [177].

The situation is not as simple as it appears, however, as is illustrated in Fig. 4.29. In this figure Eq. (4.34) is plotted in the form $\ln G + U^*/[R(T - T_\infty)]$ against $T_m^0/(T \Delta T)$. The data are the same as those used in Fig. 4.28. It is found that, with changes in the values of U^* and C , a discontinuity can be observed in the plots. The solid squares represent the results obtained using the same values of U^* and C as in Fig. 4.28. Obviously a straight line results. However, when U^* is increased from 1499 to 1525 cal mol⁻¹ and C reduced from 39 to 36, a discontinuity appears in the plot, as indicated by the open circles in Fig. 4.29. As the constants are varied the data can be represented by two intersecting straight lines. For the set of constants $U^* = 4120$ cal mol⁻¹ and $C = 74$ the slope ratio of the two intersecting straight lines is two. This ratio corresponds exactly to a sharp II–III regime transition. Similar results are found for all other polymers in this category.

The analysis of spherulite growth-rate data over an extended temperature range thus presents a major dilemma. There are two conflicting results from the above

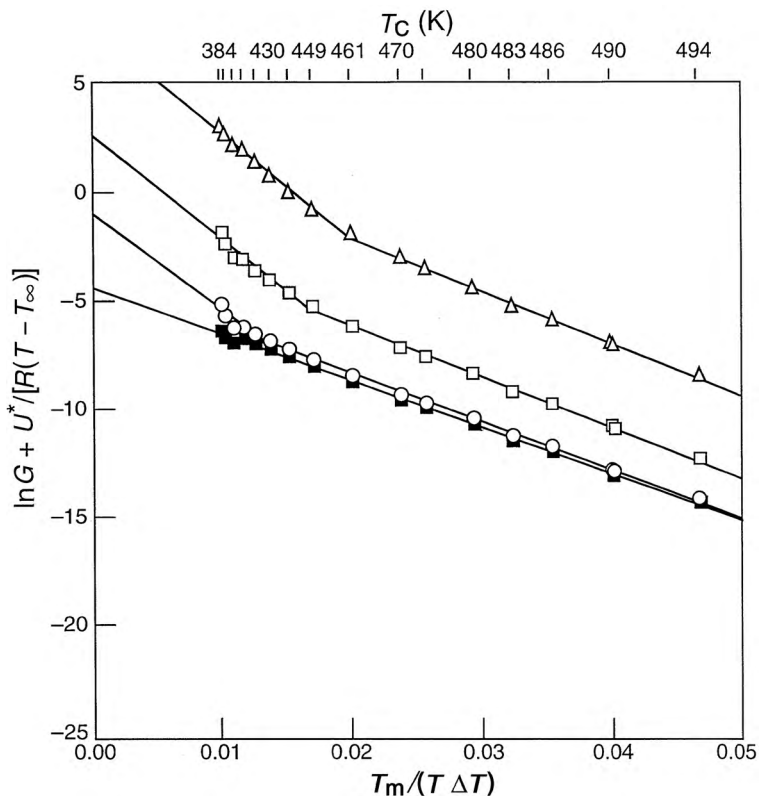


Fig. 4.29. A plot of $\ln G + U^*/[R(T - T_\infty)]$ for isotactic poly(styrene): $\blacksquare$ $U^* = 1499$ and $C = 39$; $\circ$ $U^* = 1525$ and $C = 36$; $\square$ $U^* = 2300$ and $C = 48$; and Δ $U^* = 4120$ and $C = 74$. Data are from [177].

analysis. In one case there is no evidence for a regime transition and the crystallization takes place in regime II. In the other case, there is a set of reasonable constants for a given polymer that allow the data to adhere exactly to a III–II regime transition. The reason for this problem is that the values of the constants U^* and C are not known *a priori* for any polymer. They are unique to each polymer. Unfortunately, there is in fact no set of universal constants, although its existence has often been proposed [164, 176].

The physical basis for the existence of regime III is quite plausible [165]. The nucleation rate continuously increases with decreasing temperature. At large undercoolings the rate is very rapid, resulting in a profusion of very small nuclei. Consequently there is not very much space into which nuclei can spread and grow, i.e. the rate of spreading is effectively zero. There is then a temperature region within which the steady-state nucleation rate is the dominant factor and the expression for the growth rate becomes the same as that for regime I. The physical validity

of this region is not in question. Rather it is a matter of whether a definite, sharp transition between regimes II and III occurs, with the appropriate slope ratio, or whether the changes are gradual and diffuse. Even with the large amount of suitable experimental data that is available, it is difficult to make an objective choice without prior knowledge of U^* and C for each polymer. Independent experiments are needed in order to determine these two quantities. Thus, there is a formidable problem that needs to be resolved.

There are a few polymers, such as poly(butylene terephthalate) [178], poly(trimethylene terephthalate) [179], poly(pivalolactone) [180, 181], poly(methylene oxide) [182], linear polyethylene over an extended temperature range [183–185], and isotactic poly(propylene) [186–190], that crystallize in a temperature interval well removed from T_m^0 , for which III–II regime transitions have been reported but without a maximum in the rate. There are many problems associated with the proper assignment of this transition. A major problem is the correct selection of the equilibrium melting temperature. This turns out to be a crucial matter.

Another matter of interest is the relationship between the temperature maximum, $T_{\max}$, in the rate of crystallization and the equilibrium melting temperature. The analysis of extensive experimental data for the rates of growth of spherulites and overall crystallization shows that

$$T_{\max} = (0.82 \pm 0.005)T_m^0 \quad (4.35)$$

for both cases [191]. This conclusion can be explained in a natural manner by use either of the Arrhenius expression or of the Vogel expression for the transport term [191–193].

4.5 Structure and morphology

4.5.1 General aspects

Since the basic framework of the subject, involving the thermodynamics of fusion and crystallization kinetics, is reasonably well established, one might logically and properly ask why there are problems that still remain to be resolved. One way to address this question is to consider the crystallization of a normal hydrocarbon with less than about 100 carbon atoms per molecule. For such normal hydrocarbons, it is well known that crystallization will take place very rapidly on lowering the temperature only infinitesimally below the equilibrium melting temperature. On the other hand, in order to crystallize the polymeric analog, linear polyethylene, one has to reduce the temperature well below the melting temperature even for a low molecular weight fraction. In the former case, the chains are completely extended and molecular crystals are found since each molecule is of exactly the

same length. Molecular crystals cannot develop in polymers even for the best-fractionated samples, since there will always be a distribution of chain lengths. Thus, the crystallization of long-chain molecules will occur at finite or reasonable rates only at large undercoolings, i.e. 20–40 °C below the melting temperature. As a consequence, with polymers a polycrystalline system that is only partially crystalline or semicrystalline is formed. For low molecular weight fractions containing up to several hundred chain atoms, it is possible to form extended, but not molecular, crystals. Higher molecular weight polymers usually form folded structures¹ (see later). The crystallite structure, as well as the associated morphology, is complex. It is these structures and morphological features that actually determine properties. The well-known fact that polymers can crystallize at a finite rate only under conditions well removed from equilibrium presents the basic problem. Therefore, in order to describe and understand properties, we have to deal with a very morphologically complex non-equilibrium or metastable system. These considerations bring us to the more modern aspects of the problems involving the crystalline state in polymers, i.e. the relation between structure and properties. We focus our attention on the relationship between the molecular morphology and the properties of homopolymers crystallized from the pure melt. The principles that will be established can be, and have been, extended to include polymer–diluent systems, polymer–polymer mixtures, and the various types of copolymers. Crystallization under an applied stress, or oriented crystallization, presents another distinct area that will not be discussed here.

Before proceeding, what is meant by structure and morphology should be described in more detail. The problem can be simplified by examining various levels of hierarchy in the structure: the unit cell, the crystallite, the noncrystalline region, and the supermolecular structures. The unit cells are essentially the same as those found in the conventional crystallography of low molecular weight substances. The crystallite structure, resulting from the polycrystalline nature of the system, involves a description of the structure of the actual crystallite, its associated interfacial region or zone, and the interconnections, if they exist, between crystallites. The supermolecular structure is concerned with organization of the crystallites into larger structures.

The determination of the unit-cell structure can be treated in a classical manner. The problem was initially thought to be a very complicated one. However, it became simplified when it was recognized that the whole of a long-chain molecule need not be in the unit cell. The deduction of the unit cell has not presented any major interpretative problems. In most cases the chains are parallel to one another in the

¹ Normal hydrocarbons with more than about 150 carbon atoms can also form folded structures under appropriate conditions.

unit cell. An interesting exception is the γ polymorph of isotactic poly(propylene), in which the chains are not parallel [194]. In contrast, the elucidation of the crystallite structure, particularly the interfacial region, has been a controversial, and, unfortunately, divisive matter for many decades. However, a rational analysis and resolution of this problem appears to be finally at hand. Systematic study of the supermolecular structure has also evolved, particularly by incorporating the specification of the various kinds of superstructures that can develop under different conditions of crystallization and their influence on properties.

It is important that we recognize that the molecular morphology differs in a very important and significant way from what one might term the gross morphology. Both of these concepts are important, however. The gross morphology is observed and characterized by direct microscopic examination; it specifies the form and shape of the structures of interest. The molecular morphology is a description of the arrangement and disposition of the chain units which are consistent with the gross morphology. Obviously, the molecular morphology cannot be observed directly. These two morphological descriptions must be consistent with one another.

4.5.2 Crystallite structure

We now direct our attention to the problems of crystallite structure. It is well established and accepted that a lamellar-like crystallite habit is the characteristic gross morphological form developed by homopolymers during crystallization from the pure melt. Such lamellar structures were initially observed for crystallites formed from dilute solution. The characteristic thin lamellar habit for solution-formed crystals is shown in Fig. 4.30 for linear polyethylene. Such structures have now been observed for all homopolymers studied and can be taken to be a universal mode of crystallization of homopolymers. Details of the external shape of the platelet-type crystals depend on the polymer, the solvent medium, and the crystallization temperature [195]. These crystallites possess some important features. The lamellar thickness of dilute-solution-formed crystals is of the order of 100–200 Å, depending on the crystallizing solvent and temperature. The chain axes are preferentially oriented perpendicular to the basal planes of the lamellae. Such crystal habits are found in very high molecular weight polymers. Since the thickness of the crystallites in the chain direction is only of the order of 100–200 Å, a single chain must traverse the crystallite from which it originates many times. The detailed nature of the interface that develops is quite important and unique. The interfacial structure is not obvious and cannot be deduced solely from the results of microscopic studies. It is important to emphasize that, despite the esthetic pleasantness of the crystallites shown in Fig. 4.30, the interfacial structure is not at all apparent from such images.

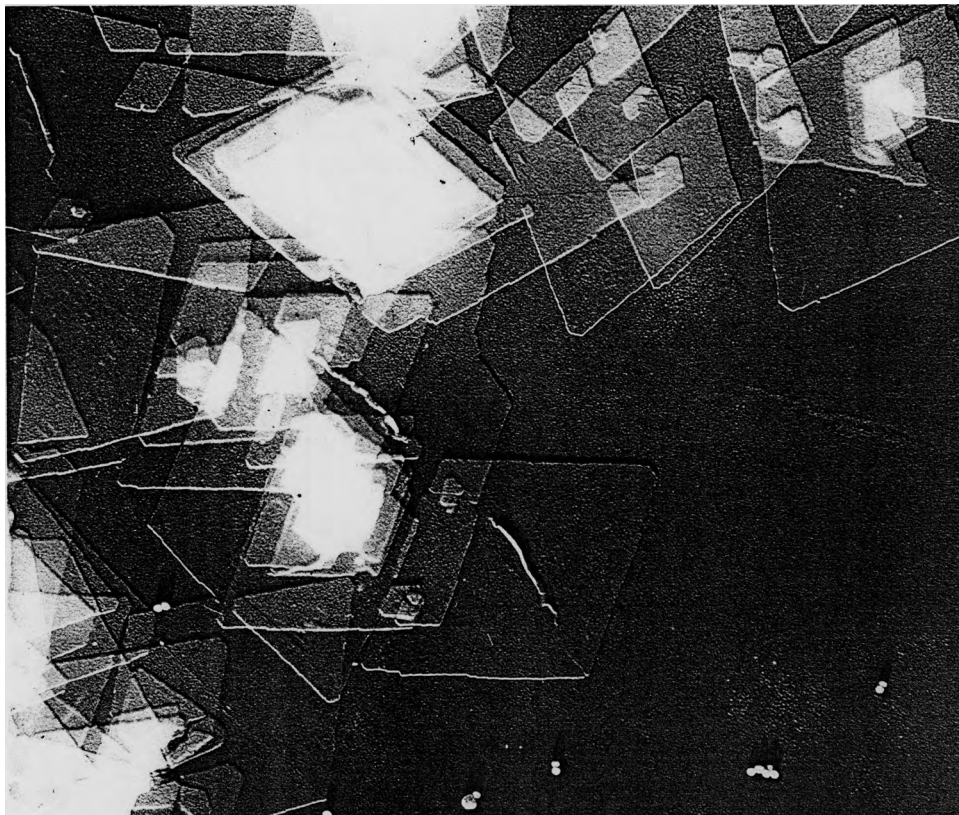


Fig. 4.30. A typical electron micrograph of lamellae formed by homopolymers crystallized from dilute solution. The example illustrated is for linear polyethylene.

Although we will not dwell in any detail on the properties of solution crystals in this chapter, it is important to recognize that electron-microscope observations of this kind do not lend themselves to a description of the interfacial structure on a molecular level. The gross morphological form and the orientation features are, however, well established. The molecular interfacial structure is consistent with several extremes, as is schematically indicated in Fig. 4.31 [196].

In one extreme, termed the regularly folded-adjacent-re-entry structure, the molecular chains appear to be accordion-like, making precise hairpin turns in order to yield the optimum level of possible crystallinity. However, equally consistent with the gross morphological features is the other model illustrated. Here, there is a distinct, disordered, amorphous overlayer. This schematic representation has popularly been termed the “switchboard” model. Both of these interfacial structures, and those in between, are consistent with the electron micrographs. The reason for introducing these concepts here is that a lamellar-type crystallite is also the universal mode of crystallization of a homopolymer from the pure melt.

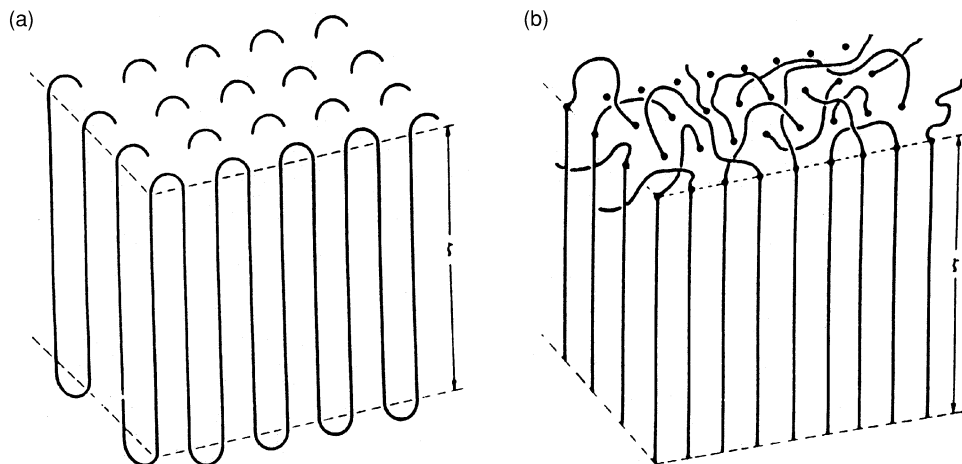


Fig. 4.31. Schematic diagrams of possible chain structures within lamellar crystallite. Key: (a), regularly folded array and (b), nonregularly folded chains; loop lengths are variable. Reproduced from [196]. Copyright 1962, American Chemical Society.

The first observations of lamellae in bulk crystallized systems were obtained by surface-replica electron microscopy. Unfortunately, the thicknesses of the lamellae in this case were only in the range 100–200 Å. These dimensions were originally thought to be typical of, and unique to, the crystallites formed during bulk crystallization. We know now that lamellar thicknesses, depending on molecular weight and crystallization temperature, can range up to 1000 Å or more, even when polymers are crystallized at atmospheric pressure. Even larger thicknesses can be obtained after crystallization at higher temperatures and pressures [197]. Since the crystallite thickness in this early work is about the same as that of solution crystals, a connection and identification between the two situations was immediately made. It was proposed that the lamellar crystallites observed in bulk crystallized polymers were comprised of regularly folded chains that formed a smooth interface, i.e. the scheme of Fig. 4.31(a) was followed. Moreover, it was also postulated that there were no molecular connections between crystallites. To put matters in another way, it was argued, principally on the basis of gross morphological observations, that noncrystalline regions did not exist. The deviation in properties, such as the density and enthalpy of fusion, from those of the completely crystalline polymer was attributed to internal defects within the crystal [198, 199].

Lamellar-type crystallites are widely recognized and universally accepted as the characteristic mode for bulk crystallization of homopolymers. Surprisingly, copolymers up to a relatively high co-unit content also form lamellar crystallites [200, 201]. The visual observation of lamellae, or even the occasional viewing of defined sectors within lamellae, is not a license to describe the interfacial structure,

the presence or absence of connecting regions, their structure if there is one, or even the type and concentration of internal defects. The apparent geometric regularity perceived by the electron microscope is a gross morphological observation, and an important one. However, it cannot be taken by itself as evidence for any detailed structure on a molecular level. This fact, unfortunately, has not always been recognized. The observation of lamellae *per se* gives us no detailed information about the disposition and arrangement of the chains within the crystallites. Results from selected-area-diffraction studies tell us only about the chain orientation.

The character of the lamellae and their arrangement relative to one another are dependent on the molecular weight and the crystallization temperature. As an example, some thin-section electron micrographs of a set of rapidly crystallized linear polyethylene fractions, for $M = 5.6 \times 10^3$ to $M = 1.89 \times 10^5$, are shown in Fig. 4.32 [202]. The samples of lower molecular weights exhibit stacked lamellae,

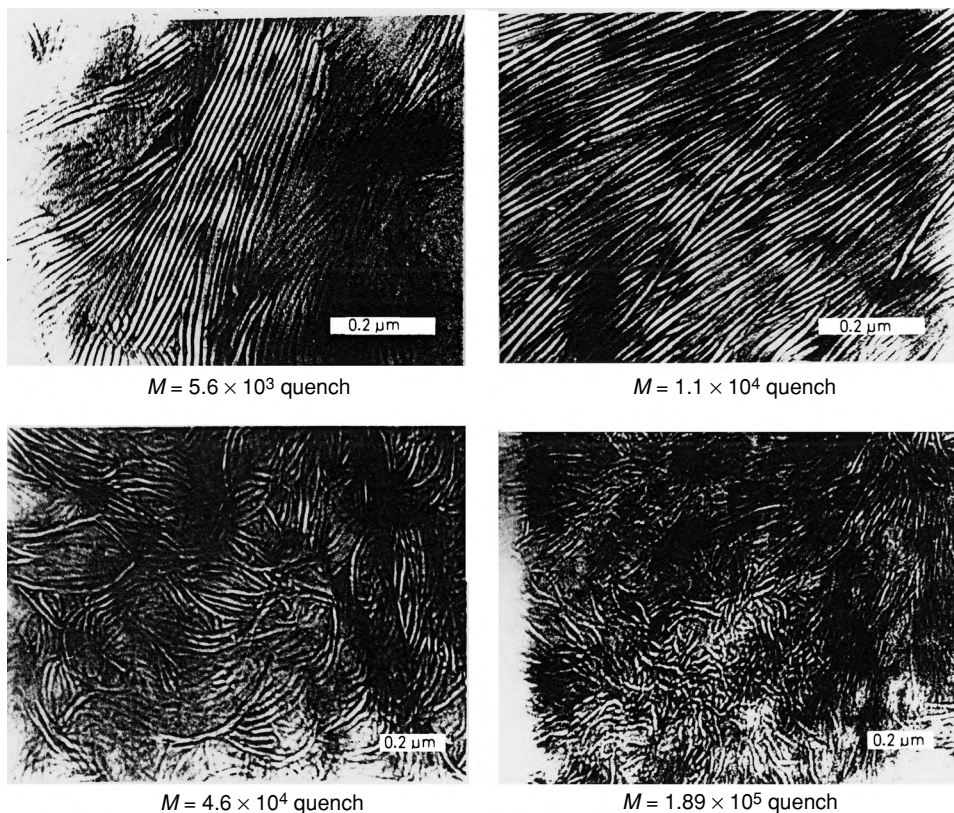


Fig. 4.32. Typical transmission electron micrographs of quenched linear polyethylene fractions for indicated molecular weights. Reproduced from [202] with permission. Copyright 1984, John Wiley & Sons, Inc.

each of the order of 100 Å thick. Their lateral extent is remarkably long, several micrometers. There is little evidence of segmentation within the lamellae. As the molecular weight increases the lamellar thickness does not change appreciably. However, the lateral dimensions decrease dramatically, as the lamellae become more curved. In addition the lamellae become segmented. For very high molecular weights, $(1-6) \times 10^6$, only short segments of crystallites are observed. The contrast is poor in this case, so the micrographs cannot be properly reproduced and are not shown here.

The influence of the crystallization temperature on the lamellar structure of a fraction of fixed molecular weight ($M_w = 1.89 \times 10^5$, $M_n = 1.79 \times 10^5$) is illustrated by a set of electron micrographs in Fig. 4.33 [203]. These micrographs demonstrate the gradual deterioration of the well-defined lamellar organization as the crystallization temperature is lowered. There is a systematic degradation of the crystallites from well-developed long lamellae formed at the high crystallization temperatures

(a)

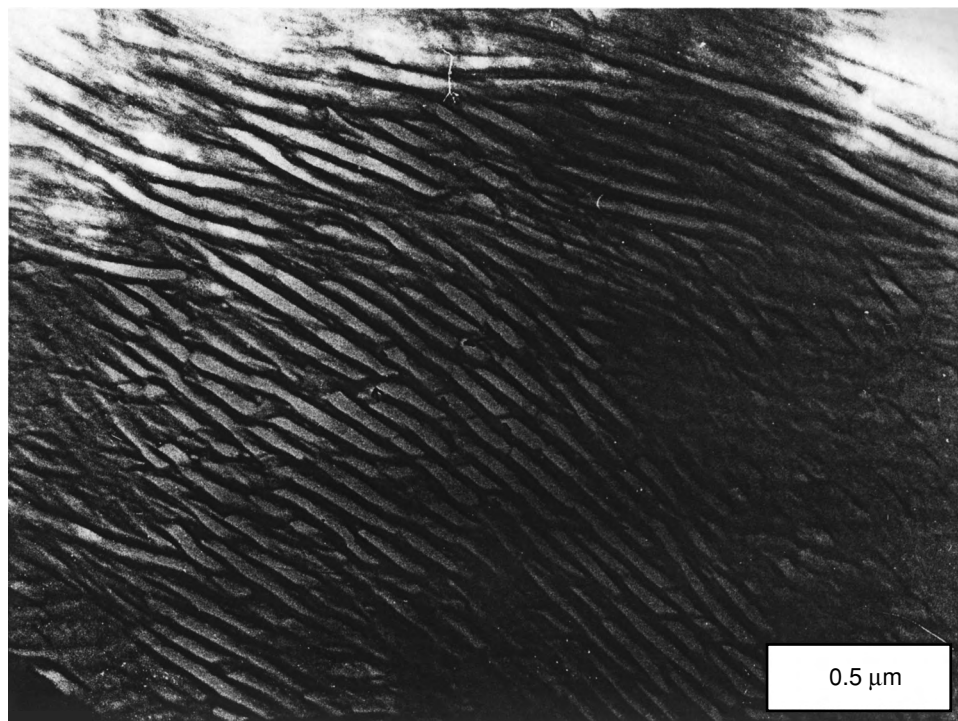
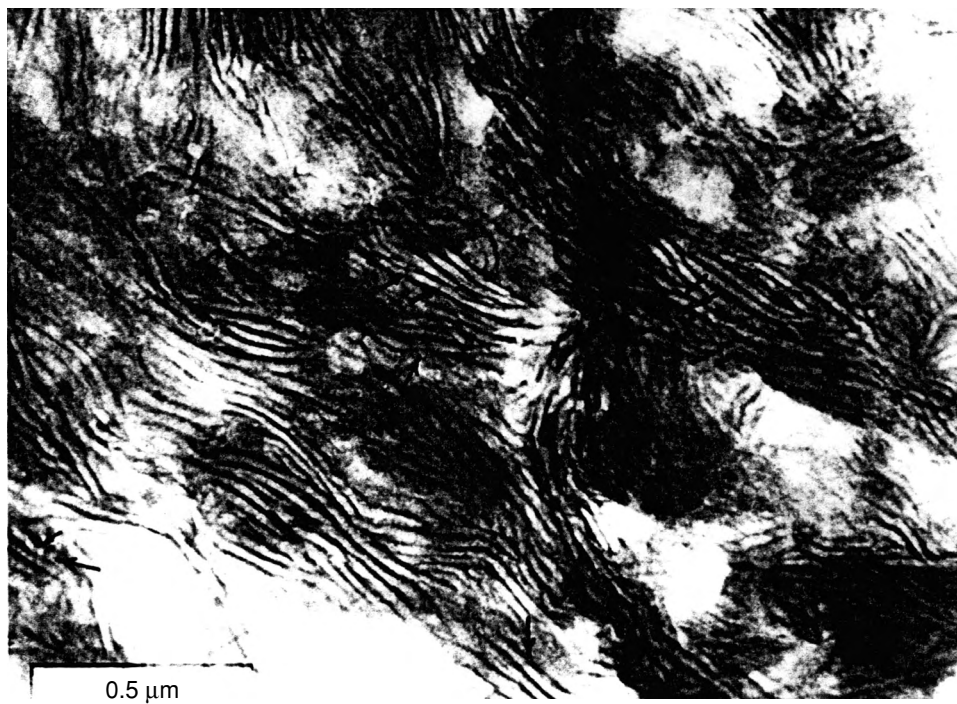


Fig. 4.33. A transmission electron micrograph of a linear polyethylene fraction crystallized at indicated temperatures T_c . (a) $T_c = 131.2^\circ\text{C}$, (b) $T_c = 116^\circ\text{C}$, and (c) $T_c = 100^\circ\text{C}$. Reproduced from [203] with permission. Copyright 1981, John Wiley & Sons, Inc.

(b)



(c)

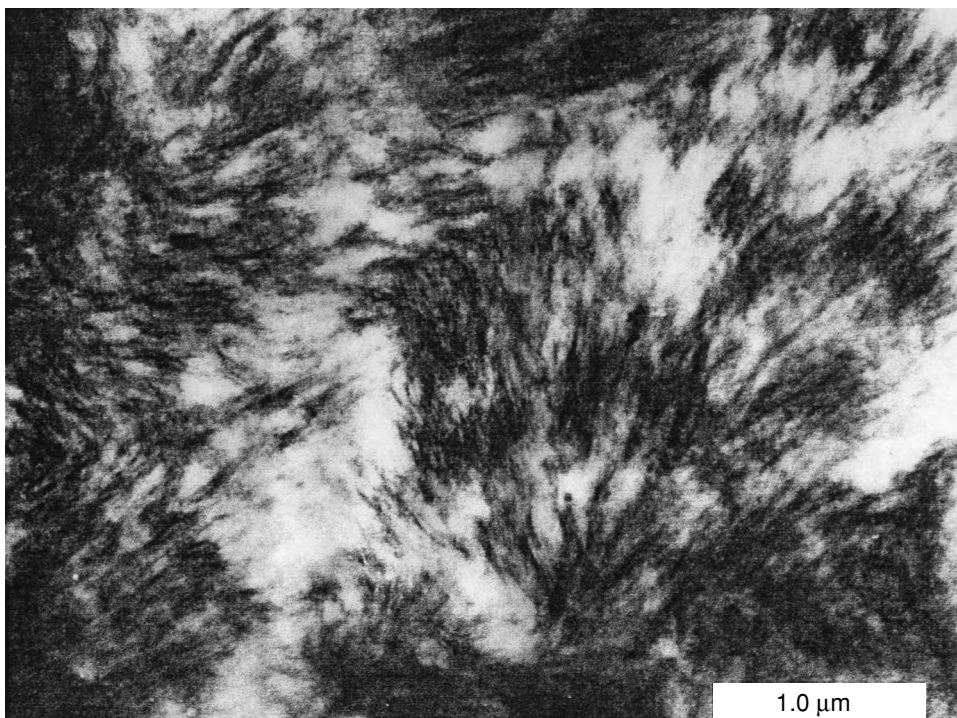


Fig. 4.33. (*Contd.*)

to short, curved lamellae at the lower temperature. Other fractions behave in a similar manner. However, for very high molecular weights, $(1-6) \times 10^6$, curved lamellae are observed even after isothermal crystallization at high temperature [204].

It is widely recognized that bulk crystallized samples exhibit major deviations in thermodynamic and other properties from those of the perfect crystal. In addition to the thermodynamic properties, these include, among others, haloes in the wide-angle X-ray-scattering pattern, the nature of the infrared and Raman spectra, and proton and carbon-13 NMR spectra. We shall discuss some of these examples in more detail subsequently. It was thought that these deviations could be accounted for by contributions from the smooth interface, since small crystals are involved, as well as by a major contribution from defects believed to exist within the interior of the crystallite. A crystalline polymer was viewed as consisting of disordered material, or defects, embedded within a crystalline matrix [198, 199]. Chain units in non-ordered conformations, which would connect crystallites, did not exist in this view. The implication of these ideas, or, stated more positively, the establishment of the structure of the crystallite on a molecular level, as opposed to the unit cell, is a crucial matter. It goes to the heart of the relationships among structure, morphology, and properties.

There is a set of independent structural variables that are important for analyzing the crystallite and related structures. These can be related to properties [205]. These variables are the degree of crystallinity; the structure of the residual or liquid-like isotropic regions, i.e. the region between lamellae; the crystallite thickness distribution; the extent and structure of the interfacial region; and the internal structure of the lamellar crystallites. There are two classes of variable involved. One is the molecular constitution, which is concerned with the molecular weight, polydispersity, and structural regularity of the chain. The other is the set of structural variables that were just described. These variables serve as the basis of relating structure to properties. There is a synergistic effect among the independent structural variables, the molecular constitution of the chain, and the crystallization conditions. We examine these structural factors in detail, including their identification and quantitative description.

4.5.3 The degree of crystallinity

Results obtained using a variety of experimental methods have conclusively demonstrated that the degree of crystallinity is a quantitative concept. These methods include measurements of density and enthalpy of fusion, infrared and Raman spectroscopies, wide- and small-angle X-ray scattering, and proton and carbon-13 NMR. The basic principle involved is the assigning of a specific value of the quantity of interest to each element of the phase structure. In general, there is qualitative

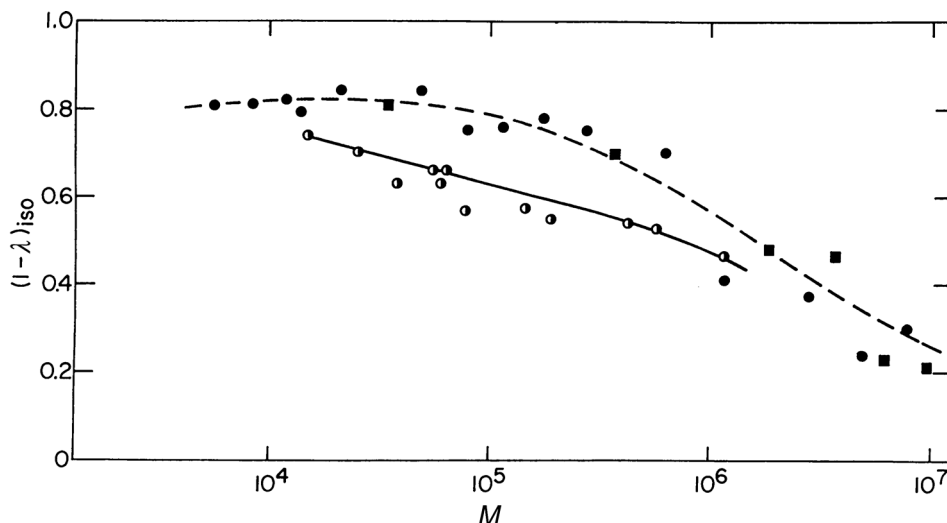


Fig. 4.34. The level of crystallinity as a function of the molecular weight under isothermal crystallization conditions: ● linear polyethylene; □ poly(ethylene oxide); ○ poly(tetramethyl-*p*-silphenylene siloxane). From [205].

agreement among results obtained with the various methods. However, small but significant differences are observed among results obtained with some of the methods. These differences can be attributed to the sensitivity of the elements of the phase structure that are being probed.

The level of crystallinity that can be attained at a given crystallization temperature is dependent on the molecular weight and the structural regularity of the chain. Figure 4.34 illustrates this point for several homopolymers that were crystallized under isothermal crystallization conditions [205]. The level of crystallinity is relatively high for the lower molecular weights. However, as the molecular weight increases, there is a monotonic decrease in the level of crystallinity until a limiting value of about 25%–30% is reached. The large range that is observed in the levels of crystallinity of homopolymers rules out the possibility that the crystallites are comprised of a regularly folded chain structure, with perhaps just minor perturbations. These results cannot be attributed to the influence of end groups, cilia, or similar structures, whose concentrations decrease with increasing molecular weight. As was noted in the discussion of crystallization kinetics, molecule-dependent topological factors, such as chain entanglements, serve as a restraint on the process of crystallization. These structures are molecular weight dependent and are reflected in the degree of crystallinity that can be attained.

The level of crystallinity is further reduced by the random introduction of non-crystallizing structural units into the chain. An example of the influence of co-unit content on the level of crystallinity, at ambient temperature, is illustrated in

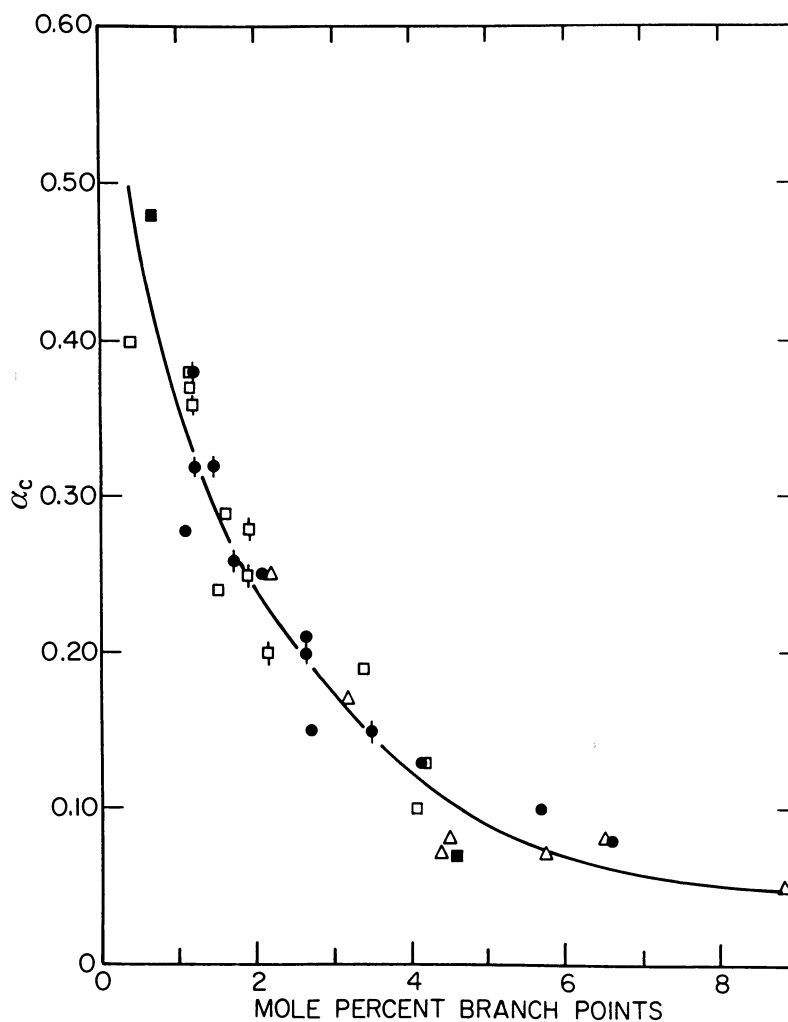


Fig. 4.35. A plot of the degree of crystallinity calculated from Raman internal modes, α_c , against the mole percentage of branch points: Δ hydrogenated polybutadiene; $\bullet$ ethylene–vinyl acetate; $\square$, $\square$ ethylene–butene; $\blacksquare$, $\blacktriangle$ ethylene–octene; and $\blacklozenge$ ethylene–hexene. From [206].

Fig. 4.35 for random ethylene copolymers [206]. In this example the molecular weights are restricted to the range 5×10^4 to 1×10^5 . It is evident that the introduction of the noncrystallizing co-units into the chain leads to a rapid and continuing decrease in the level of crystallinity with increasing side-group content. The levels of crystallinity vary from about 48% for 0.5 mol% of branches to about 7% for 6 mol% of branches. It can safely be assumed that the level of crystallinity will be reduced even further for higher co-unit contents. The chemical nature of the

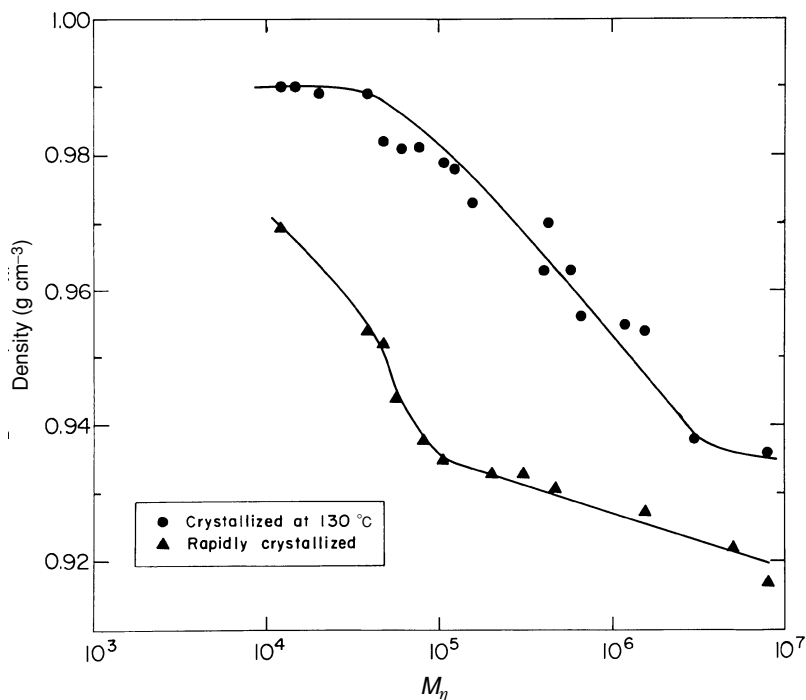


Fig. 4.36. A plot of density, measured at room temperature, as a function of the molecular weight for linear polyethylene fractions crystallized under the conditions indicated. Reproduced with permission from [206].

branches, or co-units, has virtually no influence on the level of crystallinity for a given co-unit content. As was discussed earlier, this result is to be expected for random-type copolymers when the crystalline phase remains pure.

The level of crystallinity that is obtained after cooling a homopolymer from the isothermal crystallization temperature is also of interest. The results of such a study on linear polyethylene, in terms of the density, are shown in Fig. 4.36 for two different modes of crystallization [207]. Here, the densities obtained after isothermal crystallization are compared with those observed after very rapid crystallization. The densities, and the levels of crystallinity derived therefrom, depend systematically both on the molecular weight and on the crystallization conditions. For example, the densities, measured at room temperature, range from 0.99 g cm^{-3} , which corresponds to a value very close to that of the unit cell, to 0.94 g cm^{-3} following crystallization at 130°C and subsequent cooling. For linear polyethylene, a density as low as 0.92 g cm^{-3} can be observed after the rapid crystallization of a high molecular weight fraction. After high-temperature, isothermal crystallization, and subsequent cooling, the densities of the samples of lower molecular weights

approach those expected for the unit cell. The monotonic decrease in density now starts at a slightly lower molecular weight than is the case for isothermal measurements. A constant value is reached in the very high molecular weight range. More rapid, non-isothermal crystallization results in much lower densities for comparable molecular weights. The molecular weight dependence of the density is no longer as severe. The main changes now occur at molecular weights less than about 10^5 . For molecular weights greater than 10^5 , only a small decrease in density is observed with increasing chain length.

The other experimental methods for measuring the degree of crystallinity that were mentioned give results that change in a similar manner with the molecular weight and crystallization conditions. The large range in levels of crystallinity that can be attained by control of the molecular weight, chain structure, and crystallization conditions is striking. Since many structural, physical, and mechanical properties depend, directly or indirectly, on the level of crystallinity, these results portend that large changes in many of the other properties of crystalline polymers can be achieved. The quantitative conclusion about the degree of crystallinity is quite general and is not limited to polyethylene. The classical work with natural rubber, with which much lower levels of crystallinity are obtained, substantiates this conclusion. It has also been established for other polyolefins, and for polyamides, polyesters, and poly(tetrafluoroethylene) to cite but a few examples.

Another important feature has emerged from establishing the quantitative nature of the degree of crystallinity. The deviations in degree of crystallinity from that expected for the unit cell (the perfect crystal) are systematic with the molecular weight and the mode of crystallization. These deviations are far from trivial and are, in fact, quite significant. It is clear that one must account for the wide range of values in order to develop a complete, or meaningful, picture of the crystalline state. A single piece of data, for example an isolated density value, can be interpreted in virtually any arbitrary manner desired. Focusing attention on an isolated piece of data can thus be a treacherous experience. Examining the complete set of data imposes rather extensive, rigorous demands that must be satisfied before any structural analysis can be devoted to the crystalline state.

An important feature of the internal structure of the crystallites is the angle of inclination between the chain axis and the normal to the basal plane of the lamella. For linear polyethylene at high crystallization temperatures, i.e. low undercoolings, the tilt angle is about $19\text{--}20^\circ$. It gradually decreases with decreasing crystallization temperature and at low temperatures is approximately 45° . Other polymers whose tilt angles have been determined exhibit qualitatively similar behavior. The tilt angle is an important factor that needs to be taken into consideration in developing a detailed crystallization mechanism.

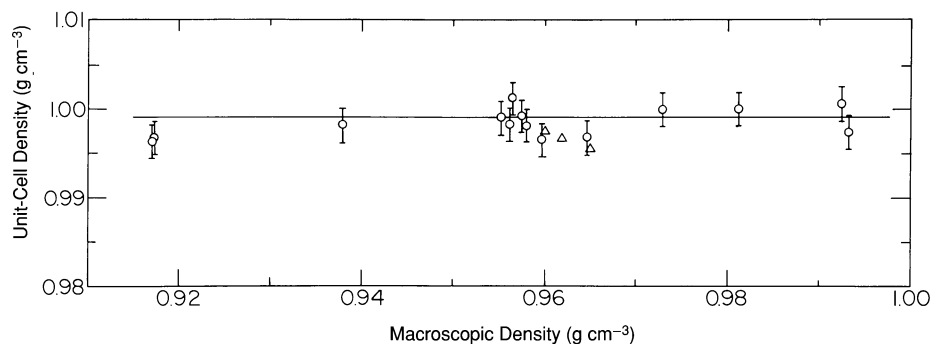


Fig. 4.37. Lattice parameters for linear polyethylene. A plot of the unit-cell density against the macroscopic density for linear polyethylene fractions. Reproduced with permission from [208]. Copyright 1970, *J. Polym. Sci.: Polym. Phys. Ed.*

A matter of concern is the influence of defects within the crystallite interior. It has already been noted that a wide range of levels of crystallinity can be obtained for many different polymers. The macroscopic density of linear polyethylene ranges from about 0.92 to 0.99 g cm⁻³ as the molecular weight decreases from 10⁶ to 10⁴. This change in the density raises the question of the integrity of the crystal structure. Put another way, do the changes in density reflect alterations within the crystallite interior or structural features that are exterior to the crystallite itself? However, as is illustrated in Fig. 4.37, as the macroscopic density of linear polyethylene is varied over the range 0.92–0.99 g cm⁻³ the actual lattice parameters, as reflected in the unit-cell density, remain constant [208]. It is concluded, therefore, that the deviations in density from that of the ideal crystal that are observed cannot be attributed in any meaningful way to a concentration of imperfections within the lattice. The origin of these deviations must be sought in specific structures that are located outside the crystalline region; that is, in structures that are external to the crystallite itself. This conclusion is consistent with the quantitative concept of the degree of crystallinity and involves analyzing the interfacial and interlamellar structures. However, we first examine the crystallite-thickness distribution.

4.5.4 The crystallite thickness distribution

There are several methods by which the crystallite-thickness distribution can be determined. These include thin-section electron microscopy, analysis of the Raman longitudinal acoustic mode, and measurement of the small-angle X-ray-scattering long period. These methods give concordant results for narrow crystallite-thickness distributions. However, agreement is not usually observed when the thickness distribution is broad. However, when cognizance of this dispersity is taken, a rational

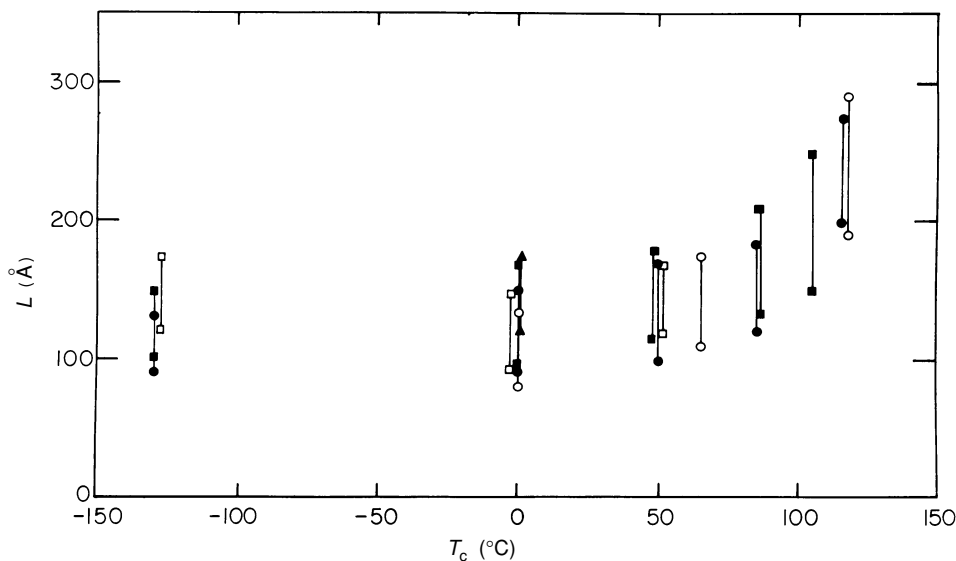


Fig. 4.38. The crystallite-thickness distribution as a function of quenching temperature for molecular weight fractions of linear polyethylene: $\circ$ 1.97×10^4 ; $\bullet$ 4.6×10^4 ; $\square$ 2.26×10^5 ; $\blacksquare$ 4.28×10^5 ; $\blacktriangle$ 1.62×10^6 . From [205].

interpretation of the size distribution can be made. After rapid, non-isothermal crystallization, a narrow size distribution is obtained, as is illustrated in Fig. 4.38 for linear polyethylene [205]. The crystallite thicknesses range from 120 to 150 Å and are independent of the molecular weight. There is only a slight dependence of the thickness on the crystallization temperature. In contrast, after isothermal crystallization a broad size distribution results. This distribution results because of the thickening of crystallites that takes place at the isothermal crystallization temperature. The rate of thickening depends on the molecular weight and temperature. Consequently, by control of these variables a wide range of sizes and distributions can be obtained. Copolymers and branched polymers, with co-unit exclusion, give thicknesses in the range of about 40–100 Å. In general, depending on the molecular weight, chain structure, and crystallization conditions, the crystallite thicknesses can vary from about 40 Å to several thousand ångström units, with a variety of size distributions.

4.5.5 The interlamellar structure

Measurements of the level of crystallinity have shown that the interlamellar region can amount to a significant portion of the total system. A detailed analysis of the structure in this region has been elusive since it is a reflection of the complex

structure of the initial melt. In the pure melt, polymer chains assume randomly coiled configurations with dimensions identical with those under theta conditions. In order for these dimensions to be maintained in a very dense system, the chains must be intertwined with one another. This requirement leads to the formation of chain entanglements, loops, knots, interlinks, and other structures that cannot be reversed, or dissipated, during the time course of crystallization. Consequently, these structures will be rejected from the growing crystallite and become concentrated within the noncrystalline regions. The level of crystallinity and the structure of the residual noncrystalline portion of the system are governed by these factors. The noncrystalline, interlamellar region influences a large number of macroscopic properties.

A large body of experiments has given strong evidence that the chain units in the interlamellar region are in non-ordered conformations without any preferential orientation, i.e. the region is isotropic. In this region, the disordered chain units, and their properties, are similar to those in the completely molten or random state. This requirement is a natural consequence of the quantitative nature of the concept of the degree of crystallinity. Certain aspects of vibrational spectroscopy support this concept of isotropy. In addition, semicrystalline polymers display well-defined glass-transition temperatures. Although there is still serious discussion regarding the mechanism of glass formation, it is universally accepted that it is a property of the liquid state. In some cases, for example natural rubber, the glass-transition temperature of the semicrystalline polymer is the same as that of the completely molten polymer [209]. In others, exemplified by linear polyethylene, it is independent of the level of crystallinity [210]. There are also examples, such as poly(ethylene terephthalate), poly(aryl ether ether ketone), and a poly(imide), for which the glass-transition temperature increases with the level of crystallinity [211–214]. What appears to be important here is the distance between lamellae and the chain conformation. The observation of glass formation then lends further support to the hypothesis of the presence of random, or close-to-random, structures in the interlamellar region. The sequences of chain units connecting crystallites are not complete molecules. The term “tie-molecule,” which has often been applied, is a misnomer. It implies that the connections are extended or straight and comprise a complete molecule. These connections represent only portions of molecules that are not ordered. A chain can adopt a variety of trajectories after it has left a crystallite. Therefore, there result many different structures that are consistent with the condition of isotropy. A highly schematic representation of the interlamellar region is given in Fig. 4.39. From this figure the highly complex interlamellar structure becomes apparent. A portion of the chain can traverse the space between lamellae unimpeded. Some chains, however, will become entangled and knotted with one another. Others will form long loops contained within the domain of a given

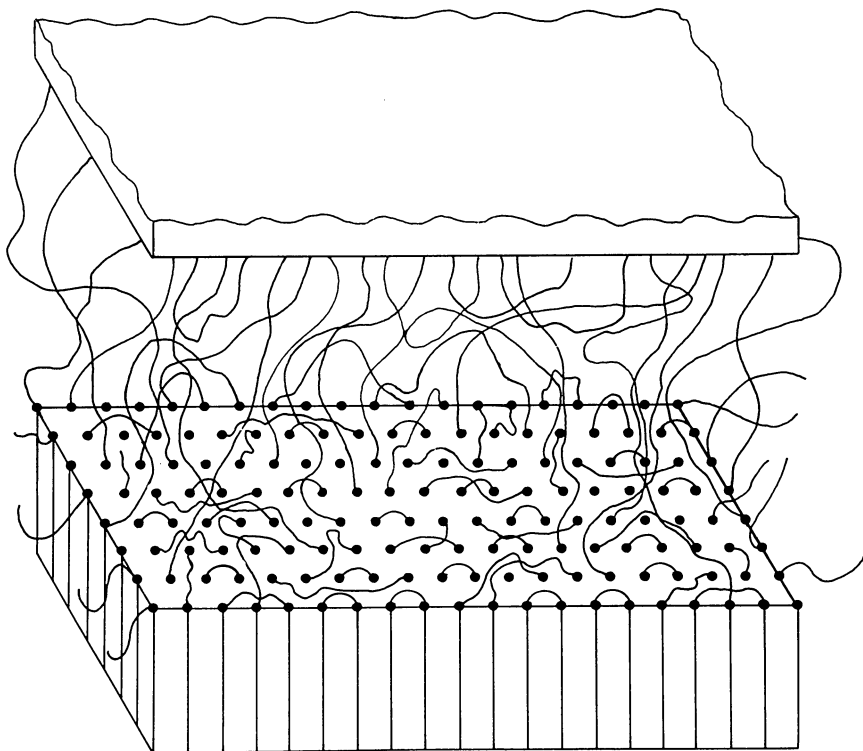


Fig. 4.39. A schematic representation of chain structure in the interlamellar region.

crystallite, while loops from two adjacent lamellae can interlink with one another and connect the crystallites.

The analysis of the small-angle neutron-scattering patterns of mixtures of hydrogenated and deuterated chains in the semicrystalline state has been informative. (For more details see Chapter 7, by G. Wignall.) For present purposes it suffices to note that the radius of gyration of a chain in the pure melt is the same as that when the polymer is crystallized from the melt. The virtual identity of the radius of gyration in the two states indicates that there is not much readjustment in chain conformation as the crystallizing growth front advances. Moreover, it becomes apparent from these results that the lamellar crystallites cannot contain a significant concentration of regularly folded chains. If this were so, the radius of gyration would be quite different from that observed.

The interlamellar region can be structurally quite complex, although isotropy is maintained. The detailed quantitative description of the molecular structure in this region remains one of the major problems still to be resolved in the area of crystalline polymers.

4.5.6 The interfacial structure

The nature of the boundary between a lamellar crystallite and the disordered interlamellar region has been a matter of intensive study and discussion for many decades. Several divergent views that are represented by the two schematic diagrams in Fig. 4.31 have emerged. Experimental and theoretical developments have led to a resolution of the problem.

The examination of thin-section transmission electron micrographs suggested that the basal planes of the lamellae were molecularly smooth. This perception was then identified with regular chain folding. However, detailed analysis of the electron micrographs, including their overall characteristics, and their decoration, sectorization, and interfacial dislocation networks for solution and bulk crystallized samples, showed that there is no *a priori* need to identify the lamellar-like crystallites with regularly folded chains in order to satisfy the gross morphological features. All of these key morphological characteristics are also found for nonfolded n-alkanes and low molecular weight polymers. They are thus not unique to regularly folded chain structures. It has already been pointed out, from the analysis of the temperature coefficient, that crystallization of polymers is a nucleation-controlled process. This conclusion is drawn on the most general grounds, irrespective of the structure of the chain within the nucleus and the type of nucleation process that is involved. Put another way, the temperature coefficient of nucleation is independent of the chain conformation within the nucleus. The assumption that the nuclei involved are composed of regularly folded chains that grow into mature crystallites of the same structure has been made [215]. This postulate was then incorporated into a theory of polymer crystallization. Since the observed temperature coefficient is typical of a nucleation process, it was concluded that the chains both in the nucleus and in the mature crystallite were regularly folded. This argument is clearly a circular one. By itself, it does not have any bearing on the structure either of the nucleus or of the crystallite.

Other structures can satisfy the established morphological and kinetic characteristics of crystallization of polymers. Some of the chains could traverse the crystallite only once and then join a nearby crystallite. Others could return to the crystallite of origin but not necessarily in juxtaposition after transversing the interfacial and interlamellar regions. Some chains could also return in adjacent re-entry positions. Results from small-angle-neutron-scattering studies, chain statistics, and many macroscopic and microscopic properties do not allow the possibility of regularly folded chain structures, as a general rule. There may very well be exceptions to this general rule. However, such exceptions have not yet been demonstrated. For example, the observed variation of the level of crystallinity with the molecular weight is not compatible with a regularly folded structure. Results from other

experimental studies involving ^1H and ^{13}C NMR, small-angle neutron scattering, specific-heat measurements, dielectric relaxation, analysis of the Raman internal modes, and electron microscopy demonstrate the presence of an appreciable interfacial region that is characterized by the partial ordering of the chain units [216]. There is no substantive basis, either experimental or theoretical, from polymers that have been studied to support the view that lamellar crystallites, formed either in the bulk or in dilute solution, are comprised of regularly folded chains. This conclusion does not preclude some type of chain folding taking place. As will be discussed in the following, some amount of adjacent re-entry can be expected, but not on the basis of nucleation theory. This conclusion, however, is not incompatible with nucleation-controlled kinetics. The basic questions that remain to be addressed are those of why a lamellar crystallite is a characteristic of crystallization of polymers, and what the true structure of the interphase is.

Flory pointed out in 1949 that the boundary between the crystalline and liquid-like regions in a polymer is not sharply defined [6]. This amounts to a fundamental difference from the behavior of low molecular weight systems. The continuity of a long-chain molecule imposes severe constraints on the transition between the two regions. The conformational differences of the chain in the two states require a boundary, or interphase, that allows the crystalline order to be dissipated [196]. The problem is that the flux of chains (the number of chains per unit area) emanating from the basal plane of the crystallite cannot usually be accommodated in the isotropic, liquid-like region.² Exceptions to this generality are crystal structures, such as those of the α -helical polypeptides, in which the chains are sufficiently far apart in the unit cell. The flux of chains is reduced and they can be accommodated in random conformations in the liquid. Chain tilting will also reduce the severity of the problem to a large extent. One obvious way to alleviate this problem is by the return of the chain to the crystallite of origin. These returns, however, do not have to be in juxtaposition. For a crystallite to grow laterally, a significant amount of chain bending, or folding, must occur. An expenditure of free energy, i.e. a gain in free energy, will be involved. This gain in free energy can be compensated for by the crystallization of long sequences, resulting in lateral growth of crystallites. There is then a straightforward mechanism by which well-developed lamellae will form at the expense of some types of folded structures without the need to manipulate monomeric nucleation theory.

Several detailed theoretical analyses have quantitatively pursued the ideas described above. Although different mathematical techniques are involved, there is essential agreement on the major conclusion [217–225]. Several principal factors

² This problem is not pertinent to the formation of a critically sized nucleus since not enough ordered sequences are involved to cause this problem.

have to be taken into account. One of these is the density of the chains at the crystal surface. This quantity is determined by the tilt angle and the ratio of the cross-sectional areas of a chain segment in the crystalline and liquid-like regions. When the cross-sectional area in the crystalline state exceeds the corresponding quantity in the liquid-like region, the problem of flux dissipation is severely reduced. Another, very important, consideration that also needs to be taken into account is the increase in free energy necessary to make a bend or tight fold. These concerns make clear that the structure of the interfacial zone is specific for a given polymer. Generalizations will be difficult to make.

As an example, consider the hypothetical polyethylene chain for which there is no expenditure of free energy in forming a fold and no conditions are placed on the chain incidence probability. For this case it is found that about 70%–75% of the sequences would return to the lamellae of origin in tight, adjacent folds. This result is not surprising since, with no free-energy cost being involved in making a bend, the regularly folded structure is clearly the easiest way in which the flux of chains can be dissipated. However, this conclusion must be tempered by reality and the properties of the actual system. For polyethylene, the incidence of a tight fold, or immediately adjacent re-entry, is reduced to 30%–40% of the sequences because of the increase in free energy necessary to make a fold. Consideration of the surface chain density (tilt angle of 45°) reduces the incidence of adjacent re-entry to about 20%. Adjacent re-entry will thus not make a major contribution to the interfacial structure for the real polyethylene chain, even for these idealized calculations. The adjacent folds that are formed will be randomly distributed along the lamellar surface.

The chemical nature of the chain, as reflected in the crystal structure and in the disordered chain conformation, will strongly influence the interfacial structure. At one extreme, we can conceive of a chain for which there is a minimal expenditure of free energy on making a bend. In this case, adjacent re-entry will predominate. For chains whose axes are positioned far from one another in the unit cell, as in the α -helical polypeptides, or have extended conformations in the disordered liquid state, as in cellulose and its derivatives, folding of any type including adjacent re-entry will be minimal.

The concepts that were outlined above with regard to the interfacial region can be subjected to experimental scrutiny utilizing several different experimental techniques [216]. The fraction of the system that is in the interfacial region, α_b , for rapidly crystallized linear polyethylene is plotted against the molecular weight (of fractions) in Fig. 4.40 [226]. These data were obtained by analysis of the Raman internal modes. There is clearly a dependence of α_b on the molecular weight. α_b is about 5% for the lower molecular weight range and it monotonically increases to 15%–17% for the higher molecular weights. Since the core level of crystallinity is

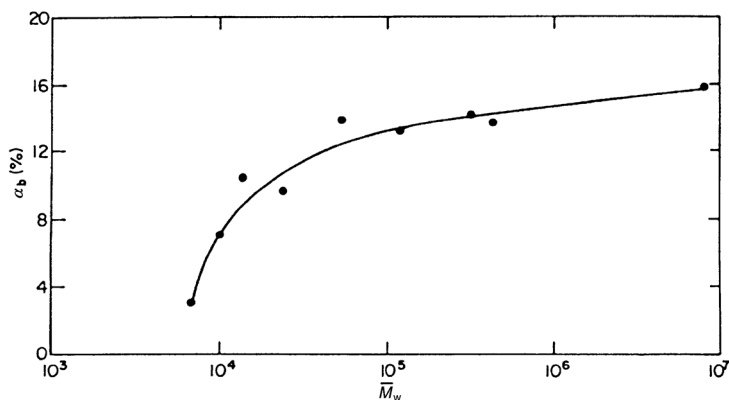


Fig. 4.40. A plot of the interfacial content (α_b) against the weight-average molecular weight for a rapidly crystallized fraction of linear polyethylene. From [226].

only about 40% for the high molecular weights, the interfacial region comprises a significant portion of the total system.

Decomposition of proton NMR spectra of linear polyethylene fractions reveals an almost quantitative agreement with the analyses of the Raman internal modes [227]. Both chemical shifts and relaxation times, obtained by solid-state ^{13}C NMR, also give information about the interfacial region. Results for linear polyethylene of high molecular weight give a value for α_b of 0.16–0.18, in agreement with the results from other methods [228]. The values of α_b for isotactic poly(propylene) and poly(tetramethylene) obtained by the same method are about 0.30 and 0.22, respectively [78, 229]. The interfacial regions of these polymers again amount to a significant portion of the total system.

Specific-heat measurements have led to the concept of a rigid amorphous phase [79, 80]. The results from thermochemical studies have shown that the increase in the specific heat at the glass-transition temperature is not as large as is theoretically expected. The portion of the noncrystalline system that does not contribute to this change in specific heat is defined as the rigid amorphous phase. This structure has been identified as the region between the crystalline and liquid-like regions, namely the interfacial region [81, 82]. The values of α_b obtained by this method have been tabulated [216]. Some typical values of α_b are 0.24 for poly(oxyethylene) [230], 0.12–0.45 for poly(phenylene sulfide) [231, 232], 0.2–0.32 for poly(aryl ether ether ketone) [231, 232], and 0.19–0.24 for poly(ethylene terephthalate) [231, 232]. The range of values listed for a given polymer is a reflection of different crystallization conditions.

The analyses of the diverse experimental data that have been given provide strong evidence for the existence of a diffuse non-ordered interfacial region that connects

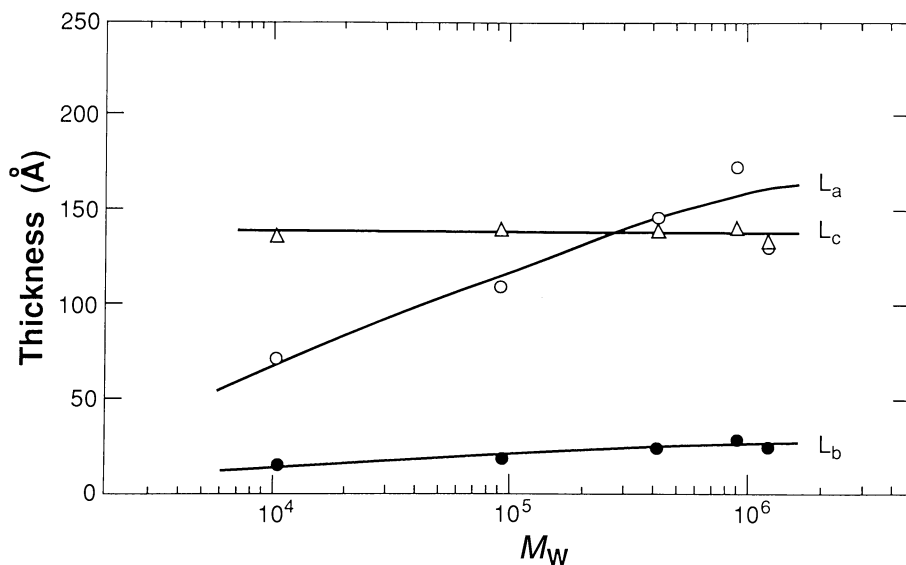


Fig. 4.41. Plot of thicknesses in ångström units against weight-average molecular weight for linear polyethylene fractions quenched to 78 °C. Δ crystallite core thickness L_c ; $\circ$ interlamellar thickness L_a ; $\bullet$ interfacial thickness L_b . Reproduced from [228]. Copyright 1990, American Chemical Society.

the ordered crystalline and disordered liquid-like regions. In all cases the interfacial region is a substantial portion of the total system. It is also of interest to determine the thickness of the interface. This can be accomplished by several experimental techniques. These include Raman spectroscopy and small-angle X-ray scattering. The thicknesses of the interface L_b , the crystallite L_c , and the interlamellar region L_a can be obtained by a combination of Raman internal and low-frequency (longitudinal acoustic) modes [233]. The results for a rapidly crystallized polyethylene fraction are given in Fig. 4.41. In this example the core crystallite thickness remains constant at about 140 Å with varying molecular weight; at the same time the thickness of the interlamellar region increases from about 75 Å to 175 Å. The interfacial thickness, L_b , also depends on the molecular weight and varies from 14 Å for $M = 10^4$ to about 25 Å for $M = 10^6$. For a linear polyethylene that has a most probable molecular weight distribution L_b is 33 Å for $M_w = 3.5 \times 10^5$ [233]. For a polydisperse sample, with $M_n = 8 \times 10^6$, L_b is equal to 45 Å [216]. By electron-spectroscopic imaging of a polydisperse sample, with $M_n = 2 \times 10^6$, L_b was found to be 60–80 Å [234]. Both α_b and L_b are thus significant and dependent on the molecular weight. The molecular weight dependence implies that the topological defects rejected by the crystalline regions are predominantly located at the crystallite boundary in the interfacial region.

By utilizing the long period obtained from small-angle X-ray scattering and the interfacial content from calorimetry, it was found that L_b varied in the range 40–50 Å, depending on the crystallization conditions [231].

The analysis of the angular dependence of the intensity of the small-angle X-ray scattering also gave information about the boundary between the crystalline and liquid-like regions [235–237]. Some typical results for the thickness of the interfacial region obtained by this method are as follows [216]: 10–15 Å for linear polyethylene; 13 Å for isotactic poly(propylene); and 13 Å for poly(ethylene terephthalate). The results here are similar to those found by other methods. The analysis of the small-angle-X-ray-scattering pattern demonstrates that a semicrystalline polymer cannot be interpreted in terms of a simple two-phase system.

The interfacial free energy associated with the basal plane of the mature polyethylene crystallite initially increases with chain length and then levels off. A constant, relatively high value of 295 erg cm^{-2} is reached at about $M \simeq 10^5$. This quantity is that of the mature crystallite rather than that of the stable nucleus. It is a reflection of the influence of the initial structure of the melt on the resulting crystallite. The fraction of interface is slightly higher for random copolymers than it is for homopolymers. For copolymers, however, it constitutes a significantly higher proportion of the core crystallite thickness. Although the interfacial fraction of copolymers depends on the co-unit content, it does not vary significantly with the molecular weight. The accumulation of the noncrystalline co-units at the surface of the crystallite is the dominant factor determining the interfacial structure in this case.

The interfacial thickness, L_b , for crystallites formed in dilute solution is about 10 Å, independently of the molecular weight [226]. Under these crystallization conditions, chain entanglements are minimal and there is no significant chain-mobility restraint on the process of crystallization. In addition to the interface, there is also a substantial disordered overlayer associated with crystals formed in solution [227]. Thus it is not surprising that results obtained using many different experimental methods indicate that crystals formed in dilute solution are only 85%–90% crystalline [3]. They are not completely crystalline.

In summary, it can be concluded that there are three major regions that characterize a semicrystalline polymer. There are the crystalline, the interfacial, and the interlamellar or liquid-like regions. In each region there is a different chain conformation. Many of the individual chains traverse all three regions. The crystalline region represents the three-dimensional ordered structure with the typical lamellar-like habit. The levels of imperfection within the crystallites are no different in concentration and type from those found in crystals formed by similar low molecular weight compounds. The crystallite, or core, thickness can be related to the nucleation requirements. However, the control by nucleation of the process of

crystallization does not mean the formation of regular folded chains. Neither does it require crystallite thicknesses that are identical, or very similar, to those of the critically sized nuclei.

Theory and experiment have led to the conclusion that there exists a significant interfacial region that is characterized by a partial order of the chain units. Although many chains return to the crystallite of origin, the number that return in an adjacent position is generally small. The interfacial region is diffuse. It is not the sharp, clearly defined boundary that one usually associates with the interfaces of crystals of low molecular weight substances. This is an important distinction that is unique to chain molecules. This boundary is characterized by a relatively high interfacial free energy.

The interlamellar liquid-like, isotropic region constitutes the main portion of the noncrystalline region. Although it is often neglected, and not discerned by many gross morphological observations, this region plays a crucial role in governing many properties. Its structure is similar, but not necessarily identical, to that of the pure melt.

Two major points have emerged from many studies. These are the importance of the initial structure of the melt and the role of the molecular weight in influencing the quantities that describe and define the crystallite and related regions. It is very important to recognize the extremely wide range of values that can be attained for a given structural parameter by control of the molecular weight and crystallization conditions. However, before addressing the relation between the properties of crystalline polymers and molecular structure, it is necessary to consider the factors governing the formation of supermolecular structures.

4.5.7 Supermolecular structure

The discussion of the supermolecular structure is concerned with the arrangement of the individual lamellar crystallites into a larger scale of organization. This aspect of structure has been studied extensively. One is aware that such higher orders of organization exist since these structures manifest themselves in the common observation of spherulites in semicrystalline polymers. Despite the widespread observation of such structures, it is only recently that they have been studied in a systematic manner. It is important to establish the conditions under which various kinds of supermolecular structures are formed and their influence, if any, on properties. A powerful technique that can be used in these studies is small-angle light scattering [238]. The light-scattering studies are usually complemented by light- and electron-microscopic observations.

The most useful light-scattering method for describing the superstructures is the H_v mode, which is dependent on fluctuations in orientation [238]. In this mode the

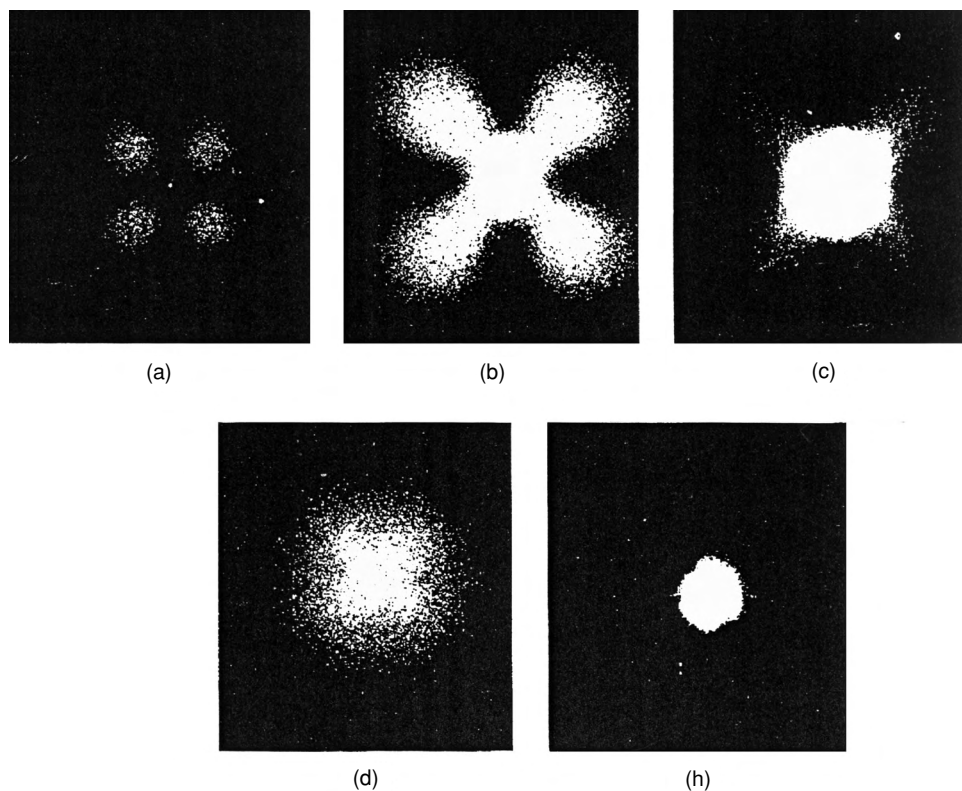


Fig. 4.42. Types of light-scattering patterns observed with polyethylenes. Reproduced with permission from [3]. Copyright 1979, *Faraday Discuss. Chem. Soc.*

incident light is polarized in the vertical direction and the observed scattered light is polarized in the horizontal direction. Although only the results for polyethylene will be discussed in detail, molecular weight fractions of poly(ethylene oxide) and isotactic poly(propylene) behave similarly. Thus the trend described for polyethylene can be taken to be quite general, although the specific molecular weight ranges involved may differ from polymer to polymer.

The polyethylenes display five distinctly different types of light-scattering patterns, which are illustrated in Fig. 4.42 and are designated by the letters of the alphabet [239]. These patterns range from that of the classical cloverleaf (a), to one which is circularly symmetric (h). The light-scattering patterns can be related by theory to different supermolecular structures that are listed in Table 4.4. In Table 4.4, patterns (a), (b), and (c) represent spherulites of decreasing order, that is, the spherulitic structure is deteriorating. Pattern (a), the classical cloverleaf with zero intensity at the center, represents the ideal, best-developed spherulite. Pattern (d), which has an azimuthally dependent light-scattering pattern, represents lamellae

Table 4.4. *Light scattering and supermolecular structure*

Small-angle light scattering	Supermolecular structure
(a), (b), (c) (cloverleaf)	(a)-, (b)-, (c)-type spherulites
(d) (some azimuthal dependence)	(d), thin rods or rod-like aggregates
(h) (no angular dependence)	(g), rods (breadth comparable to length); sheet-like (h), randomly oriented lamellae

that are organized into thin rods or rod-like aggregates. The circularly symmetric pattern, designated (h), does not represent a unique morphological situation. It can represent rods, or sheets of which the breadth is comparable to the width. We designate this structure as a (g)-type morphology. The same light-scattering pattern can also represent a random collection of uncorrelated lamellae. We designate this structural situation as an (h)-type morphology. Hence, the (h)-type scattering pattern can represent either of two superstructures, which can be discriminated only by the application of some complementary microscopic method.

The supermolecular structures that are formed depend on the molecular weight, the crystallization conditions, such as the isothermal crystallization temperature and the cooling rate, the molecular constitution, and the polydispersity of the molecular weight. The formation of supermolecular structures is found to be sensitive to polydispersity.

It is possible to establish a morphological map depicting the dependence of the supermolecular structure on the molecular weight and crystallization conditions. An example of such a morphological map is given in Fig. 4.43. In this diagram the almost vertical dashed line represents the boundary for isothermal crystallization. The temperatures below this demarcation are that of the quenching bath to which the sample is rapidly transferred from the melt. Although this is a subjective experiment, it is a reproducible one, and accomplishes the main purpose of varying the superstructures that are formed. The non-isothermal portion of the diagram merges in a continuous manner with the isothermal region. The regions where the various superstructures are formed are given the letter designations of Table 4.4. One of the important highlights of this map is the strong statement that spherulitic structures are not always observed. They are clearly not the universal mode of crystallization of homopolymers, although they are very common for polydisperse whole polymers. In fact, as the map clearly indicates, superstructures do not always develop. An (h)-type morphology is found under isothermal, as well as non-isothermal, crystallization conditions, for molecular weights greater than 10^5 . Thus, although no organized superstructures are observed for the highest molecular weights, the level of crystallinity is still of the order of 0.50–0.60 for these samples. When the map

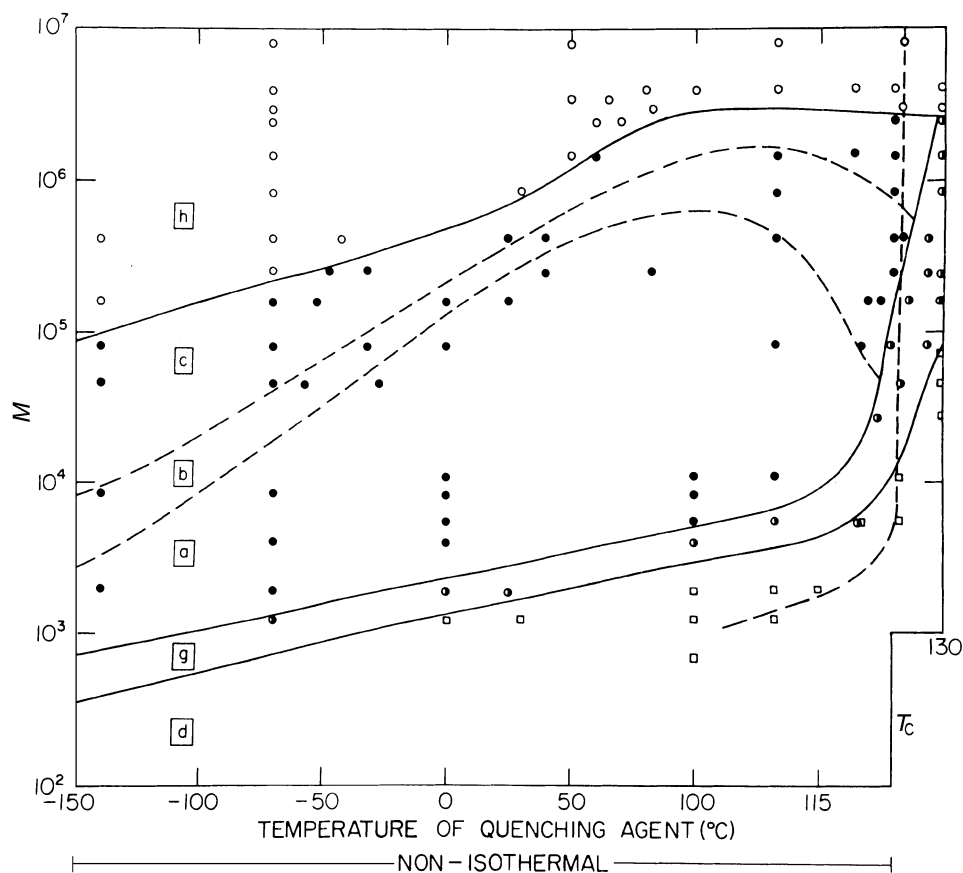


Fig. 4.43. A morphological map for molecular weight fractions of linear polyethylene. A plot of molecular weight against either quenching or isothermal crystallization temperature. Reproduced from [239]. Copyright 1981, American Chemical Society.

of Fig. 4.43 is examined in detail, we find that the low molecular weight polymers form thin rod-like structures. As the molecular weight is increased, a (g)-type morphology is observed at the higher crystallization temperatures. Here, the length and breadth of the rod-like structure are comparable to one another, i.e. sheet-like structures are observed. If the crystallization temperature is lowered, then, in this molecular weight range, spherulites will form. The spherulitic structure deteriorates as the chain length increases. Well-developed (a)-type spherulites are also generated at low temperatures for very low molecular weight fractions.

By examining the map of Fig. 4.43, it is possible to work out how to prepare various supermolecular structures from samples of the same molecular weight by choosing the appropriate crystallization conditions. In certain situations the various

superstructures can be formed with the same molecular weight at the same level of crystallinity. There is, therefore, another well-defined independent variable that must be taken into account in discussing the properties and behavior of crystalline polymers.

It is of interest to compare the superstructure observed by small-angle light scattering with the lamellar structure and organization found by thin-section electron microscopy. Detailed comparison has shown that there are very strong correlations between the electron-microscope observation and the presence or absence of superstructures and the particular type [204]. For example, in Fig. 4.33(a) the sheet-like structures, of (g)-type morphology, obtained from a fraction with $M = 1.89 \times 10^5$ isothermally crystallized at 131.2°C are illustrated. For a sample of the same molecular weight quenched at 100°C , well-developed spherulites are observed, as is shown in Fig. 4.33(b). Other structures (such as those of (h) type) can also be demonstrated by electron microscopy. Comparison of the two methods shows that there is a one-to-one correspondence between the morphological map deduced from small-angle light scattering and the direct electron-microscopic observations.

The influence of chain microstructure on the supermolecular structure can also be examined. The incorporation of branched (side) groups, copolymeric units, and other irregularities into the chain will alter the major characteristics of the morphological map. As a general proposition, insofar as the supermolecular structure is concerned, a chain with structural or chemical irregularities behaves as though it were of a higher molecular weight relative to the results obtained for linear polymers. Analysis of isothermally crystallized samples for these polymers is complicated by the limitation of the small amount of the transformation under these conditions and the substantial amount that develops on cooling. To avoid such complexities, the discussion here is limited to the reproducible, non-isothermally crystallized systems.

A typical morphological map obtained in the standard way for a set of molecular weight fractions of ethylene-1-alkene random copolymers is given in Fig. 4.44 [240]. Each of these fractions contains about 1.5 mol% of branch points. For a given branching content and molecular weight, there is a very limited temperature range within which spherulites of different degrees of order can form. Low molecular weights are conducive to the formation of more highly ordered spherulites. When the superstructures that are formed are examined as a function of the molecular weight, one observes a dome-shaped curve that forms the boundary for spherulite formation. Both for higher and for lower temperatures outside the boundary delineated by the dome, the (h)-type morphology of random lamellae usually develops. Within the dome, spherulites are formed. This morphological conclusion is confirmed by thin-section transmission electron micrographs. A strong correlation between the lamellar structure and the formation and character of the

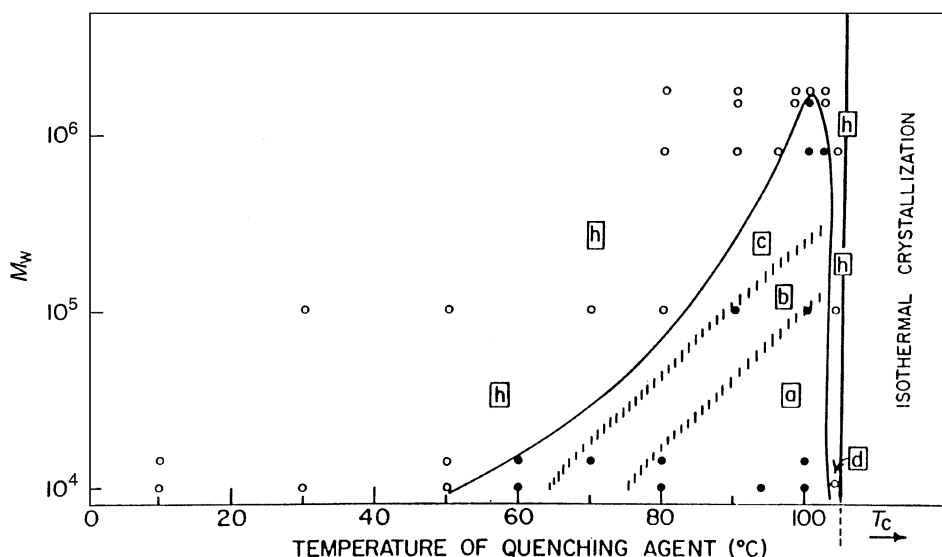


Fig. 4.44. A morphological map for molecular weight fractions of branched polyethylenes, with 1.5 mol% of branched groups. The solid line delineates the region of spherulite formation. Reproduced from [240]. Copyright 1981, American Chemical Society.

spherulites for ethylene–1-alkene and ethylene–vinyl acetate copolymers has been found [30].

A schematic representation based on results from experiments with fractions of varying contents and molecular weights of the changes that take place at the boundary for spherulite formation is given in Fig. 4.45. For a given molecular weight, as the concentration of branching decreases, the temperature range over which spherulites can be formed becomes larger. The height of the dome which encloses the region for formation of spherulites decreases with increasing branching content. Thus, increases both in molecular weight and in co-unit content reduce the probability of spherulite formation and favor the random arrangement of the lamellae. A correlation between the occurrence of lamellar structures and the formation of superstructures has been found for long-chain branched polyethylys.

4.6 Properties

The basic thermodynamic, kinetic, and structural principles which govern the crystallization behavior of polymers have been developed so far. These principles can now be applied to give an understanding of the properties of semicrystalline polymers. There is a continuing interest in understanding the properties of crystalline polymers in terms of structure. Because of the non-equilibrium character of the

However, before proceeding with this analysis the factors governing the crystallinity of homopolymers will be reviewed and the role of the supermolecular structures assessed. Figures 4.34 and 4.36 illustrate the influence of the molecular weight and crystallization temperature on the level of crystallinity that is attained by linear polyethylene. At a fixed molecular weight the density, or level of crystallinity, decreases with the crystallization temperature. When the isothermal crystallization temperature is fixed, a very large range in the level of crystallinity can be achieved by varying the molecular weight.

Figure 4.46 illustrates the relationship among the supermolecular structure, the density, and the degree of crystallinity. The densities are plotted for various crystallization temperatures for a set of molecular weight fractions. The various supermolecular structures that are formed are also indicated. There are no morphological changes for $M = 10^4$ and the density changes smoothly with the crystallization temperature. In contrast, for molecular weights of 10^5 and 10^6 there are major changes in the supermolecular structure. However, these structural changes are not reflected in any changes in the density under comparable crystallization conditions since the

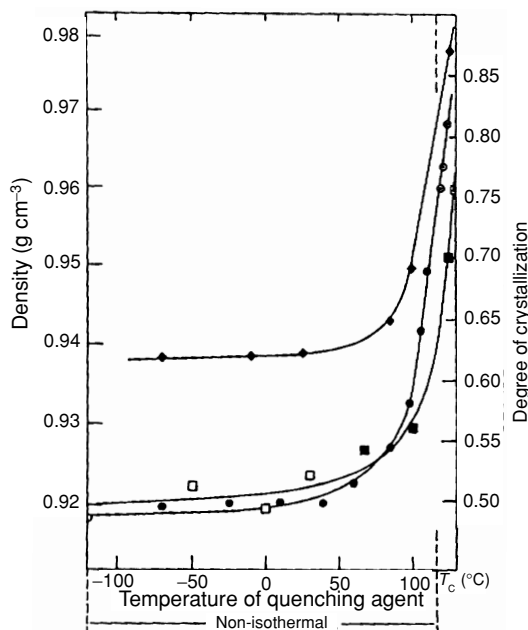


Fig. 4.46. A plot of density, or the degree of crystallinity, as a function of the isothermal crystallization temperature for three linear polyethylene fractions. For $M_w = 2.78 \times 10^4$, spherulites $\blacklozenge$, rods (d) $\diamond$; for $M_w = 1.61 \times 10^5$, random lamellae $\circ$, spherulites $\bullet$, rods (g) $\odot$; for $M_w = 1.50 \times 10^6$, random lamellae $\square$, spherulites $\blacksquare$, and rods (g) $\boxtimes$. Reproduced with permission from [3]. Copyright 1979, *Faraday Discuss. Chem. Soc.*

density changes smoothly with properties. The enthalpies of fusion and the measured melting temperatures exhibit a similar insensitivity to the supermolecular structure. The superstructure thus has very little influence on the thermodynamic quantities. Results of studies using various types of spectroscopy also show that there is little, if any, effect of the supermolecular structure. Many physical and mechanical properties are similarly unaffected. The type and size of the supermolecular structures must obviously influence optical properties. Besides these, any influence of the superstructure on properties has yet to be established.

Dynamic mechanical measurements of crystalline polymers yield a set of relaxation transitions, in addition to melting. A typical, low-frequency dynamic-mechanical spectrum for a branched polyethylene (with short- and long-chain branching) is illustrated in Fig. 4.47 [241]. Such a spectrum, with but occasional minor variations, is characteristic of crystalline polymers. In the order of decreasing temperature below the melting temperature these transitions, or relaxations, for the polyethylenes have been designated α , β , and γ respectively.³ The transition is usually observed in the range -150 to $+120$ °C; the β transition in the range -30 to $+10$ °C, and the α transition is usually found between 30 and 120 °C. Utilizing the strategy that has been outlined, the molecular and structural basis for these relaxations can be analyzed.

The α transition is observed in all of the polyethylenes, i.e. linear polymers, copolymers, and long-chain branched polymers. It can be concluded from the change in the intensity of the transition with the level of crystallinity that this relaxation results from the motion of chain units that are located within the crystalline portion of the polymer. The next questions that need to be addressed are the following: what are the structural and molecular factors that govern this transition, and why can it be observed over such a wide temperature interval? From examination of the influence of the independent variables, and the wide range of values that can be developed, it can be concluded that the temperature of the α transition, T_α , depends on the crystallite thickness, irrespective of the molecular weight, type and concentration of branching, and level of crystallinity [242]. This point is illustrated by the plot in Fig. 4.48. Here T_α ranges from about -20 °C to $+60$ °C for crystallite thicknesses of 60 – 300 Å. Examination of the data in Fig. 4.48, using the code in the inset, shows quite clearly that the superstructure does not play a role in determining T_α . There are examples in which different types of supermolecular structures have the same value for T_α . The controlling factor, for the various types of polyethylene, and their morphologies, is the crystallite thickness. For a closely related phenomenon, it has been found that the carbon-13 crystalline spin–lattice

³ For other polymers, the designation may be different. If they are labeled in the same order, the transitions could possibly reflect the involvement of different structures. Therefore, each polymer needs to be analyzed individually in order to avoid confusion between the molecular basis of the relaxation and the Greek alphabet.

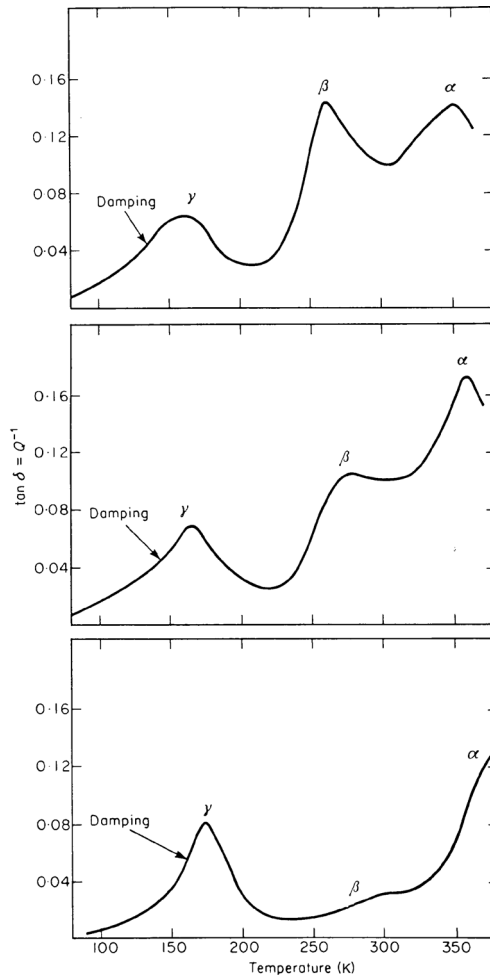


Fig. 4.47. The effect of branch concentration on the magnitude of β relaxation in polyethylene. Upper, middle, and lower curves are for specimens containing 32 branches, 16 branches, and one branch per 1000 carbon atoms, respectively. From [241].

relaxation time, T_1 , at ambient temperatures, increases directly with the crystallite thickness [243]. A correlation between the NMR results and the location of the α transitions has been found. However, when the interfacial structure is drastically altered, either by selective oxidation or by the use of extended chain crystals, there is a significant increase in T_1 . This result indicates that the interfacial structure influences, and is coupled with, the motion within the interior of the crystallite. The coupling of the motion of these two regions is also expected in dynamic-mechanical and dielectric-relaxation phenomena.

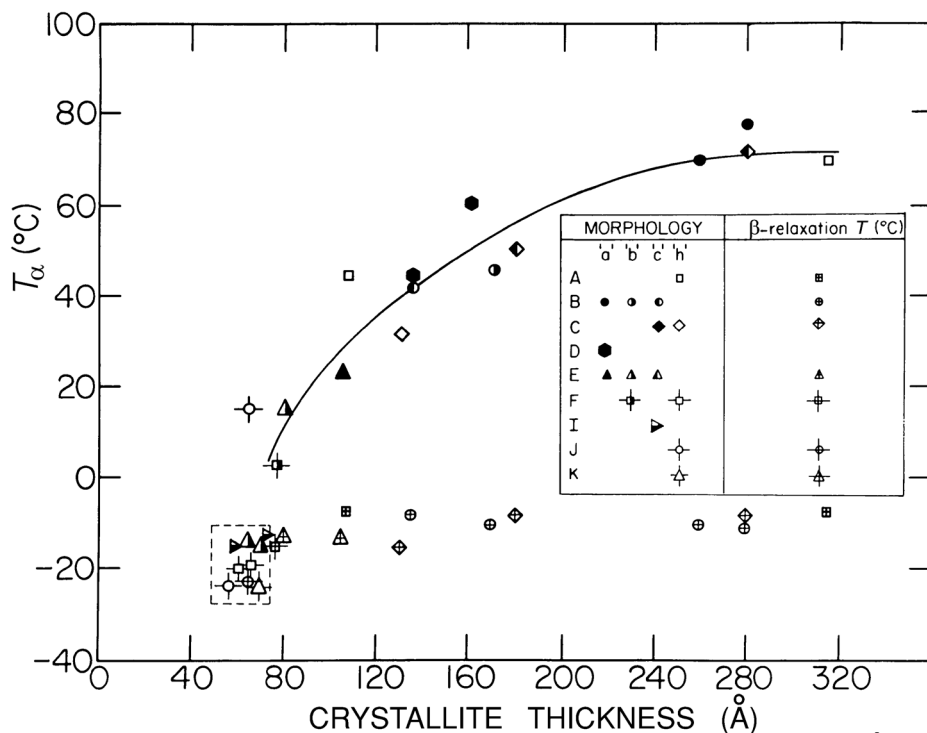


Fig. 4.48. A plot of α - and β -transition temperatures, at frequency 3.5 Hz, for a variety of linear and branched polyethylenes representing the complete range of supermolecular structures. From [242].

An intense β transition is universally observed for all branched polyethylenes (short and long chains). However, this transition is found only for a very high molecular weight linear polyethylene. The data plotted in Fig. 4.48 show that, in contrast to the α transition, the temperature of the β transition does not depend on the crystallite thickness. The location of the β transition, T_β , depends on the chemical nature and concentration of the co-unit. Thus, each copolymer has its own β transition [244].

The universal observation of the β transition in copolymers, in long-chain branched polymers, and in the high molecular weight linear polymers suggests that there could be a relation between the interfacial content and the intensity of the β transition [244]. The highest fraction of chain units in polymers of these types is located in the interfacial region. Analysis of experimental data indicates that merely having a high noncrystalline content in these polymers is not sufficient for the observation of a β transition. Furthermore, at a constant level of crystallinity, the intensity of the β transition substantially increases with the interfacial content. A compilation of the structures and conditions under which a β transition is observed

Table 4.5. *A summary of the β transition in polyethylenes*

	Observation	Interfacial content $\alpha_b(\%)$
Solution crystals of linear polyethylene	Not observed	<5
Solution crystals of branched polyethylene	Transition observed ^a	11–17
Bulk crystallized linear polyethylene	Not observed for low molecular weights ($<2 \times 10^5$)	7
	Observed for high molecular weights ($>2 \times 10^5$)	>10
Bulk crystallized branched polyethylene	Strong relaxation always observed	11–21

^a No dynamic-mechanical studies on such systems have been reported. The transition is observed by indirect measurement of the coefficient of thermal expansion.

is given in Table 4.5 [244]. It is correlated with the interfacial content α_b . This summary emphasizes the relation between the interfacial content and the intensity, or even the existence, of the β transition for various situations. When the interfacial content is small, less than about 5%–7%, the β transition is not observed. This conclusion is exemplified by the results for the solution-formed crystals and for low and medium molecular weight bulk crystallized linear polyethylene. When the interfacial content is greater than about 10%, well-defined β transitions are observed in high molecular weight bulk-crystallized linear polyethylene and in both solution and bulk crystallized branched polyethylenes. One can now understand why the β transition in linear polyethylene has been elusive and its interpretation controversial. The value of α_b needs to be sufficiently high to insure the observation of this transition. This is the reason why it is observed only in high molecular weight linear polyethylenes.

Although a detailed analysis has been given for the polyethylenes, because of the extensive amount of experimental data that is available, a similar basis for the β transition also exists in other crystalline polymers. The dynamic-mechanical behavior of poly(oxymethylene) is in fact very similar to that of polyethylene. This polymer displays a crystalline relaxation and two others, which are usually referred to as the β and γ relaxations. The introduction of small amounts of ethylene oxide co-units into the chain greatly enhances the intensity of the originally weak β transition. These results parallel those for copolymers of ethylene and indicate that they have a common origin. Since the ethylene oxide co-units are effectively excluded from the crystal lattice, an enhanced interfacial structure would be expected.

The analysis of the experimental data makes it evident that the β transition can be taken as resulting from the motion of disordered chain units, which are associated with the interfacial regions of semicrystalline homopolymers and copolymers. The presence of crystalline and noncrystalline material is a necessary requirement. Although it might be convenient to consider this transition as some type of pseudoglass temperature, the correlation time for segmental relaxation is many orders of magnitude too large. The transition, or relaxation, is unique to the partially ordered interfacial region. The assignment of the β transition to the interfacial region also explains the unique dependence on co-unit composition that is observed.

It is well established that the γ transition can be assigned to segmental motions within the interlamellar or liquid-like regions. The basis for this conclusion is that the intensity of the transition parallels the change in level of crystallinity. Specific-heat measurements in the temperature range of the γ transition show all the characteristics of glass formation [245–247]. The assignment of the γ transition to glass formation is also consistent with carbon-13 NMR relaxation measurements [248]. A compilation of the experimental techniques and results that indicate that the γ transition can be identified with the glass temperature is given in [249].

Another example of a complex property that can be analyzed and understood by the strategy outlined is the tensile behavior. Although this property is not yet completely understood in molecular terms, sufficient progress has been made that a discussion of this problem is worthwhile. A highly schematic illustration of the ductile deformation in tension of crystalline polymers is given in Fig. 4.49. The initial portion of the deformation, about 2% or 3% strain, is usually reversible.

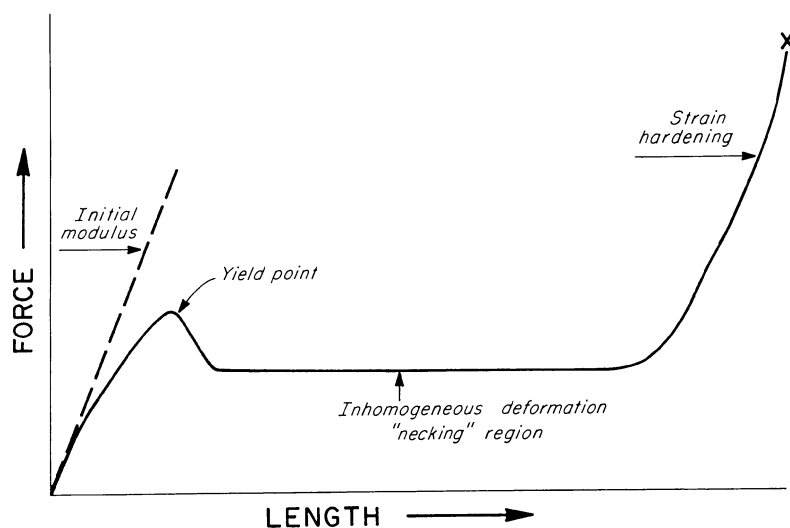


Fig. 4.49. A schematic representation of the force–length relation for semicrystalline polymers.

The dashed line in Fig. 4.49 accentuates this initial deformation. The initial modulus can be calculated from the slope of the straight line. As the deformation proceeds, a yield point is reached, which is followed by a decrease in the force or stress. Subsequently, the deformation becomes inhomogeneous, or “necking” is said to occur. In this region, the force becomes invariant with length. There is a final upsweep in the force–length curve, called “strain-hardening,” which terminates in the fracture or rupture of the sample. Figure 4.49 represents a specimen undergoing a ductile-type deformation. Brittle fracture can also occur in certain types of samples. There appear to be two main types of brittle failure. In one case, fracture occurs just past the yield point. In the other, the specimen does not reach the yield point. The overall process of deformation is time-dependent in that the quantitative force–length curve depends on the rate of strain. A major challenge is to explain the major characteristics of the deformation, as illustrated in Fig. 4.49, in terms of molecular and structural factors.

Figure 4.49 gives an overall idealized view of tensile deformation. In real situations, major variations can be observed, depending on the molecular weight, the structural regularity of the chain, and the values of the other independent structural parameters. As an example, Fig. 4.50 illustrates the force–length curves for various molecular weight fractions of rapidly crystallized linear polyethylene [250]. All of these samples display ductile behavior and the yield for each is well defined.

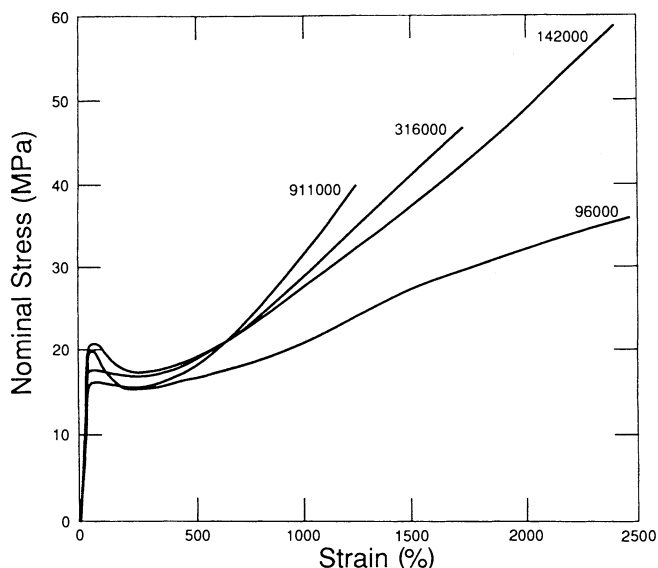


Fig. 4.50. A plot of nominal stress against nominal strain for a series of rapidly quenched molecular weight fractions of linear polyethylene having indicated values of M_w . Reproduced from [50]. Copyright 1994, American Chemical Society.

However, the yield becomes more diffuse as the molecular weight increases and the value of the yield stress decreases. At the yield point a neck is initiated, this neck becoming established as the stress falls. With increasing molecular weight, the length of the plateau region beyond the yield point decreases and the slope of the strain-hardening region becomes steeper. At the highest molecular weight the yield is diffuse and poorly defined. No neck forms and the deformation is homogeneous. The strain-hardening process dominates.

The initial modulus is determined in the limit of small strain. The initial portion of the force-length curve is usually reversible. The deformation of the disordered interlamellar region is involved and the lamellar structure remains essentially intact. Interpreting the modulus, in terms of the basic structural and molecular parameters that define a semicrystalline polymer, is complex. In this region of very small strain, the primary effect is a rubber-like elastic deformation, whereby chain entanglements and other topological features act as effective cross-links. The total system is constrained by the bounding lamellae and their broad basal planes.

It is well established that the yield stress depends on the level of crystallinity [244, 251]. This dependence is illustrated in more detail in Fig. 4.51, where the

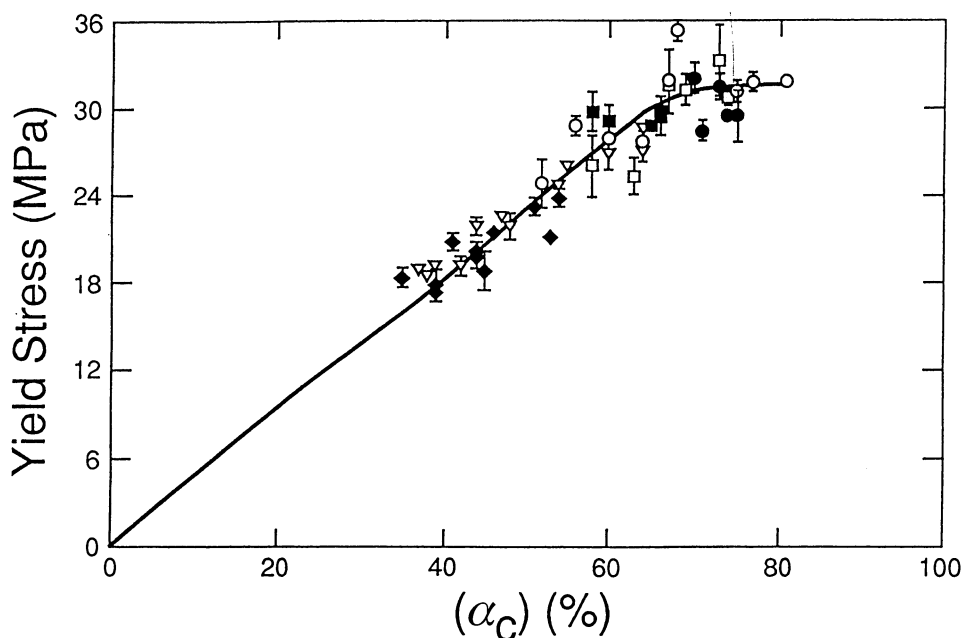


Fig. 4.51. A plot of yield stress against the level of crystallinity determined from Raman internal modes for a linear polyethylene fraction and samples with most probable molecular weight distributions. Reproduced from [50]. Copyright 1994, American Chemical Society.

yield stress is plotted against the core level of crystallinity for molecular weight fractions of linear polyethylene and samples with the most probable molecular weight distribution [250]. The data for both sets of polymers fall on the same straight line, as do data for unfractionated linear polyethylenes that are not plotted. There is a linear relation between the yield stress and core level of crystallinity that passes through the origin; i.e. the yield stress is directly proportional to the core crystallinity. It is also found that there is no direct influence either of the molecular weight or of the supermolecular structure on the magnitude of the yield stress. The key factor here is the level of crystallinity. Data for the yield stress plotted against the core level of crystallinity for a variety of random-type copolymers of ethylene with butene-1, hexene-1, octene-1, 4-methylpentene, vinyl acetate, and methacrylic acid as comonomers also fall on a common straight line that also extrapolates to the origin [251, 252]. However, the values of the yield stress are lower than those of the linear homopolymer.

The strong dependence of the yield stress on crystallinity suggests that the crystallites, or regions associated with them, undergo some type of structural change during the process of yielding. Two distinctly different mechanisms have been suggested for yielding. Flory and Yoon have proposed that a partial melting–recrystallization process is involved in the deformation [253]. During the deformation the adiabatic heating that takes place, coupled with the applied stress, should result in partial melting and recrystallization. The orientation of the recrystallized material will be governed by the stress and the recrystallization will result in a decrease in the stress. Wignall and Wu [254] have demonstrated by means of small-angle neutron scattering that partial melting–recrystallization is involved in the complete deformation of linear polyethylene. This is in accord with the hypothesis put forth by Flory and Yoon. However, the neutron-scattering experiments have not involved the yield region [255].

Alternatively, it has been postulated that yielding in crystalline polymers in general, and in polyethylene in particular, involves the thermal activation of screw dislocations with Burgers vectors that are parallel to the chain direction [256–258]. Without going into the details, this theory requires that the reduced yield stress (the yield stress divided by the core crystallinity) increase with the crystallite thickness. However, it has been shown that the reduced yield stress is independent of the crystallite thickness [250]. This postulate does in fact predict the correct order of magnitude for the yield stress. Taking into account these considerations, and the neutron-scattering results, one cannot at present assign a unique molecular mechanism to the process of yielding.

Finally, the ultimate properties of crystalline polymers will be considered. Attention is focused on the draw ratio at breakage after a ductile deformation. The interest here is in assessing the influences of the molecular weight, supermolecular

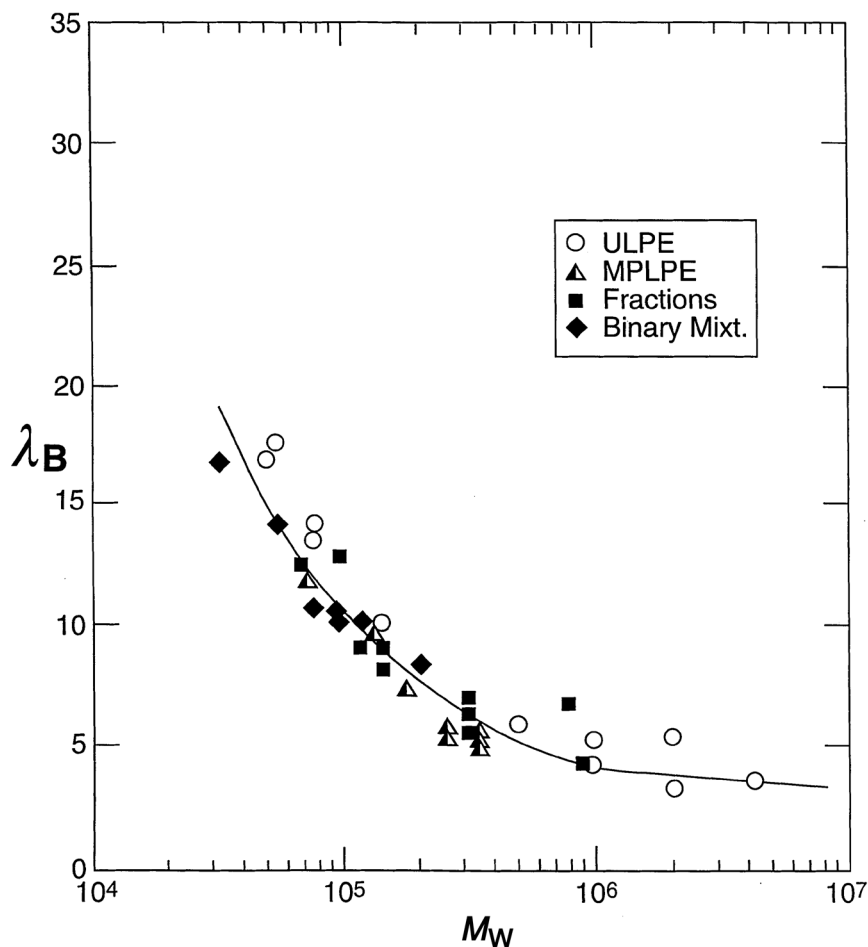


Fig. 4.52. A plot of the draw ratio after breakage against M_w for the linear polyethylene samples indicated in the insert. $T = 25^\circ\text{C}$; strain rate 10^{-1} s^{-1} . From [226, 250].

structure, degree of crystallinity, crystallite thickness, and structural irregularities on this property. The draw ratio at breakage, λ_b , for a given sample, will depend on the rate of deformation and the temperature. A plot of λ_b against the logarithm of the weight-average molecular weight, M_w , for various linear polyethylenes at ambient temperature at a draw rate of $1''\text{ min}^{-1}$ is given in Fig. 4.52. The symbols in this figure represent molecular weight fractions and samples with most probable molecular weight distributions, unfractionated polymers, and binary mixtures of fractions [250]. There is a definite and major influence of the chain length on λ_b . Over the molecular weight range 5×10^3 to 8×10^6 , λ_b decreases from about 18 to 3. An extrapolation of the data indicates that there would be essentially no deformation at still higher molecular weights, despite the fact that the level of crystallinity

would be extremely low. It has been shown that, for ductile deformation, λ_b is independent of the level of crystallinity, crystallite thickness, interlamellar thickness, and supermolecular structure [250]. The true ultimate tensile stress exhibits a very similar behavior.

From detailed studies that were outlined above one can draw the important conclusion that the ultimate properties in the ductile region depend only on the weight-average molecular weight, irrespective of whether the sample is a fraction, a well-defined molecular weight distribution, a very polydisperse sample, or a binary mixture. The draw ratio at breakage decreases with the chain length. It might have been expected that samples with high molecular weights, with the accompanying low level of crystallinity, would be more deformable. The unit cell is independent of the molecular weight, as are the general characteristics of the lamellar crystallites. The observation that λ_b and the ultimate tensile stress depend only on M_w indicates the importance of the noncrystalline, interlamellar region to the process of deformation. The chain topology in the noncrystalline region is important.

There has been a tendency to focus attention primarily upon the structural changes that take place within the crystalline region when one is discussing the tensile properties of semicrystalline polymers. Attempts to treat the deformation of structurally complex semicrystalline polymers in analogy with the plastic deformation of metals and other monomeric systems have been made. Polymeric crystallites, like other substances, can undergo plastic deformation through several mechanisms. These include slip, thinning, dislocation mechanisms, and a martensite-type phase transition. However, which, if any, of these processes serves as the structural basis for the deformation of crystalline polymers has yet to be established. The experimental results that have been described above make it evident that the major mechanisms involved in the deformation of polymers after yield are not of crystallographic origin. An important conclusion that can be drawn from present results is that small deformations (beyond the initial reversible region) are governed by the crystallite and associated regions, whereas for large deformations the ultimate properties depend on the structure of the liquid-like region.

It is evident from the preceding discussion that many aspects of the deformation of crystalline polymers have yet to be understood on a molecular basis. A great deal of work remains to be done. However, progress has been made by focusing on the independent structural variables that define the crystalline states.

4.7 General conclusions

Starting from an analysis of the conformation of a polymer chain in the liquid (amorphous) and crystalline (ordered) states, it has been possible to develop the basic thermodynamic, kinetic, and structural principles that govern the crystallization

behavior of polymers. The quantitative description of the kinetics of crystallization and the thermodynamic analysis of the melting–crystallization process are found to be generalized manifestations of the classical processes applicable to low molecular weight systems. Consequently, these two subjects have reached a relatively high level of comprehension and maturity.

Because of the non-equilibrium character of the crystalline state in polymers, both microscopic and macroscopic properties depend on the specific structural and morphological features that are present. Various independent structural variables have been identified, at different levels of hierarchy, which, together with the molecular constitution of the chain, determine properties. These structural variables can be determined experimentally. A striking feature of the structure of a crystalline polymer is the wide range of values that a given variable can be made to attain by control of the molecular constitution and crystallization conditions. Taking advantage of this feature, a specific variable can be isolated and its influence singly, or in conjunction with others, on a specific property can be assessed. By implementing this strategy, a molecular understanding of spectroscopic, physical, and mechanical properties can and is being developed. This approach should be applicable to virtually all properties of crystalline polymers.

References

- [1] S. Z. D. Cheng and A. Keller, *Ann. Rev. Mater. Sci.*, **28** (1998), 533.
- [2] L. Mandelkern, *J. Macromol. Sci. Chem.*, **A15** (1981), 1211.
- [3] L. Mandelkern, *Faraday Discuss. Chem. Soc.*, **68** (1979), 310.
- [4] F. A. Quinn, Jr and L. Mandelkern, *J. Am. Chem. Soc.*, **83** (1961), 2857.
- [5] J. E. Mayer and S. F. Streeter, *J. Chem. Phys.*, **7** (1939), 1019.
- [6] P. J. Flory, *J. Chem. Phys.*, **17** (1949), 223.
- [7] T. Nakaoki, R. Kitamaru, R. G. Alamo, W. T. Huang, and L. Mandelkern, *Polym. J.*, **32** (2000), 876.
- [8] J. B. Jackson, P. J. Flory, and R. Chiang, *Trans. Faraday Soc.*, **59** (1963), 1906.
- [9] J. Chatterjee and R. G. Alamo, *J. Polym. Sci. Pt B: Polym. Phys.*, **40** (2002), 872.
- [10] S. Miyata, M. Sorioka, T. Arikawa, and K. Akaoki, *Prog. Polym. Phys. Japan*, **17** (1974), 233.
- [11] L. Mandelkern, *Crystallization of Polymers*, 2nd Edition, Vol.1 (Cambridge University Press, Cambridge, 2002).
- [12] L. Mandelkern and R. G. Alamo, in *Handbook of Polymer Properties*, edited by J. E. Mark (American Institute of Physics Press, New York, 1996).
- [13] A. E. Tonelli, *J. Chem. Phys.*, **53** (1970), 4339.
- [14] P. J. Flory, *Trans. Faraday Soc.*, **51** (1955), 848.
- [15] C. H. Baker and L. Mandelkern, *Polymer*, **7** (1966), 7.
- [16] J. F. Kenney, *Polym. Sci. Eng.*, **8** (1968), 216.
- [17] M. J. Richardson, P. J. Flory, and J. B. Jackson, *Polymer*, **4** (1963), 21.
- [18] L. Mandelkern, M. Tryon, and F. A. Quinn Jr, *J. Polym. Sci.*, **19** (1956), 77.
- [19] S. Newman, *J. Polym. Sci.*, **47** (1960), 111.
- [20] R. H. Colby, G. E. Milliman, and W. W. Graessley, *Macromolecules*, **19** (1986), 1261.

- [21] L. Mandelkern, M. Hellman, D. W. Brown, D. Roberts, and F. A. Quinn Jr, *J. Am. Chem. Soc.* **75** (1953), 4093.
- [22] P. J. Manaresi, A. Munari, F. Pilati, G. C. Alfonso, S. Russo, and M. L. Sartirana, *Polymer*, **27** (1986), 955.
- [23] L. L. Lopez, G. L. Wilkes, and J. F. Geibel, *Polymer*, **30** (1989), 147.
- [24] G. Guerra, C. Venditto, C. Natale, P. Rizzo, and C. DeRosa, *Polymer*, **39** (1998), 3205.
- [25] M. Inoue, *J. Appl. Polym. Sci.*, **8** (1964), 2225.
- [26] M. J. Richardson, P. J. Flory, and J. B. Jackson, *Polymer*, **4** (1963), 21.
- [27] N. Naga, K. Mizunama, H. Sadatoslei, and A. Kakugo, *Macromolecules*, **20** (1987), 2197.
- [28] R. Kyotokura, T. Masuda, and N. Tsutsumi, *Polymer*, **35** (1994), 1275.
- [29] K. Okuda, *J. Polym. Sci. Pt A*, **2** (1961), 1719.
- [30] J. R. Isasi, J. A. Haigh, J. T. Graham, L. Mandelkern, and R. G. Alamo, *Polymer*, **41** (2000), 8813.
- [31] R. G. Alamo and L. Mandelkern, *Thermochim. Acta*, **238** (1994), 155.
- [32] A. G. Simanke and R. G. Alamo, private communication.
- [33] C. Garbuglio, M. Ragazzini, O. Pilat, D. Carcono, and G. Cevidalli, *Eur. Polym. J.*, **3** (1967), 137.
- [34] M. M. Brubaker, D. A. Coffman, and H. H. Hoehn, *J. Am. Chem. Soc.*, **74** (1952), 1509.
- [35] P. Colombo, L. E. Kuckaka, J. Fontana, R. N. Chapman, and M. Steinberg, *J. Polym. Sci. Pt A-1*, **4** (1966), 29.
- [36] S. DeVito, F. Ciardelli, E. Benedette, and E. Bramanti, *Polym. Adv. Technol.*, **8** (1977), 53.
- [37] A. Sonmazzi and F. Garbassi, *Prog. Polym. Sci.*, **22** (1997), 1547.
- [38] E. Drent, A. M. Brookhaven, and M. I. Doyle, *J. Organomet. Chem.*, **417** (1991), 235.
- [39] B. J. Lommerts, E. Z. Klop, and J. Aerts, *J. Polym. Sci. Pt B: Polym. Phys.*, **31** (1993), 1319.
- [40] M. Modena, C. Garbuglio, and M. Ragozzina, *J. Polym. Sci. Polym. Lett.*, **10B** (1972), 153.
- [41] C. Garbuglio, M. Modena, M. Valera, and M. Ragozzini, *Eur. Polym. J.*, **10** (1974), 91.
- [42] D. W. Brown, R. E. Lowry, and L. A. Wall, *J. Polym. Sci.: Polym. Phys. Ed.*, **12** (1974), 1302.
- [43] H. Chien, D. McIntyre, J. Cheng, and M. Fone, *Polymer*, **36** (1995), 2559.
- [44] R. W. Waymouth and M. K. Leclerc, *Angew. Chem.*, **37** (1998), 922.
- [45] T. Vozumi, K. Miyazana, T. Sono, and K. Soga, *Macromol. Rapid Commun.*, **18** (1997), 833.
- [46] P. J. Flory, *Principles of Polymer Chemistry* (Cornell University Press, New York, 1955), p. 555.
- [47] M. W. Matsen and M. Schick, *Macromolecules*, **27** (1994), 6761.
- [48] R. A. Brown, A. J. Masters, C. Price, and X. F. Yuan, *Comprehensive Polymer Science*, Vol. 2 (Pergamon Press, Oxford, 1989), p. 155.
- [49] F. S. Bates and G. H. Frederickson, *Phys. Today*, February (1999), 37.
- [50] F. S. Bates, M. F. Schulz, A. K. Khandpres, S. Förster, J. H. Rosedale, K. Almdal, and K. Mortensen, *Faraday Discuss. Chem. Soc.*, **98** (1994), 7.
- [51] M. F. Schulz and F. S. Bates, in *Physical Properties of Polymers Handbook*, edited by J. E. Mark (American Institute of Physics, New York, 1996), p. 427.

- [52] P. K. Seow, Y. Gallot, and A. Skoulios, *Makromol. Chem.*, **177** (1976), 177.
- [53] D. J. Quiram, R. A. Register, and G. R. Marchand, *Macromolecules*, **30** (1997), 4551.
- [54] J. Heuschen, R. Jérôme, and Ph. Teyssié, *J. Polym. Sci. Pt B: Polym. Phys.*, **27** (1989), 523.
- [55] Y. Mohajer, G. L. Wilkes, J. C. Wang, and J. E. McGrath, *Polymer*, **23** (1982), 1523.
- [56] P. A. Weimann, D. A. Hajduk, C. Chu, K. A. Chaffin, J. C. Brodel, and F. S. Bates, *J. Polym. Sci. Pt B: Polym. Phys.*, **37** (1999), 2068.
- [57] P. C. Ashman and C. Booth, *Polymer*, **16** (1975), 889.
- [58] C. Booth and D. V. Dodgson, *J. Polym. Sci.: Polym. Phys. Ed.*, **11** (1973), 265.
- [59] P. C. Ashman, C. Booth, D. R. Cooper, and C. Price, *Polymer*, **16** (1975), 897.
- [60] C. Booth and C. J. Pickles, *J. Polym. Sci.: Polym. Phys. Ed.*, **11** (1973), 249.
- [61] P. C. Ashman and C. Booth, *Polymer*, **17** (1976), 105.
- [62] A. Misra and S. R. Gang, *J. Polym. Sci. Pt B: Polym. Phys.*, **24** (1986), 983; *J. Polym. Sci.*, **24** (1986), 999.
- [63] R. Perret and A. Skoulios, *Makromol. Chem.*, **156** (1972), 143.
- [64] R. Perret and A. Skoulios, *Makromol. Chem.*, **162** (1972), 147.
- [65] R. Perret and A. Skoulios, *Makromol. Chem.*, **162** (1972), 163.
- [66] A. Skoulios, in *Block and Graft Copolymers*, edited by J. J. Burke and V. Weiss (Syracuse University Press, New York, 1973), p. 121.
- [67] S. Nojima, M. Ohno, and T. Ashida, *Polymer J.*, **24** (1992), 1271.
- [68] D. H. Coffey and T. J. Meyrick, *Proceedings of the Rubber Technology Conference* (1954), p. 170.
- [69] J. J. O'Malley, *J. Polym. Sci.: Polym. Phys. Ed.*, **13** (1975), 1353.
- [70] J. J. O'Malley, T. J. Pacansky, and W. J. Stanffor, *Macromolecules*, **10** (1977), 1197.
- [71] M. H. Theil and L. Mandelkern, *J. Polym. Sci. A-2*, **8** (1970), 957.
- [72] L. L. Harrell, Jr, *Macromolecules*, **2** (1969), 607.
- [73] J. C. Stevenson and S. L. Cooper, *Macromolecules*, **21** (1988), 1309.
- [74] R. J. Cella, *Encyclopedia of Polymer Science and Technology Supplement No. 2* (John Wiley and Sons, New York, 1977), p. 481.
- [75] J. R. Wolfe Jr, *Rubber Chem. Technol.*, **50** (1977), 688.
- [76] M. A. Valance and S. L. Cooper, *Macromolecules*, **17** (1984), 1208.
- [77] A. Lilanontkiel, J. G. West, and S. L. Cooper, *J. Macromol. Sci. Phys.*, **12** (1976), 563.
- [78] A. Hirai, F. Horii, R. Kitamaru, J. G. Fatou, and A. Bello, *Macromolecules*, **23** (1990), 2913.
- [79] B. Wunderlich and S. Z. D. Cheng, *Gaz. Chim. Ital.*, **116** (1986), 345.
- [80] S. Z. D. Cheng, D. P. Heberer, H.-S. Lieu, and F. W. Harris, *J. Polym. Sci.: Polym. Phys. Ed.*, **28** (1990), 655.
- [81] P. Huo and P. Cebe, *Macromolecules*, **25** (1992), 902.
- [82] D. P. Heberer, S. Z. D. Cheng, J. S. Barley, S. H. S. Lieu, R. G. Bryard, and F. W. Harris, *Macromolecules*, **24** (1991), 1896.
- [83] I. W. Hamley, *The Physics of Block Copolymers* (Oxford University Press, Oxford, 1998), p. 281.
- [84] M. Scandala, G. Ceccoralli, M. Pizzoli, and M. Grazzani, *Macromolecules*, **25** (1992), 1405.
- [85] N. Kamiya, M. Sakurai, Y. Inoue, R. Chugo, and Y. Doi, *Macromolecules*, **24** (1991), 2178.
- [86] M. Kunioka, A. Tamaki, and Y. Doi, *Macromolecules*, **22** (1989), 694.
- [87] D. L. VanderHart, W. J. Orts, and R. H. Marchessault, *Macromolecules*, **28** (1995), 6394.

- [88] Y. Doi, S. Kitamura, and H. Abe, *Macromolecules*, **28** (1985), 4822.
- [89] T. L. Bluhm, G. K. Hamer, R. S. Marchessault, C. A. Fyfe, and R. P. Verigin, *Macromolecules*, **19** (1986), 2871.
- [90] X. Lu and A. H. Windle, *Polymer*, **36** (1995), 451; **37** (1996), 2027.
- [91] R. D. Evans, H. R. Mighton, and P. J. Flory, *J. Am. Chem. Soc.*, **72** (1951), 2018.
- [92] E. Perez and D. L. VanderHart, *J. Polym. Sci.: Polym. Phys. Ed.*, **25** (1987), 1637.
- [93] W. Hu, S. Srinivas, and E. B. Sirota, *Macromolecules*, **35** (2002), 5013.
- [94] T. W. Bowmer and A. E. Tonelli, *Polymer*, **26** (1985), 1195.
- [95] L. Mandelkern, in *Comprehensive Polymer Sciences: Polymer Properties*, Vol. 2 (Pergamon Press, Oxford, 1989), p. 363.
- [96] G. Natta, *Makromol. Chem.*, **35** (1960), 93.
- [97] O. B. Edgar and R. Hill, *J. Polym. Sci.*, **8** (1952), 1.
- [98] A. J. Yu and R. D. Evans, *J. Am. Chem. Soc.*, **81** (1959), 5361.
- [99] A. J. Yu and R. D. Evans, *J. Am. Polym. Sci.*, **20** (1959), 5361.
- [100] M. Levine and S. C. Temin, *J. Polym. Sci.*, **49** (1961), 241.
- [101] T. C. Tranter, *J. Polym. Sci. Pt A*, **2** (1964), 4289.
- [102] F. R. Prince, E. M. Pearce, and R. J. Fredericks, *J. Polym. Sci. Pt A-1*, **8** (1970), 3533.
- [103] F. R. Prince and R. J. Fredericks, *Macromolecules*, **5** (1972), 168.
- [104] M. Hachiboshi, T. Fukud, and S. Koyayashi, *J. Macromol. Sci. Phys.*, **35** (1960), 94.
- [105] N. Yoshie, Y. Inoue, H. Y. Yoo, and N. Okui, *Polymers*, **35** (1994), 1931.
- [106] S. S. Park, I. H. Kim, and S. S. Im, *Polymer*, **37** (1996), 2165.
- [107] Y. Doi, *Microbiol Polyesters* (VCH, Weinheim, 1996).
- [108] G. Natta, P. Corradini, D. S. Sianezi, and D. Moreio, *J. Polym. Sci.*, **54** (1965), 527.
- [109] G. Natta, G. Allegra, I. W. Bass, D. Sianesi, G. Capericcio, and E. Torta, *J. Polym. Sci. Pt A*, **3** (1965), 4263.
- [110] G. Natta, L. Pornis, A. Carbanaro, and G. Lugli, *Makromol. Chem.*, **53** (1960), 52.
- [111] F. P. Reding and E. R. Walter, *J. Polym. Sci.*, **37** (1959), 555.
- [112] A. T. Jones, *Polymer*, **6** (1965), 249; *Polymer*, **7** (1965), 23.
- [113] T. W. Campbell, *J. Appl. Polym. Sci.*, **5** (1961), 184.
- [114] G. Natta, G. Allegra, I. W. Bassi, C. Carloni, E. Chielline, and G. Montagnol, *Macromolecules*, **2** (1969), 311.
- [115] K. H. Gardner, B. S. Hsiao, R. M. Matheson Jr, and B. A. Wood, *Polymer*, **33** (1992), 2483.
- [116] G. Montandi, G. Bruno, P. Manavigna, P. Finocchiario, and G. Centines, *J. Polym. Sci.: Polym. Chem. Ed.*, **11** (1973), 65.
- [117] G. Allegra and I. W. Bassi, *Adv. Polym. Sci.*, **6** (1969), 549.
- [118] A. W. Adamson, *Textbook of Physical Chemistry* (Academic Press, New York, 1973).
- [119] G. Allegra, R. H. Marchessault, and S. Bloembergen, *J. Polym. Sci.: Polym. Phys. Ed.*, **30** (1990), 809.
- [120] G. Allegra and S. V. Meille, *Crystallization of Polymers* (Kluwer Academic, Dordrecht, 1993), p. 226.
- [121] E. Helfand and J. I. Lauritzen Jr, *Macromolecules*, **6** (1973), 631.
- [122] I. C. Sanchez and R. K. Eby, *J. Res. Nat. Bur. Stand.*, **77A** (1973), 353.
- [123] I. C. Sanchez and R. K. Eby, *Macromolecules*, **8** (1975), 638.
- [124] J. Wendling and V. W. Suter, *Macromolecules*, **31** (1998), 2516.
- [125] H. G. Kilian, *Thermochim. Acta*, **238** (1994), 113.
- [126] H. G. Kilian, *Koll. Z. Z. Polym.*, **202** (1965), 97.
- [127] H. Baur, *Makromol. Chem.*, **98** (1966), 297.
- [128] B. Obi, P. DeLassur, and E. A. Gruelbe, *Macromolecules*, **27** (1994), 5491.

- [129] H. Baur, *Koll. Z. Z. Polym.*, **212** (1966), 97.
- [130] D. M. Sadler and G. H. Gilmer, *Phys. Rev. Lett.*, **56** (1986), 2708; *Phys. Rev. B*, **38** (1988), 5686.
- [131] G. Goldbeck-Wood, *Polymer*, **33** (1992), 778.
- [132] F. von Göler and G. Sachs, *Z. Phys.*, **77** (1932), 281.
- [133] W. A. Johnson and R. F. Mehl, *Trans. Am. Inst. Mining Met. Engrs*, **135** (1939), 416.
- [134] M. Avrami, *J. Chem. Phys.*, **7** (1939), 1103; *J. Chem. Phys.*, **8** (1940), 212; *J. Chem. Phys.*, **9** (1941), 177.
- [135] R. U. Evans, *Trans. Faraday Soc.*, **41** (1945), 365.
- [136] A. N. Kolmogorov, *Bull. Acad. Sci. USSR Phys. Ser.*, **1** (1937), 355.
- [137] L. Mandelkern, F. A. Quinn Jr, and P. J. Flory, *J. Appl. Phys.*, **25** (1954), 830.
- [138] L. Mandelkern, *Crystallization of Polymers* (McGraw-Hill, New York, 1964).
- [139] E. Ergoz, J. G. Fatou, and L. Mandelkern, *Macromolecules*, **5** (1972), 147.
- [140] R. G. Alamo and L. Mandelkern, *Macromolecules*, **24** (1991), 6480.
- [141] F. Gornick and L. Mandelkern, *J. Appl. Phys.*, **33** (1962), 907.
- [142] D. Jadraque and J. G. Fatou, *Anales Quim.*, **73** (1977), 639.
- [143] Magill, J. H., *Macromol. Chem. Phys.*, **199** (1998), 2365.
- [144] C. Devoy, L. Mandelkern, and L. Bourland, *J. Polym. Sci. Pt A-2*, **8** (1970), 869.
- [145] J. Q. G. Maclaine and C. Booth, *Polymer*, **16** (1975), 191.
- [146] H. L. Chen, L. J. Li, W. C. O. Yang, J. C. Hwang, and W. Y. Wong, *Macromolecules*, **30** (1997), 1718.
- [147] J. H. Magill, *J. Polym. Sci. Pt A-2*, **5** (1967), 89.
- [148] E. C. Lovering, *J. Polym. Sci.*, **30C** (1970), 329.
- [149] Y. Deslandes, F. N. Sabir, and J. Roover, *Polymer*, **32** (1991), 1267.
- [150] J. J. Labaig, Ph.D. Thesis, Louis Pasteur University, Strasbourg (1978).
- [151] J. D. Hoffman, L. J. Frolen, G. S. Ross, and J. I. Lauritzen Jr, *J. Res. Nat. Bur. Stand.*, **79A** (1975), 671.
- [152] L. A. Wood and N. Bekkedahl, *J. Appl. Phys.*, **17** (1946), 362.
- [153] T. Suzuki and A. Kovacs, *Polym. J.*, **1** (1970), 82.
- [154] A. E. Nielsen, *Kinetics of Precipitation* (Pergamon Press, Oxford, 1964), pp. 40ff.
- [155] F. P. Price, in *Nucleation*, edited by A. C. Zettlemoyer (Marcel Dekker, New York, 1969), pp. 405ff.
- [156] D. Turnbull and J. C. Fisher, *J. Chem. Phys.*, **17** (1949), 7.
- [157] L. Mandelkern, J. G. Fatou, and C. Howard, *J. Phys. Chem.*, **69** (1965), 956.
- [158] J. W. Gibbs, in *Collected Works*, Vol. 1 (Longmans, Green & Co., Inc., New York, 1931), pp. 55–371.
- [159] A. J. Kovacs and J. Gonthier, *Koll. Z. Z. Polym.*, **250** (1974), 530.
- [160] J. D. Hoffman and J. J. Weeks, *J. Chem. Phys.*, **37** (1962), 1723.
- [161] L. Mandelkern and R. G. Alamo, in *Handbook of Polymer Properties*, edited by J. E. Mark (American Institute of Physics Press, New York, 1996).
- [162] P. D. Calvert and D. R. Uhlmann, *J. Appl. Phys.*, **43** (1972), 944.
- [163] W. B. Hillig, *Acta Metall.*, **14** (1966), 1868.
- [164] J. D. Hoffman, G. T. Davis, and J. I. Lauritzen, in *Treatise on Solid State Chemistry*, Vol. 3, edited by N. B. Hannay (Plenum, New York, 1976), p. 497.
- [165] J. D. Hoffman and R. L. Miller, *Macromolecules*, **22** (1989), 3502.
- [166] I. C. Sanchez and E. A. DiMarzio, *J. Res. Nat. Bur. Stand.*, **76A** (1972), 213.
- [167] J. I. Lauritzen Jr, *J. Appl. Phys.*, **44** (1973), 4653.
- [168] F. C. Frank, *J. Cryst. Growth*, **22** (1974), 233.
- [169] P. J. Phillips, *Rep. Prog. Phys.*, **53** (1990), 549.

- [170] J. J. Point and M. Dosi    , *Polymer*, **30** (1989), 2292.
- [171] J. J. Point and M. Dosi    , *Macromolecules*, **22** (1989), 3501.
- [172] J. J. Point and J. J. Janimak, in *Crystallization of Polymers*, edited by M. Dosi     (Kluwer Academic, Dordrecht, 1993), p. 119.
- [173] J. A. Haigh, L. Mandelkern, and L. Howard, unpublished results.
- [174] H. Vogel, *Phys. Z.*, **22** (1921), 645.
- [175] J. D. Hoffman, *J. Chem. Phys.*, **29** (1958), 1192.
- [176] J. D. Hoffman, *Polymer*, **24** (1983), 3.
- [177] J. Miyamoto, Y. Tanzawa, H. Miyaji, and H. Koho, *Polymer*, **33** (1992), 2496.
- [178] J. D. Runt, M. Miley, X. Zhang, K. P. Gallagher, K. McFeaters, and J. Fishburg, *Macromolecules*, **25** (1992), 1929.
- [179] J. M. Huang and I. C. Chang, *J. Polym. Sci. Pt B: Polym. Phys.*, **38** (2000), 934.
- [180] D. B. Roitman, H. Marand, R. L. Miller, and J. D. Hoffman, *J. Phys. Chem.*, **93** (1989), 6919.
- [181] J. Huang, A. Prasad, and H. Marand, *Polymer*, **35** (1994), 1986.
- [182] Z. Pelzbauer and A. Galeski, *J. Polym. Sci.*, **38C** (1972), 23.
- [183] J. D. Hoffman and J. P. Armistead, *Macromolecules*, **35** (2002), 3895.
- [184] J. G. Fatou, C. Marco, and L. Mandelkern, *Polymer*, **31** (1990), 1685.
- [185] J. G. Fatou, C. Marco, and L. Mandelkern, *Polymer*, **31** (1990), 890.
- [186] E. J. Clark and J. D. Hoffman, *Macromolecules*, **17** (1980), 878.
- [187] S. Z. D. Cheng, J. J. Janimak, A. Zhang, and H. N. Cheng, *Macromolecules*, **23** (1990), 298.
- [188] B. Monasse and J. M. Haudin, *Coll. Polym. Sci.*, **263** (1985), 822.
- [189] R. G. Alamo and C. Chi, in *Molecular Interactions and Time-Space Organization in Macromolecules*, edited by Y. Morishima, T. Norisaye, and K. Tashiro (Springer, Berlin, 1998), p. 29.
- [190] J. Xu, S. Srinivas, H. Marand, and P. Agarwal, *Macromolecules*, **31** (1998), 8230.
- [191] L. Mandelkern, unpublished observations.
- [192] N. Okui, *Polymer*, **31** (1990), 92.
- [193] N. Okui, in *Crystallization of Polymers*, edited by M. Dosi     (Kluwer Academic, Dordrecht, 1993), p. 593.
- [194] S. Br        , S. V. Meille, V. Petraccone, and B. Pinozzi, *Prog. Polym. Sci.*, **16** (1991), 361.
- [195] S. J. Organ and A. Keller, *J. Mater. Sci.*, **20** (1985), 1602.
- [196] P. J. Flory, *J. Am. Chem. Soc.*, **84** (1962), 2857.
- [197] B. Wunderlich and T. Arakawa, *J. Polym. Sci.*, **A2** (1964), 3694.
- [198] P. H. Lindenmeyer, *J. Polym. Sci.*, **1c** (1963), 5.
- [199] P. H. Lindenmeyer, *Koll. Z. Z. Polym.*, **231** (1966), 593.
- [200] I. G. Voigt-Martin, R. Alamo, and L. Mandelkern, *J. Polym. Sci.: Polym. Phys. Ed.*, **24** (1986), 1283.
- [201] J. R. Isasi, J. A. Haigh, J. T. Graham, L. Mandelkern, and R. G. Alamo, *Polymer*, **41** (2000), 8813.
- [202] I. G. Voigt-Martin and L. Mandelkern, *J. Polym. Sci.: Polym. Phys. Ed.*, **22** (1984), 1901.
- [203] I. G. Voight-Martin and L. Mandelkern, *J. Polym. Sci.: Polym. Phys. Ed.*, **19** (1981), 1769.
- [204] I. G. Voight-Martin, E. W. Fischer, and L. Mandelkern, *J. Polym. Sci.: Polym. Phys. Ed.*, **18** (1980), 2347.
- [205] L. Mandelkern, *Acc. Chem. Res.*, **23** (1990), 380.
- [206] R. G. Alamo and L. Mandelkern, *Macromolecules*, **22** (1989), 1273.

- [207] L. Mandelkern, *J. Phys. Chem.*, **75** (1971), 3920.
- [208] R. Kitamaru and L. Mandelkern, *J. Polym. Sci. Pt A-2*, **8** (1970), 2079.
- [209] N. Bekkedahl and H. Matheson, *J. Res. Nat. Bur. Stand.*, **15** (1935), 503.
- [210] F. C. Stehling and L. Mandelkern, *Macromolecules*, **3** (1970), 242.
- [211] K. H. Illers, *Koll. Z. Z. Polym.*, **231** (1969), 628.
- [212] J. Dobbertin, A. Hensel, and C. Schich, *J. Therm. Anal.*, **47** (1990), 1027.
- [213] D. S. Kalika, D. G. Gibson, D. J. Quiram, and R. A. Register, *J. Polym. Sci.: Polym. Phys. Ed.*, **36** (1998), 65.
- [214] P. P. Huo, J. B. Friller, and P. Cebe, *Polymer*, **34** (1993), 4387.
- [215] J. I. Lauritzen Jr and J. D. Hoffman, *J. Res. Nat. Bur. Stand.*, **64A** (1960), 73; **65** (1961), 297.
- [216] L. Mandelkern, *Chemtracts – Macromol. Chem.*, **3** (1992), 347.
- [217] M. L. Mansfield, *Macromolecules*, **16** (1983), 914.
- [218] P. J. Flory, D. Y. Yoon, and K. A. Dill, *Macromolecules*, **17** (1984), 82.
- [219] D. Y. Yoon and P. J. Flory, *Macromolecules*, **17** (1984), 868.
- [220] J. A. Marqusee and K. A. Dill, *Macromolecules*, **19** (1986), 2420.
- [221] J. A. Marqusee, *Macromolecules*, **22** (1989), 472.
- [222] S. K. Kumar and D. Y. Yoon, *Macromolecules*, **22** (1989), 3458.
- [223] I. Zumiga, K. Rodrigues, and W. L. Mattice, *Macromolecules*, **23** (1990), 4108.
- [224] K. A. Dill, J. Naghizadeh, and J. A. Marqusee, *Ann. Rev. Phys. Chem.*, **39** (1988), 425.
- [225] F. A. M. Leemaker, J. M. H. M. Scheatjens, and R. Gaylord, *Polymer*, **25** (1984), 1577.
- [226] L. Mandelkern and A. J. Peacock, in *Studies in Physical and Theoretical Chemistry*, Vol. 54 (Elsevier, Amsterdam, 1988), p. 201.
- [227] R. Kitamaru and F. Horii, *Adv. Polym. Sci.*, **26** (1978), 139.
- [228] S. Saito, Y. Moteki, M. Nakagawa, F. Horii, and R. Kitamaru, *Macromolecules*, **23** (1990), 3256.
- [229] R. Kitamaru, F. Horii, and K. Murayama, *Macromolecules*, **19** (1985), 636.
- [230] H. Suzakai, I. Grebowicz, and B. Weinderlich, *Macromol. Chem.*, **186** (1985), 1109.
- [231] P. Huo and P. Cebe, *Coll. Polym. Sci.*, **270** (1992), 840.
- [232] S. Z. D. Cheng, Z. Q. Wu, and B. Wunderlich, *Macromolecules*, **20** (1987), 2802.
- [233] L. Mandelkern, R. G. Alamo, and M. A. Kennedy, *Macromolecules*, **23** (1990), 4721.
- [234] M. Kunz, M. Möller, V.-R. Heirich, and H. J. Cantow, *Makromol. Chem., Makromol. Symp.*, **20–21** (1988), 147; *Makromol. Chem., Makromol. Symp.*, **23** (1989), 57.
- [235] B. Crist, *J. Polym. Sci.: Polym. Phys. Ed.*, **11** (1973), 635.
- [236] D. S. Brown and R. E. Welton, in *Developments in Polymer Characterization*, edited by J. V. Dawkins (Applied Science Publishers, New York, 1978), p. 157.
- [237] G. Porod, *Koll. Z. Z. Polym.*, **124** (1951), 83; *Koll. Z. Z. Polym.*, **125** (1952), 51.
- [238] R. S. Stein, in *New Methods of Polymer Characterization*, edited by B. Ke (Wiley-Interscience, New York, 1964).
- [239] I. Maxfield and L. Mandelkern, *Macromolecules*, **10** (1977), 1141.
- [240] L. Mandelkern, M. Glotin, and R. A. Benson, *Macromolecules*, **14** (1981), 22.
- [241] D. E. Kline, J. A. Sauer, and A. E. Woodward, *J. Polym. Sci.*, **22** (1956), 455.
- [242] R. Popli, M. Glotin, L. Mandelkern, and R. S. Benson, *J. Polym. Sci.: Polym. Phys. Ed.*, **22** (1984), 407.
- [243] D. E. Axelson, L. Mandelkern, R. Popli, and P. Mathie, *J. Polym. Sci.: Polym. Phys. Ed.*, **21** (1983), 2319.
- [244] R. Popli and L. Mandelkern, *J. Polym. Sci.: Polym. Phys. Ed.*, **25** (1987), 441.

- [245] F. C. Stehling and L. Mandelkern, *Macromolecules*, **3** (1970), 242.
- [246] C. L. Beatty and F. E. Karasz, *J. Macromol. Sci. Rev. Macromol. Chem.*, **C17** (1971), 37.
- [247] J. Simon, C. L. Beatty, and F. E. Karasz, *J. Therm. Anal.*, **7** (1975), 187.
- [248] J. J. Dechter, D. E. Axelson, A. Dekmazian, M. Glotin, and L. Mandelkern, *J. Polym. Sci.: Polym. Phys. Ed.*, **20** (1982), 641.
- [249] L. Mandelkern and R. G. Alamo, in *Polymer Data Handbook*, edited by J. E. Mark (Oxford University Press, Oxford, 1999), p. 493.
- [250] M. A. Kennedy, J. J. Peacock, and L. Mandelkern, *Macromolecules*, **27** (1994), 5297.
- [251] A. J. Peacock and L. Mandelkern, *J. Polym. Sci.: Polym. Phys. Ed.*, **28** (1990), 1917.
- [252] M. A. Kennedy, A. J. Peacock, M. D. Failla, J. C. Lucas, and L. Mandelkern, *Macromolecules*, **28** (1995), 1407.
- [253] P. J. Flory and D. Y. Yoon, *Nature*, **272** (1978), 226.
- [254] G. D. Wignall and W. Wu, *Polym. Commun.*, **24** (1983), 354.
- [255] W. Wu, G. D. Wignall, and L. Mandelkern, *Polymers*, **33** (1992), 4137.
- [256] R. J. Young, *Phil. Mag.*, **30** (1974), 85.
- [257] R. J. Young, *Mater. Forum*, **11** (1988), 210.
- [258] B. Crist, C. J. Fischer, and P. R. Howard, *Macromolecules*, **22** (1989), 1709.

Further reading

- L. Mandelkern, *Crystallization of Polymers* (McGraw-Hill, New York, 1964).
- L. Mandelkern, *Crystallization of Polymers*, 2nd edition, Vol. 1 (Cambridge University Press, Cambridge, 2002).
- B. Wunderlich, *Macromolecular Physics* (Academic Press, New York, 1980).
- Faraday Discussions of the Chemical Society*, "Organization of Macromolecules in the Condensed Phase," No. 68 (1979).
- J. H. Magill, in *Treatise on Materials Science and Technology*, Vol. 10, edited by J. M. Schultz (Academic Press, New York, 1977), p. 3.
- A. Keller, *Rep. Prog. Phys.*, **31** (1968), 623.
- L. Mandelkern, *Acc. Chem. Res.*, **23** (1990), 380.
- L. Mandelkern, *Comprehensive Polymer Sciences, Volume 2, Polymer Properties*, edited by C. Booth and C. Price (Pergamon Press, Oxford, 1989).
- Selected Works of Paul J. Flory*, Vol. 3, edited by L. Mandelkern, J. E. Mark, U. Suter, and D. Y. Yoon (Stanford University Press, Stanford, California, 1985).
- J. G. Fatou, "Crystallization kinetics," in *Encyclopedia of Polymer Science and Engineering Supplement Volume*, 2nd edition (John Wiley and Son, New York, 1989).
- D. C. Bassett, *Principles of Polymer Morphology* (Cambridge University Press, Cambridge, 1981).

5

The mesomorphic state

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5.1 Introduction

The term mesomorphism (exhibiting an intermediate form) is generally reserved for spontaneously ordered fluids – liquid crystals. Liquid crystals were discovered in 1888 and studied extensively in the early 1900s, but essentially remained a laboratory curiosity until the 1960s when electro-optic applications for these unusual fluids were initiated and prototypes of the now-commonplace liquid-crystal display (LCD) were first demonstrated. During this period of renewal of interest in liquid crystals, polymer scientists discovered that the unusually good mechanical properties of ultra-high-strength synthetic poly(arylamide) fibers were in part due to the fact that such fibers were spun from liquid-crystalline polymer solutions, e.g. DuPont’s Kevlar® and Akzo’s Twaron®. Consequently, macromolecular-design strategies for synthesizing new high-performance polymers and modeling polymer processing now routinely consider the potential role of the mesomorphic state. In this chapter we will try to develop an understanding of the liquid-crystalline state in materials of low molecular weight, since the author is convinced that this is a prerequisite for appreciating how mesomorphism affects high molecular weight polymers.

5.2 General concepts

The mesomorphic state may be realized in two ways, namely, the two ways in which ordinary fluid phases are formed from solids: *dissolution* and *fusion*. These two categories of mesomorphism are called *lyotropic* (liquid-crystalline solutions) and *thermotropic* (liquid-crystalline melts), respectively. The latter category consists of single-component substances and encompasses the large variety of low molecular weight mesogens used in LCDs. More recently, thermotropic “specialty” polymers

have been commercialized. Generally these are polyesters similar to Vectra[®], which was commercialized by Hoechst-Celanese, and Amoco's Xydar[®]. Lyotropics, on the other hand, are multicomponent mixtures (solute plus solvent). In the case of low molecular weight molecules, lyotropism requires specific solute–solvent interactions, e.g. hydrophobic–hydrophilic interactions in amphiphile (soap)–water mixtures. Such interactions drive the assembly of solutes into aggregates with a variety of shapes (micelles). At high solute concentrations, anisometric aggregates with high aspect ratios, L/d (aggregate length/aggregate diameter), will in turn organize in the excess solvent medium to give fluid, orientationally ordered arrangements of aggregates (e.g. cubic, hexagonal, lamellar, and bicontinuous gyroid phases). However, in the case of lyotropic polymer mesophases, specific solute–solvent interactions are not necessary, apart from those interactions needed to solubilize the polymer; the local high aspect ratio (persistence length) of rod-like polymers is sufficient to induce orientational order in such solutions. Solutions of rigid, high-aspect-ratio macromolecules will spontaneously order above some critical polymer concentration ϕ that depends merely on geometry (L/d); excluded-volume interactions among the rod-like polymers simply force the adoption of long-range, quasiparallel organization of discrete, mobile macromolecules in the fluid solvent continuum.

The phenomenon of spontaneously ordered “macromolecular” solutions was first observed in the 1930s. Solutions of the rod-like virus particle TMV (tobacco mosaic virus) exhibited spontaneous birefringence above some critical volume fraction of TMV. Curiously, despite the dominance of thermotropic systems both in experimental and in theoretical activity in liquid-crystal research prior to 1950, the first valid theoretical model of the phenomenon of liquid-crystal formation, i.e. modeling the disorder–order transformation in a fluid phase, was developed in the late 1940s by Lars Onsager to describe this rather esoteric, lyotropic TMV solution. Herein we will briefly review subsequent theories of the disorder–order transition exhibited by liquid crystals, including extensions of the original Onsager model. The implications of mesomorphism for the viscoelastic behavior of fluid phases of polymers will also be considered. This aspect of polymer mesomorphism is especially important since the rheological behavior of polymer fluids is intimately related to the morphology that forms in the solid state. In turn, this morphology determines the ultimate bulk properties of the polymer.

In certain high molecular weight materials (e.g. deformed elastomers, amorphous regions in semicrystalline polymers, and phase-separated block copolymers) some characteristics of the mesomorphic state are observed, namely local orientational order in the absence of translational order. In some instances researchers have tried to describe the deviation from isotropy observed on a local scale in these materials with the vocabulary used for liquid crystals. Indiscriminate applications

of terminology are confusing, however, leading to misconceptions both about the nature of liquid crystallinity and about the nature of order in amorphous polymers. A consistent manner of describing such superficially related, conventional polymer morphologies is lacking, so we will try to place these nonmesogenic materials into a proper context when they are encountered.

Herein we shall interchange the descriptors *mesogen* and *liquid crystal* (LC) when referring to a *molecule* that exhibits mesomorphism. Additionally, we will introduce the abbreviation MLC to represent both “low molecular weight liquid crystal” and “monomer liquid crystal.” PLC and LCP will be used to differentiate between mesogenic polymers synthesized from MLCs and those prepared from conventional (commercial) monomers, respectively. Initially the qualitative features of low molecular weight liquid crystals will be considered in a manner that facilitates the transfer of the underlying physics and characteristics of these materials to macromolecular systems. Generally we will not dwell on differences among either low molecular weight or macromolecular mesogens that derive from idiosyncratic chemical origins, i.e. differences stemming from the primary atomic constitutions of the mesogens. Rather, we stress throughout only the general features of mesomorphism. In keeping with this goal, both for polymerized monomer liquid crystals (PLCs) and for liquid-crystalline polymers (LCPs) derived from conventional monomers (e.g. aromatic esters and amides), we need examine only a few primary structural types: *linear* (main-chain) polymers, *side-chain* (comb-like) polymers, and *dendritic* (star and hyperbranched) polymers. We will adhere to the nomenclature advocated by the International Union of Pure and Applied Chemistry (IUPAC) [1]. The references begin with a reverse chronological list of books and substantial reviews intended to expedite searching the literature for more in-depth treatments of the mesomorphic state, especially as it relates to polymers [2–26].

5.2.1 Definitions and terminology

In order to appreciate the mesomorphic state in polymers, it is necessary to understand the subtleties of long-range molecular organization in fluid phases of simple molecules by first examining mesomorphism in low molecular weight materials. This examination, in turn, necessitates the identification of the variables which quantify translational and orientational order in fluid states. To introduce these variables in a systematic way starting from a familiar frame of reference, we will begin with some brief remarks about the molecular structural features of low molecular weight liquid crystals.

Figure 5.1 illustrates example molecular primary structures, associated schematic secondary structures, and idealized shapes for representative thermotropic MLCs – organic molecules that melt into ordered, fluid, mesophases. The so-called

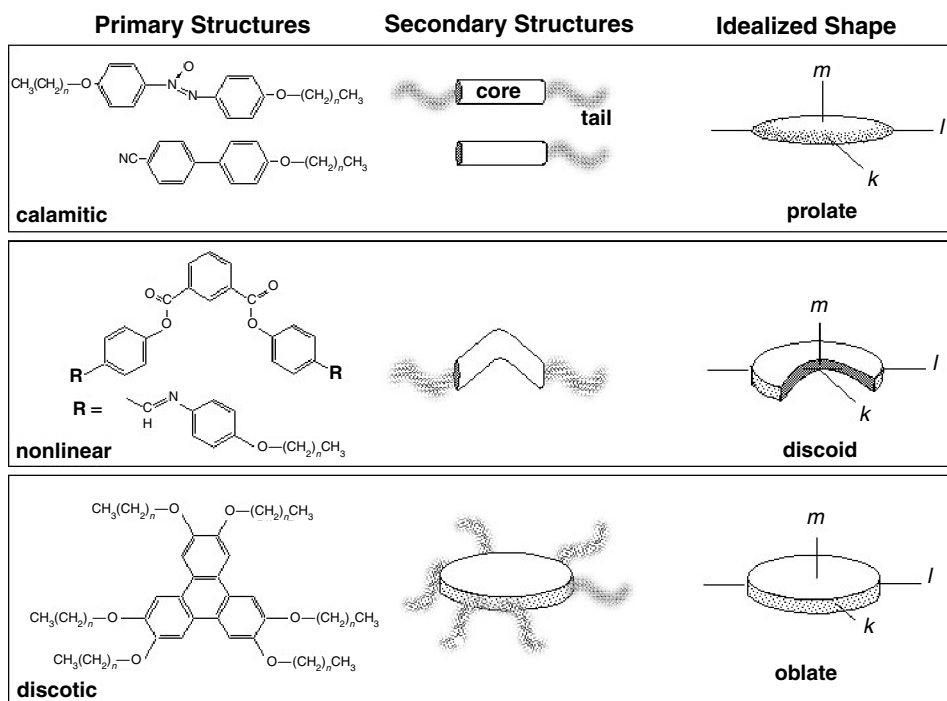


Fig. 5.1. Example molecular structures of low molecular weight liquid crystals. From left to right, primary chemical constitutions, low-resolution secondary structures, and lastly the idealized shapes for calamitic (prolate, rod-like, or lathe-like), nonlinear (discoid-, banana- or boomerang-shaped), and discotic (oblate or disk-like) mesogens.

mesogenic core is that primitive central segment of the mesogen (usually comprised of aromatic rings) possessing the requisite excluded-volume interactions – correlated dynamic packing of anisometric shapes – for inducing liquid crystallinity in the melt. The flexible *tails*, generally hydrocarbon chains, which terminate the rigid mesogenic core facilitate the transformation from the solid state to the fluid LC phase: the flexible tails lower the melting temperature of the crystal by weakening (diluting) attractive intermolecular interactions between rigid mesogenic cores in the solid state, and isomerization of the tails provides an entropic stabilization of the LC phase. Phenomenological modeling is facilitated if the secondary structures of MLCs are further abstracted into idealized prolate or oblate ellipsoids of revolution. Liquid crystals comprised of such extreme molecular shapes are called *calamitic* and *discotic*, respectively. A prolate mesogen's axis of symmetry is denoted by **l** (see Fig. 5.1) and **l** is usually referred to as the *molecular long axis*. More recently, considerable attention has been focused on intermediate-shaped nonlinear or bent mesogens, sometimes referred to as *banana-* or *boomerang-shaped*

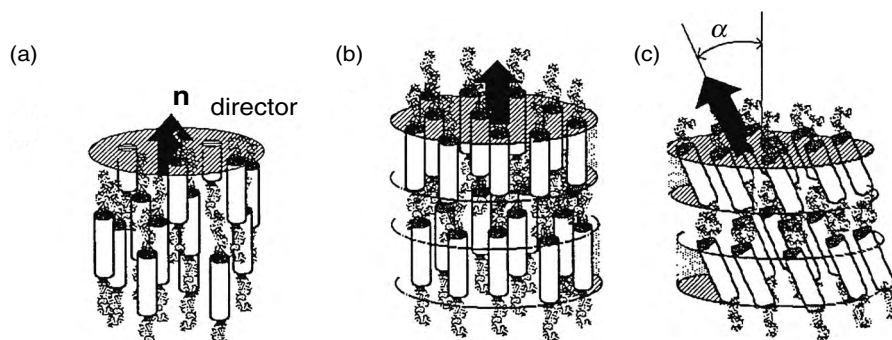


Fig. 5.2. Schematic idealized pictures of calamitic mesogen supramolecular organization in (a) uniaxial nematic (N), (b) uniaxial smectic-A (S_A), and (c) biaxial smectic-C (S_C) with an average tilt α depicted in the layers; conservation of the tilt direction from layer to layer is called a *synclinal stacking motif*.

molecules. When the mesogen is sufficiently bent new LC phases called *banana phases* may be observed. Nonlinear mesogens of the type shown in Fig. 5.1 were originally reported by Vorländer in 1927 [27]; their idealized shape is intermediate between that of calamitics and that of discotics and might best be illustrated as a discoid shape. Using the low-resolution depiction of mesogen shapes in Fig. 5.1, we can proceed to describe the common types of supramolecular organizations found in mesophases composed of these three categories of MLCs.

Figure 5.2 exaggerates the kinds of organization found in fluid mesophases of calamitic MLCs. The nematic is the most common mesophase. It is a fluid with cylindrical symmetry and there is no preference for the molecule's sense (up or down), i.e. the nematic LC is an apolar phase. The freeze-frame cartoon image of the nematic depicted in Figure 5.2 has the centers of mass of the mesogen randomly located, emphasizing the phase's translational disorder. The signature of LC phases is molecular orientational order and this is shown by having the mesogen's long axis $\mathbf{l}$ more or less parallel to the fluid's axis of symmetry, $\mathbf{n}$, which is called the *director*. The director $\mathbf{n}$ is defined to be the local average orientation of the long axes of the mesogen, and $\mathbf{n}$ is also the unique optic axis of the phase. Local uniaxial molecular orientational order is also found in the common *smectic* phases, but, in addition to this order, smectic phases exhibit some degree of molecular translational ordering: the mesogens exhibit a tendency to stratify into layers. (This layering is also extremely exaggerated in Fig. 5.2; the stratification in many smectics is detectable only by using diffraction techniques that are sensitive to subtle, periodic, spatial variations in the electron density.) In smectic LCs, the presence of translational segregation merely modifies this phase's fluidity. Translation is anisotropic, with molecules moving more readily within layers; translation ("jumps") between layers is also possible. There is a large variety, almost a continuum, of variations on

stratified organization. Hence smectics are called *polymorphic* [28]. The simplest smectic, illustrated in Fig. 5.2(b), is called a *smectic A* (S_A) phase with the molecular **l**-axis *on average* normal to the plane of the layer, i.e. in the S_A phase the local director **n** is perpendicular to the smectic layers. Tilted smectics are also common; the *smectic C* (S_C) phase has the molecular **l** axis on average tilted with respect to the layer normal; hence the local director **n** makes an angle α with respect to the layer normal. If the direction of the tilt – the orientation of the projection of **n** on to the smectic plane ($\sin \alpha$) – is conserved from layer to layer within a macroscopic volume element in the mesophase, the interlayer stacking motif is called *synclinic* (shown in Fig. 5.2(b)). A stacking motif having an alternation of the tilt direction by 180° from layer to layer is called *anticlinic*. There are corresponding normal and tilted smectic phases with more subtle features: stratified calamitics with antiferroelectric organization (mutually canceling polar orientations in neighboring layers; S_{A_2} and S_{C_2} , smectics with pronounced interdigitation (layers comprised of dimers of associated pairs of mesogens, S_{A_d} and S_{C_d}), and smectics with mesogens exhibiting both long-range layer definition and short-range in-plane packing preferences (hexagonal and hexatic order) with normal (S_B) and tilted (S_I and S_F) local directors [3].

The nematic phase of nonlinear mesogens may be biaxial – a translationally disordered fluid phase with two directors **n** and **o** specifying the orientational order (Fig. 5.3). Biaxial order in a nematic is predicted to occur [29] if the shape anisotropy of the idealized molecule (discoid) representing the nonlinear mesogen is appropriately intermediate between the prolate shape of calamitics and the oblate shape of discotics. Discoid-shaped mesogens lend themselves to a variety of stratified phases. Ferroelectric (S_{AP_F}) and antiferroelectric (S_{AP_A}) layer motifs in the normal smectic phases of discoid-shaped mesogens are readily envisioned (Fig. 5.4), but less obvious is the possibility of generating chiral supramolecular structures from such achiral discoid-shaped mesogens (Fig. 5.5) [30].

There are related supramolecular arrangements of discotic mesogens: the uniaxial nematic phase (D_N) having the molecular symmetry axes, **m** axes, aligned parallel to **n** (Fig. 5.6(a)), the uniaxial hexagonally arranged columns with ordered (D_{ho}) and disordered (D_{hd}) stacking of the disk-like mesogens in the columns (Figs. 5.6(b) and (c), respectively), and, analogously to the tilted calamitic smectics, orthorhombic, biaxial arrangements can form a D_{obd} phase having a translationally disordered stack of disk-like molecules wherein the **m** axes make an oblique angle with the column axis. Perhaps the most technologically important discotic mesophase is that produced by heating “pitch” – fused-ring, graphitic molecules comprising the residue of coal tar. The resulting birefringent melt is a carbonaceous mesophase that is the precursor to ultra-high-strength carbon fibers [31].

There exist also *cubic* arrangements of mesogens (called S_D phases in calamitic liquid crystals). Such isotropic supramolecular structures typically are found

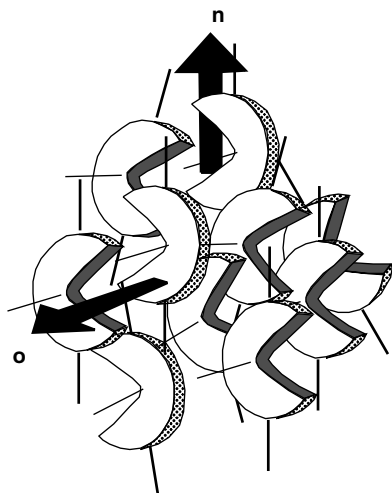


Fig. 5.3. A Schematic diagram of the molecular arrangement in a biaxial nematic phase (N_b) comprised of discoid-shaped mesogens. The primary director is designated by the usual letter, $\mathbf{n}$, and the secondary director, $\mathbf{o}$, is orthogonal to $\mathbf{n}$.

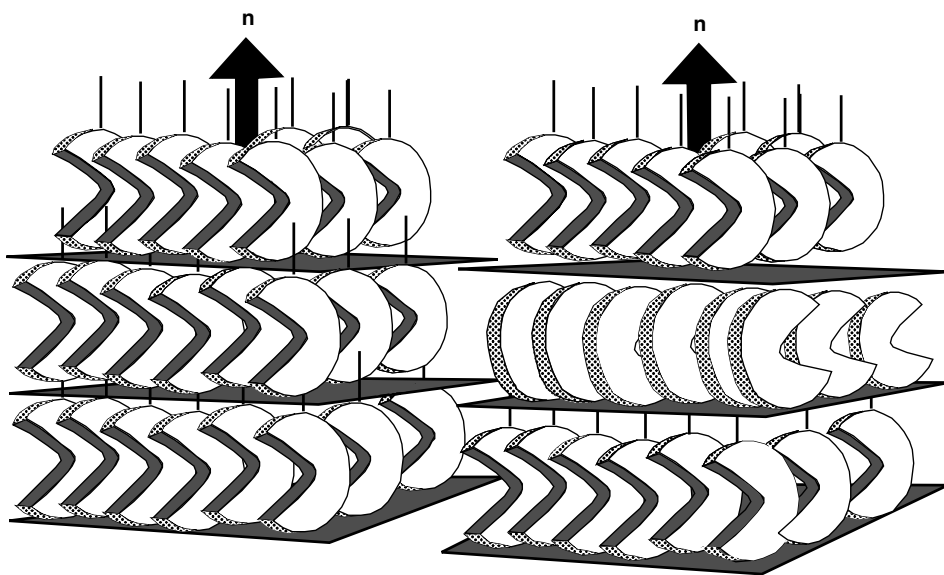


Fig. 5.4. Polar packing motifs exhibited by vertically aligned, discoid-shaped mesogens in smectic strata (the $\mathbf{l}$ axes are normal to the strata). On the left the polar orientation of the discoids in each layer is the same and the phase is ferroelectric (S_{AP_F}); on the right the polar orientations are opposed in neighboring layers and the phase is antiferroelectric (S_{AP_A}).

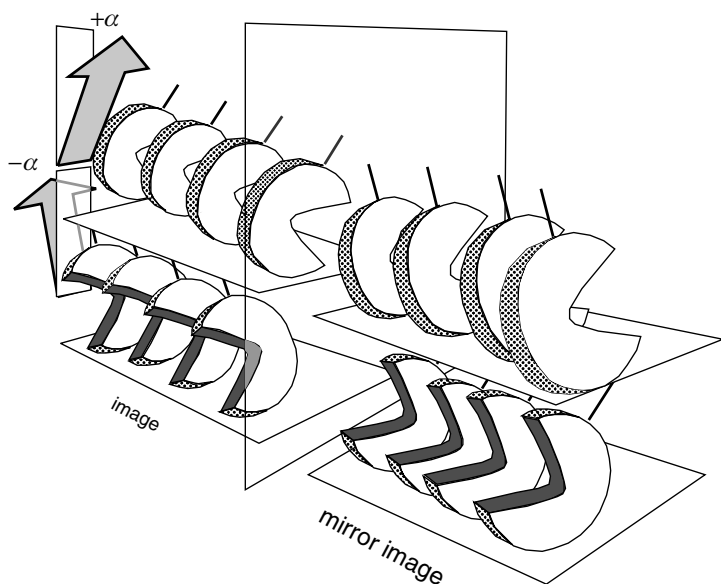


Fig. 5.5. Chiral phases can result for tilted packing motifs in the smectics composed of achiral discoid mesogens. An antiferroelectric polar sense is shown for discoids with opposite tilts ($\pm\alpha$) in neighboring layers. The mirror image of this packing motif is not superposable on its original.

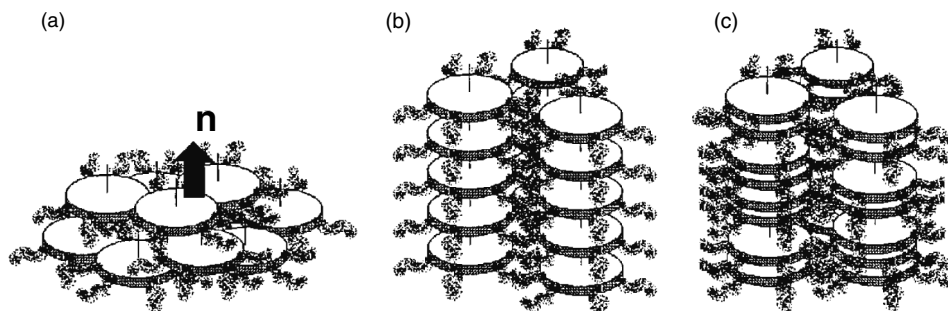


Fig. 5.6. Schematic pictures of discotic uniaxial supramolecular organizations: (a) nematic (D_N), (b) hexagonal ordered (D_{ho}), and (c) hexagonal disordered (D_{hd}).

between more conventional smectic phases (i.e. between the S_C and S_A phases in polymorphic calamitic mesogens) or in the so-called “blue phase” exhibited by chiral nematics. In such cubic liquid crystals the bulk properties obviously would appear to be isotropic just as in an ordinary liquid. However, the local molecular arrangements are anisotropic and generate overall cubic symmetry via higher-scale organization of the anisotropic substructures [32].

Some smectic phases possess substantial orientational and translational order, and such molecular organization really begs the following question: *How do you distinguish a liquid crystal from a crystal?* Despite there being a high degree of local order in some smectics (e.g. S_B) it is important to distinguish such order from that in molecular crystals: perfect translational and orientational order. The focus of this chapter is on fluid phases wherein molecules exhibit some degree of order *on average*. That is, if one performs an average over many millions of molecules in a local region of the fluid mesophase, or equivalently, if one conducts a time average over the motion of a single molecule, the result is that a preferred direction of molecular alignment, $\mathbf{n}$, is detected in the mesophase. It is orientational order, with or without some degree of translational order, in a fluid phase that is the distinguishing characteristic of the mesomorphic state. We next consider properties of these fluids that allow us to confirm the existence of long-range, motionally averaged molecular order.

5.2.2 Birefringent fluids

A cubic molecular arrangement in the unit cells of certain crystals or the random arrangement of molecules in ordinary liquids results in isotropy of the refractive index – that is, a single number characterizes the speed of light in isotropic matter. The transmission of visible light by substances placed between crossed polars (a linear polarizer–analyzer pair with principal dichroic axes at right angles to one another) is observed in crystals having direction-dependent refractive indices – this is called *birefringence*. Birefringence is a convenient indicator of long-range molecular orientational order. The detection of birefringence in a homogeneous fluid melt or solution comprised of dispersed, individual particles (single molecules or aggregates of molecules) is a key signature of thermotropic and lyotropic mesomorphism. This unique indicator of mesophases might best be understood by recalling the properties and molecular organization in the solid state of a molecular crystal. Certain space-group symmetries excepted (e.g. crystals with cubic symmetry), most molecular crystals exhibit anisotropic physical properties – direction-dependent properties, relative to the crystallographic axes – such as in their thermal expansion, refraction of visible light, dichroism (visible, UV, and IR), and magnetic and dielectric susceptibilities. This *macroscopic anisotropy* of various properties has its origins in the replication of the anisotropic molecular arrangements in the crystal's unit cell throughout the entire crystal. Such long-range and unvarying relative placements and orientations of molecules may amplify a particular intrinsic *molecular anisotropy*. For example, the refractive index of a crystal is ultimately related to the (anisotropic) molecular electronic polarizability. Coarsely speaking, the molecular polarizability is additive and collectively anisotropic if all molecules have the same orientation in the crystal. Rotation of plane-polarized light by birefringent

crystals is one dramatic macroscopic indicator of anisotropy at the molecular and supramolecular level. Birefringence is conspicuously absent for ordinary liquids and other isotropic media (glasses) because there is no long-range structure¹ to manifest the anisotropy of the molecules in these materials.

5.2.3 Thermodynamic properties

On heating a molecular crystal composed of low molecular weight mesogens (MLCs), very rapid but severely restricted thermal motions gradually increase in amplitude up to the melting point (T_m). In some crystals there may be one or more discrete, small structural reorganizations in the solid before T_m is reached, e.g. a conformational change such as the population of a *gauche* rotational isomer in an alkyl tail, or a translational shift in the packing motif of the mesogen within the crystal's unit cell. However, in such crystals the material remains solid and those structural reorganizations are called *solid-state transitions*. At T_m there is an abrupt collapse of the long-range translational and orientational order in the crystal. In the resulting fluid phase, the molecules interact with one another via motionally averaged intermolecular forces. In fluids composed of anisometric calamitic molecules having an aspect ratio $L/d > 3$ (or $d/L < 3$ for oblate discotic mesogens), the averaged dispersion forces must conform to anisotropic, steric (excluded-volume) packing considerations. This steric constraint results in an attractive intermolecular interaction that depends on the relative orientations of molecules. A delicate balance between the residual anisotropy of the interactions that promote orientational order in the melt and the thermal energy that tries to minimize the angular dependence of the interactions may be established. Sometimes this balance results in a range of temperature (thermal energies) wherein long-range orientational order is able to persist in the fluid, i.e. a mesophase is thermodynamically stable. This delicate balance is eventually overwhelmed by the chaotic molecular motion at higher temperatures, and, above the so-called *clearing temperature*, T_{cl} , all remnants of orientational order in the fluid disappear.

At the nominal melting point T_m there is a first-order phase transition from the crystal to the mesophase with the usual discontinuities in the extensive properties (e.g. volume and entropy). In Fig. 5.7, we schematically illustrate a hypothetical differential-scanning-calorimetry (DSC) trace and the variation in volume of the sample versus temperature for an ideal nematic. The values for the changes in enthalpy ($\Delta H \sim 45 \text{ kJ mol}^{-1}$) and volume ($\Delta V \sim 10\%$) at T_m are typical of those changes in extensive properties that occur on melting ordinary organic molecular crystals. However, if you continue to heat the opalescent-looking mesophase, there is a second transition to a transparent isotropic state above T_{cl} . Nematic melts

¹ Molecular organization extending over distances comparable to the wavelength of visible light ($\sim 10^{-6} \text{ m}$).

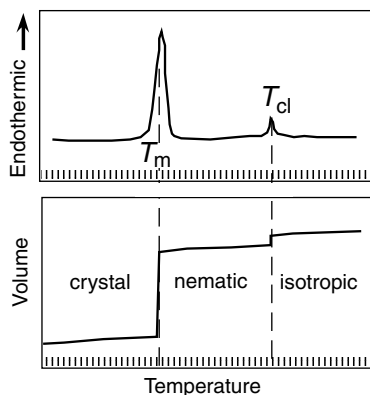
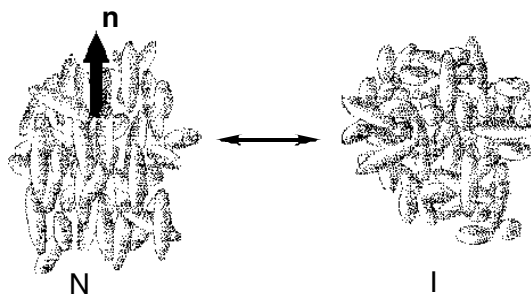


Fig. 5.7. An illustration of hypothetical endothermic transitions (DSC trace) and changes in volume that occur on melting a molecular crystal into a nematic mesophase at T_m , and the subsequent melting of the nematic phase into the isotropic liquid at the clearing temperature T_{cl} .

appear milky and opalescent because thermal energy excites fluctuations in the (bi)refractive index and these fluctuations scatter light. At T_{cl} , the magnitudes of the changes ΔH and ΔV associated with the nematic–isotropic transition ($N \leftrightarrow I$) are much smaller than those observed at T_m , but nevertheless are indicative of a first-order phase transition. The very small value of ΔH and the slight discontinuity in ΔV at the $N \leftrightarrow I$ transition imply that there are only very subtle differences between the “structure” in these two fluid phases. That is, despite the apparently dramatic changes in macroscopic properties (e.g. scattering of light and birefringence) at the $N \leftrightarrow I$ transition, the fact that very small thermodynamic changes are observed at T_{cl} suggests that a nematic mesophase is a homogeneous fluid with molecular motion and molecular order very similar to those in an ordinary isotropic liquid. Hence, rather than the exaggerated features of the nematic organization depicted in Fig. 5.2(a), a more realistic cartoon stressing the subtle differences between a mesophase and the isotropic liquid should be considered:



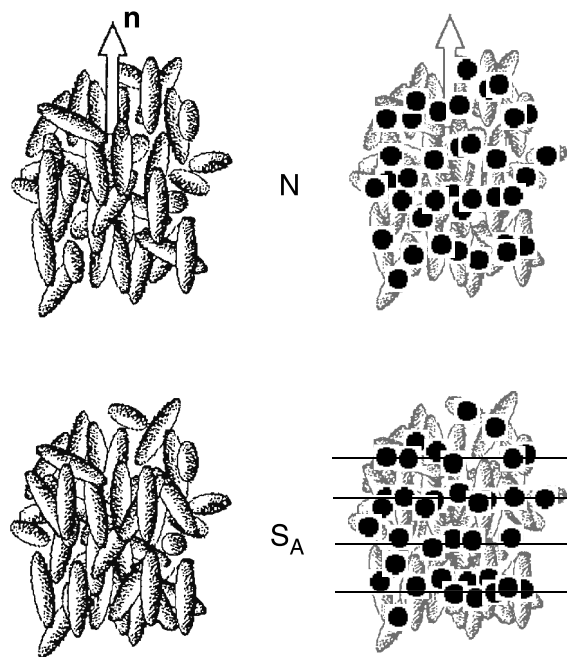
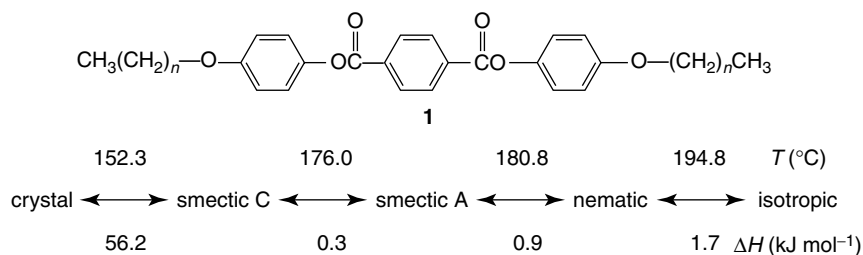


Fig. 5.8. Nematic versus smectic A molecular organization. In the nematic phase a translationally disordered distribution of molecular centers of mass is found along the director (top). For a smectic phase a Fourier analysis of the distribution of centers of mass along n exhibits a fundamental frequency component with a wavelength approximately equal to the molecular length (bottom). This subtle tendency toward stratification is frequently exaggerated in diagrams (e.g. Fig. 5.2), giving the false impression of there being well-delineated layers in the fluid smectic phases (e.g. the S_A and S_C phases).

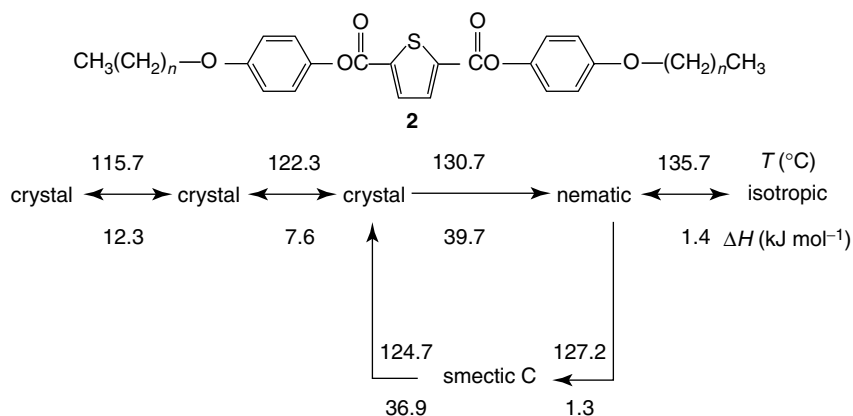
In actuality it is very difficult to discern the differences between the isotropic liquid and the nematic at the molecular level (the sketch on p. 326 also exaggerates the local packing differences). Likewise, the stratification characteristic of the S_A phase is very exaggerated in Fig. 5.2; it is more aptly represented by the cartoons in Fig. 5.8, where we attempt to emphasize the similarity between the uniaxial N and S_A phases by showing the distribution of the centers of mass on the right-hand side of the figure.

Some mesogens are *polymorphic*, exhibiting more than one type of liquid-crystalline phase as the temperature is changed. When the transitions are reversible, they are called *enantiotropic* transitions. Enantiotropic polymorphism is observed for bis(*p*-heptyloxyphenyl) terephthalate (**1**): with $n = 6$. The transition temperatures ($^{\circ}\text{C}$) and changes in enthalpy (kJ mol^{-1}) experimentally observed for **1** are indicated on the *transition map* shown below the molecular formula. Mesogen **1** exhibits two smectics and a nematic phase; the more ordered S_C phase occurs at



the lower temperature, followed by increasingly less ordered mesophases at higher temperatures (S_A and N). On heating **1**, the crystal melts into a S_C phase, which in turn melts into a S_A phase; the delicate organizational differences between these two smectic phases – they differ only in terms of by the average molecular tilt (Figs. 5.2(b) and (c)) – are reflected in the very small change in enthalpy ($0.3\ \text{kJ mol}^{-1}$) associated with the $S_C \leftrightarrow S_A$ transition. At a higher temperature the nematic phase forms and eventually it melts into the isotropic liquid.

Monotropic transitions describe mesophases that are not thermally reversible; they are encountered on heating only or on cooling only. This phenomenon is exhibited by the nonlinear mesogen bis(*p*-heptyloxyphenyl)-2,5-thiophene dicarboxylate (**2**) with $n = 6$:



Mesogen **2** exhibits an enantiotropic $N \leftrightarrow I$ transition at $135.7\ ^{\circ}\text{C}$ and a monotropic $N \leftrightarrow S_C$ transition on cooling at $127.2\ ^{\circ}\text{C}$ [33]. Monotropism can occur, for example, when energetic intermolecular interactions (e.g. hydrogen bonds, and dipole–dipole interactions) are present in the crystal making T_m higher than the upper temperature limit for a particular mesophase. In such cases the material bypasses a lower-temperature phase and melts directly into a higher-temperature mesophase or the isotropic melt. On cooling, however, a monotropic mesophase might appear and remain stable at temperatures lower than T_m (before crystallization occurs). In

this instance we say that the mesophase is *supercooled*. In polymers, supercooling and the concomitant intervention of a *glass transition* will be a common occurrence. Mesogen **2** also exhibits two *solid-state transitions*, at 115.7 and 122.3 °C, delineating three distinct crystal phases with relatively large changes in enthalpy on going between them (12.3 and 7.6 kJ mol⁻¹, respectively). Glass formation is one way to obtain a solid replica of the molecular organization in the mesophase and may have practical technological implications, especially for optical applications in which the mesophase is a host matrix for a guest molecule with special orientation-dependent optical characteristics [34].

5.2.4 Mesophase textures

It is possible to identify the various types of molecular organization in mesophases by the *texture* – the pattern of light and dark morphological features superposed on a (colored) birefringent field when the mesophase is observed with a polarizing microscope. When nematics are confined between two glass plates, they exhibit a so-called *schlieren texture* with two- and four-armed *brushes* – an intersecting pattern of dark bands (Fig. 5.9, left-hand side). These brush-like patterns arise from *disclinations*, the analog of dislocations in a crystal, where the director changes orientation abruptly in the mesophase. There is a dramatic change in the texture at the nematic–smectic phase transition, with the S_A phase typically exhibiting a *focal conic texture* (Fig. 5.9, right-hand side).

With some practice and the aid of published photomicrographs of mesophase textures [3, 28], it is possible to recognize features that are specific to nematic and smectic phases and, moreover, to differentiate among various smectics. Additionally, via specific surface treatments – rubbing and sometimes also chemically

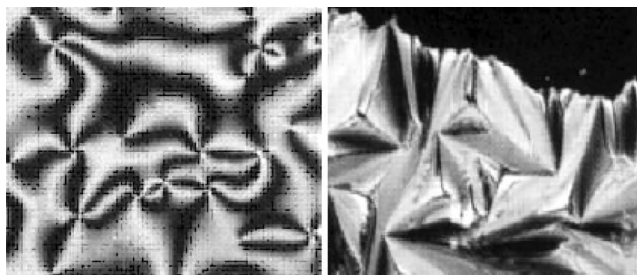


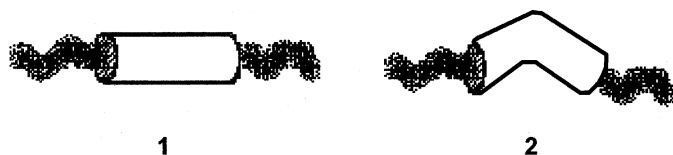
Fig. 5.9. Polarizing-microscope images of the nematic *schlieren* texture (left) and the focal conic texture of a smectic A phase (right). The reader should not try to infer any three-dimensional character from these images. The subtle variation from light to dark is merely a two-dimensional mapping of the birefringence in the plane of the samples.

modifying substrates – it is possible to *anchor* the director $\mathbf{n}$ either normal or parallel to a flat substrate (e.g. a glass microscope slide or cover slip). The former anchoring mode is called *homeotropic* alignment. In the case of a uniaxial phase with $\mathbf{n}$ coincident with the viewing direction, homeotropic alignment does not rotate the polarization of the incident light and consequently this anchoring mode appears dark in the polarizing microscope as no light passes through the orthogonal polarizer and analyzer optics. (The dark region in Fig. 5.9, right-hand side, corresponds to a homeotropically aligned section of the sample where the smectic layers are tangential to the glass substrates.) In *planar alignment* $\mathbf{n}$ is parallel to the substrate and usually anchored in a particular direction. The nominally bright birefringence of such a sample viewed between crossed polars is dark only when the planar, aligned sample is rotated so that the director is parallel either to the polarizer or to the analyzer.

5.2.5 Molecular structures of mesogens

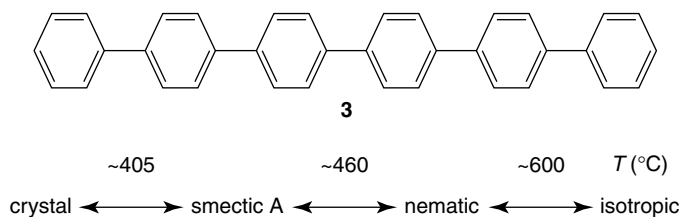
It is well known that significant differences in supramolecular organization (nematic, smectic, etc.) and stability (the temperature range wherein mesomorphism is exhibited) of a mesogen may be affected by apparently small chemical changes in the mesogen's primary structure (e.g. substituting a halogen for a hydrogen atom). However, such a high-resolution description of how mesomorphism is related to subtle chemical structural changes is beyond the scope of this chapter and we refer readers to the numerous tabulations of correlations between chemical structures of mesogens and types of LC phase exhibited [35]. A lower-resolution description of the phenomenon of liquid crystallinity is accessible if we focus on the coarse secondary structure of the mesogen and its influence by promoting specific kinds of organization. In fact, many of the physical attributes of liquid crystals can be understood in terms of the simplified idealized shapes of mesogens given in Fig. 5.1, without reference to the primary chemical composition of the mesogen at all.

In actuality, we cannot totally avoid molecular structural features. A particularly instructive case in point arises when we attempt to answer the following question: *How far can one distort the calamitic mesogenic core from the shape of a prolate ellipsoid?* In going from mesogen **1** to mesogen **2** (p. 328), we substituted the 1,4-phenylene ring with the 2,5-thiophene ring, introducing a bend into the mesogenic core as depicted schematically below:



The bend derives from the geometry of the thiophene ring: there is an angle of about 150° subtended by the 2,5-exocyclic bonds in **2**. Correspondingly the stability (temperature range) of the mesophase for compound **2** is less than that found for compound **1**, e.g. the nematic range is only five degrees with $T_{\text{cl}} = 135.7^\circ\text{C}$ for **2**, whereas for **1** the nematic persists for 14 degrees and is stable up to a higher temperature, $T_{\text{cl}} = 194.8^\circ\text{C}$. Molecules in which the 1,4-phenylene of **1** is replaced by the 1,3-phenylene unit are not mesomorphic at all. The 120° bend in the core of the 1,3-derivative frustrates the kinds of molecular packing required for a stable mesophase. However, with larger mesogenic core units the 120° bend is compatible with liquid crystallinity (for example, the Schiff's base nonlinear mesogen shown in Fig. 5.1).

Another example of the relevance of molecular structure is encountered when one asks *Why do smectic phases form?* There is no single answer to this deceptively simple question. A contemporary reply based on excluded-volume considerations alone using the idealized ellipsoidal shapes in Fig. 5.1 would stress a mechanism of stabilization of the smectic phase that is based on an increase in translational freedom. Increases in translational entropy can occur when the mesogens condense into layers, because, relative to that in the layered smectic, lateral diffusion (normal to the director) is impeded in the nematic with its randomly disposed centers of mass of the mesogens (see Fig. 5.8). In mesogens with higher aspect ratios (and in monodisperse polymers), the free volume associated with the molecule's ends is isolated near the ends of a mesogen in the nematic phase, whereas it is "shared" by many mesogens in the stratified smectic phase, thereby contributing to stabilization due to the entropy of mixing of this free volume [36]. Such concepts allow one to rationalize the appearance of the smectic phase in the all-aromatic mesogen sexiphenyl (**3**) [37]:



More-traditional replies to the question of why smectics form implicate molecular secondary structural features (Figs. 5.1 and 5.2). Consider the bis(*p*-alkyloxyphenyl) terephthalate homologous series – a fixed mesogenic core with a systematic progression of the terminal alkyl chain length y . (The homologue with $y = 7$ corresponds to mesogen **1** considered earlier.) The experimental transition temperatures ($^{\circ}\text{C}$) for the members of the series are plotted on the phase diagram (versus chain length y) in Fig. 5.10. Within the homologous series the more ordered

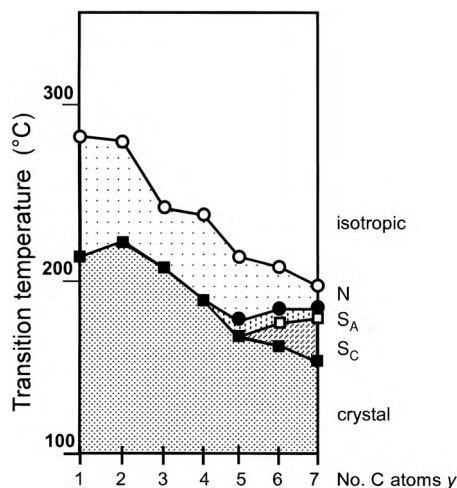
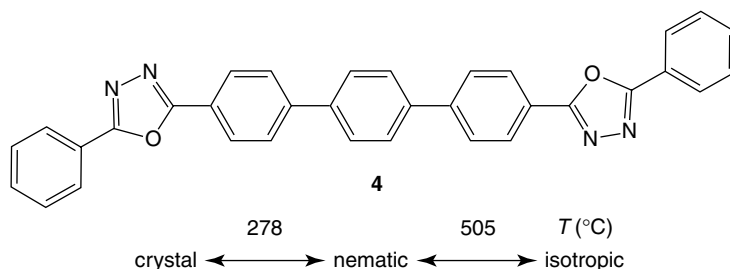


Fig. 5.10. A phase diagram showing the transition temperatures ($^{\circ}\text{C}$) versus the alkyl-tail length (number of atoms $y = n + 1$) for the homologous series of bis(*p*-alkyloxyphenyl) terephthalates (after [33]).

S_A phase begins to displace the nematic phase at greater chain length ($y = 5$). Then, for longer chains, the slightly more ordered (tilted) S_C phase grows into the phase diagram (Fig. 5.10, $y = 6$). It is as if there were a tendency, with increasing chain length, for *nanophase separation* to occur, wherein molecular cores reside preferentially next to neighboring cores separated from a chain-rich stratum to give the exaggerated, alternating *... tails-cores-tails-cores ...* motif shown in Figs. 5.2(b) and (c). This secondary-structure-driven hypothesis for formation of the smectic phase has an entropic stabilization component also; the conformational freedom of chains is larger in the aliphatic-rich stratum than it is when tails are constrained by excluded-volume interactions with neighboring mesogenic cores [38]. Smectic stratification is also reinforced by thermodynamic considerations: chemically similar parts of the mesogens associate in the smectic organization; such chemical segregation may be enhanced by increasing the difference between the chemical characters of the cores through the use of perfluorinated [39] or siloxane [40] pendant chains.

Primary-structure-based mechanisms for formation of the smectic phase also exist: there are putative correlations between formation of the tilted S_C phase and the location of permanent electric dipoles on the mesogenic core. However, attempts to induce the formation of tilted smectic phases in an aromatic analog of sexiphenyl by adding large “outboard” dipoles failed; compound **4**, with ~ 4 -Debye dipoles associated with the oxadiazole rings, in fact exhibits an unusually large nematic phase spanning more than 225°C [41]:



In the case of copolymer LCs there is speculation that the alternating primary structure...*core-spacer-core-spacer*... restricts inter-core translations and thereby stabilizes smectic phases. While we remain cognizant of the potentially important role that primary and secondary molecular structure of mesogens can play, in the remainder of this chapter, however, we will focus on aspects of mesomorphism that, for the most part, can be described in terms of the idealized prolate (oblate) shape of calamitic (discotic) mesogens (Fig. 5.1). We consider the nature and implications of the local molecular order in the nematic state after briefly reviewing the molecular crystal and the isotropic liquid.

5.3 Monomer liquid crystals

5.3.1 Molecular crystals

The perfect order in a molecular crystal allows one to interrogate its structural features – molecular organization – with X-ray diffraction. The regular, periodic variation in electron density diffracts X-rays, allowing one to reconstruct the relative positions and orientations of molecules in the crystal's unit cell. Consider for heuristic reasons the packing of the idealized shapes of calamitic low molecular weight mesogens. The nature of how the coarse features of a crystal's structure are related to the scattered X-ray intensity is schematically illustrated in Fig. 5.11. A microscopic fragment of a crystal composed of prolate molecules having the **l** axes parallel to the **c** axis of the crystal is shown in the cartoon inset of Fig. 5.11.

X-rays incident along the **b** axis will be diffracted when the Bragg condition, $n\lambda = 2d \sin \theta$ is satisfied. In the idealized diffraction pattern shown in Fig. 5.11, two sets of diffraction spots are indicated. Those along the meridian (vertical direction, parallel to the **c** axis) correspond to multiple-order diffraction ($n = 1, 2, 3, \dots$) with a spacing that is reciprocally related to the molecular length L . The larger-spaced diffraction maxima on the equator (horizontal direction) correspond to the smaller, regular lateral spacing D between molecules (along the **a** axis). The absence of azimuthal diffraction intensity (well-defined spots rather than arcs

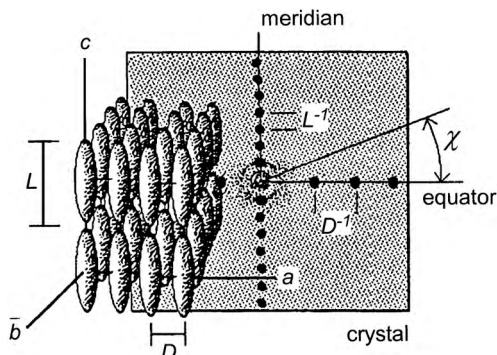


Fig. 5.11. Schematic representations of the molecular crystal of calamitic molecules and the associated idealized diffraction pattern for incident X-rays parallel to **b**. The intermolecular distances L (the approximate length of the molecule) and D (the lateral spacing) correspond to diffraction spots on the meridian and equator, respectively; there is no appreciable azimuthal spread of the diffraction along χ .

of intensity along χ) indicates that there is perfect orientational order within the crystal, i.e. $\mathbf{l} \parallel \mathbf{c}$. We may use this schematic diffraction pattern as a benchmark for characterizing structure – molecular translational and orientational order – in mesophases. However, in an effort to place the molecular organization present in the mesomorphic state into a more general context, it is instructive to review the nature of structure in the state of complete disorder at the other extreme of condensed matter, the ordinary molecular-liquid state.

5.3.2 Molecular liquids

The relative positions of molecules in a liquid may be characterized by the pair-distribution function, $g(R)$, where $g(R) dR$ is the probability of finding the center of mass of a second molecule within the range dR at a distance R from a given molecule (independent of the direction of R). The pair distribution function can be measured experimentally using X-ray diffraction. Analogously to the way in which the precise and regular periodic electron density associated with a molecular crystal Bragg-diffracts X-rays, there are diffraction phenomena characteristic of the “structure” in liquids. In ordinary liquids it is common to refer to “liquid structure,” the short-range biasing of relative (average) orientations and separations of neighboring molecules originating primarily from excluded-volume (local packing) considerations [42]. This local packing anisotropy is more pronounced in liquids composed of anisometric molecular shapes (rods or disks). However, the persistence of such packing correlations (i.e. structure in the radial distribution function) is limited to a few molecular diameters (~ 1 nm). On larger distance

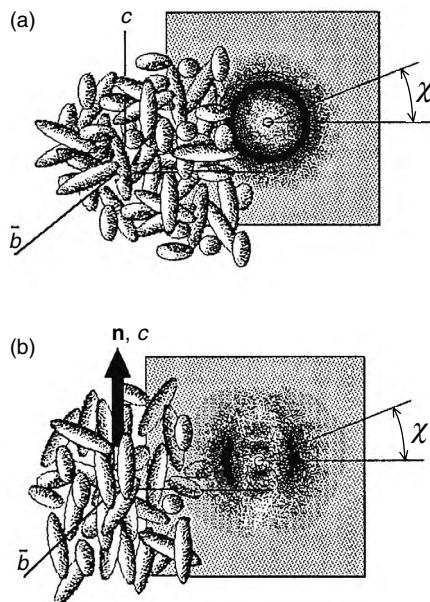


Fig. 5.12. Diffraction patterns from fluid phases: (a) for the isotropic liquid there is a uniform azimuthal X-ray-diffraction-intensity distribution; and (b) for the (aligned) nematic with the director $\mathbf{n}$ along the vertical direction remnants of local intermolecular order are revealed in the form of diffraction-intensity maxima corresponding to the molecular length (along the meridian) and the lateral intermolecular spacing (along the equator).

scales, molecular orientations and positions are random; the dynamically averaged or ensemble-averaged properties of a molecular liquid are isotropic. Consequently, the diffracted X-ray intensity is very diffuse and exhibits a broad intensity maximum located radially at $\theta = \sin^{-1} [n\lambda/(2\langle d \rangle)]$, where $\langle d \rangle$ corresponds to an average intermolecular distance in the liquid. The uniform azimuthal intensity distribution $I(\chi)$ in Fig. 5.12(a) (the circular diffraction pattern) indicates that there is no preferred orientational order in the liquid; the cartoon depicts an instantaneous (freeze-frame) “snapshot” of a microscopic volume element of a calamitic fluid taken with an extremely fast “shutter speed” (within 10^{-10} s) to freeze molecular reorientation and translation. The half-width of the *radial* intensity distribution is inversely related to the distance over which the molecules are positionally ordered. The absence of significant higher-order ($n > 1$) diffraction intensity is evidence for the very-short-range nature of the local structure of liquids. We now use this brief characterization of molecular crystals and isotropic liquids as a benchmark to contrast their diffraction features with those of monomer liquid crystals.

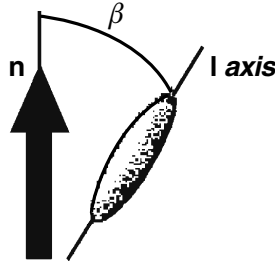
5.3.3 Nematic liquid crystals

Figure 5.12(b) shows the diffraction pattern from an idealized MLC – an aligned² nematic phase. By referring to the crystal and liquid diffraction patterns (Figs. 5.11 and 5.12(a)), we are able to infer that there is “structure” in the liquid crystal. However, we conclude that significant long-range positional order is absent (there are no high-order ($n > 1$) diffraction spots); in fact the first-order ($n = 1$) reflection along the meridian is just visible. Its reciprocal spacing corresponds to the approximate length of the mesogen while the diffraction maximum along the equator is indicative of a nominal lateral intermolecular distance. These features of the diffraction pattern are reminiscent of a liquid but with one very significant difference: the azimuthal intensity is not evenly distributed over χ . Closer examination of the distribution $I(\chi)$ leads us to conclude that, while the translational “structure” is liquid-like, on average the molecules are aligned along a direction parallel to the meridian (i.e. parallel to **c**). That is, this otherwise-normal fluid exhibits orientational order of the mesogens about a preferred direction in the fluid called the director and symbolized by **n**, an *apolar* vector. Moreover, this orientational ordering is of long range; it is uniform and coherent over the entire diffracting volume element of the nematic fluid. If we take the latter volume element to be of order 1 mm^3 , and the volume of the mesogen to be of order $100 \text{ \AA}^3$, then this orientational order extends over $\sim 10^{19}$ molecules! *What kinds of intermolecular interactions are responsible for this long-range orientational order in an otherwise purely liquid state?* Before we attempt to answer this question it is useful to continue the analysis of the static features of the nematic apparent in the diffraction pattern shown in Fig. 5.12(b).

5.3.4 The order parameter

We want to consider in more detail the origins of the diffracted azimuthal X-ray intensity distribution (the arcs at fixed Bragg angle in $I(\chi)$, Fig. 5.12(b)). The scattering intensity $I(\omega)$ from a single prolate mesogen of length L is a thin line (for large L) with a negligible intrinsic angular width $\lambda/(L \sin \omega)$, where λ is the wavelength of the X-rays and ω is the angle between the **l** axis and the direction of incidence of the beam [43]. The observed $I(\chi)$ comes from a superposition of the scattering from many mesogens. This can be represented by a continuous orientation distribution, $W(\beta)$, describing the disposition of **l** about the director **n**, where β is the angle between **l** and **n**.

² Here “aligned nematic” implies that the director **n** has the same orientation throughout the diffracting volume element ($\sim 1 \text{ mm}^3$).



$I(\chi)$ is related to $I(\omega)$ and $W(\beta)$ via an integral equation (which must be solved numerically):

$$I(\chi) \cong \int W(\beta) I(\omega) \sin \omega \, d\omega \quad (5.1)$$

The molecular quantity of interest, the average orientation of $\mathbf{l}$ relative to $\mathbf{n}$ – the nematic order parameter S – is defined in terms of $W(\beta)$:

$$S \equiv \int_0^{\pi/2} P_2(\cos \beta) W(\beta) \sin \beta \, d\beta \quad (5.2)$$

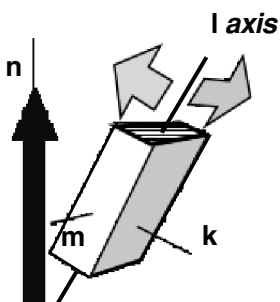
$W(\beta) \sin \beta \, d\beta$ is the (normalized) probability of finding $\mathbf{l}$ in the range $d\beta$ about the direction β with respect to the director; $W(\beta)$ is independent of β in a normal isotropic liquid. In Eq. (5.2) the order parameter S , the average of the second Legendre polynomial $P_2(\cos \beta) = 1/[2(3 \cos^2 \beta - 1)]$, assumes the value *unity* in a perfectly ordered system (when $\mathbf{l} \parallel \mathbf{n}$ as in the molecular crystal idealized in Fig. 5.11), and the value *zero* when $\mathbf{l}$ is isotropically distributed (Fig. 5.12(a)). In order to extract S from the experimental observable $I(\chi)$, one can use Eq. (5.1) (recognizing that $\cos \beta = \cos \chi \sin \omega$) with an *assumed* form for $W(\beta)$ to fit $I(\chi)$ (numerically) [44]. If, for example, one assumes the validity of a Gaussian distribution,

$$W(\beta) = A \exp[-\beta^2/(2\beta_0^2)] \quad (5.3)$$

then $I(\chi)$ may be fit by adjusting A and the distribution width β_0 to obtain $W(\beta)$ and thereby obtaining S with Eq. (5.2).

In nematic phases of MLCs, S typically ranges from about 0.25 to 0.75. We will pursue the meaning of these magnitudes for S in order to obtain a better feel for the nature of orientational order in nematics. First, however, we should recognize that we are able to describe nematic order with a single number (the scalar S) because we have made assumptions about the molecular symmetry in this uniaxial phase.

Namely, we have assumed that we have an idealized prolate-shaped molecule with cylindrical symmetry. If we remove this assumption, the orientation of the k, l, m Cartesian frame fixed to the molecule (see Fig. 5.1) is described by a second-rank tensor, $\mathbf{S}$, the order tensor with five independent elements $S_{ij} = (3\langle \cos \beta_i \cos \beta_j \rangle - \delta_{ij})/2$, where the β_i specify the orientation of the $\mathbf{i}$ axis relative to $\mathbf{n}$ and δ_{ij} is the delta function ($\delta_{ij} = 0$ for $i \neq j$; $\delta_{ij} = 1$ for $i = j$). $\mathbf{S}$ is a traceless tensor (the sum of its diagonal elements is $\sum S_{ii} = 0$), and gives the average orientation of any molecule-fixed frame relative to the director. If the k, l, m axis system is the *principal axis system* (PAS), $\mathbf{S}$ is diagonal in the k, l, m frame ($S_{ij} = 0$ for $i \neq j$). If the mesogen's shape deviates from cylindrical symmetry (e.g. a biphenyl mesogenic core approximated as a parallelepiped), it is necessary to specify the average orientation of the mesogen with two order parameters, S_{ll} and $S_{kk} - S_{mm}$; the latter is referred to as the *molecular biaxiality* – the preference for having the l - m plane rather than the l - k plane of the parallelepiped remain tangential to $\mathbf{n}$ while the molecular long axis executes angular librations. (Molecular biaxial orientational order is a local attribute deriving from the shape of the molecule; it applies to molecules in uniaxial phases and is distinct from the phase biaxiality depicted in Fig. 5.3.) When the molecule has cylindrical symmetry the orientation



of the k, l, m PAS is specified by a single element $S \equiv S_{ll} (= -2S_{kk} = -2S_{mm})$, the average orientation of the molecular symmetry axis $\mathbf{l}$; S is the nematic order parameter referred to in Eq. (5.2).

Returning to a discussion of the meaning of the magnitude of S , Fig. 5.13(a) shows the probability distribution $W(\beta) \sin \beta$ for various Gaussian widths β_0 centered about 0° (and, equivalently, 180° in the apolar nematic phase); the value of S obtained from Eq. (5.2) is plotted versus β_0 in Fig. 5.13(b). When, for example, an angular spread of $\beta_0 = 60^\circ$ is used in the Gaussian distribution (Eq. (5.3)) the mesogen order parameter $S = 0.5$; the average inclination³ $\langle \beta \rangle$ of $\mathbf{l}$ relative to

³ It makes no physical sense to invert the expression $S = \langle P_2(\cos \beta) \rangle$ and find an average β (35° for the example $\beta_0 = 60^\circ$). Although this is widely practiced in the literature, such an inversion is valid only if the distribution $W(\beta)$ is a delta function.

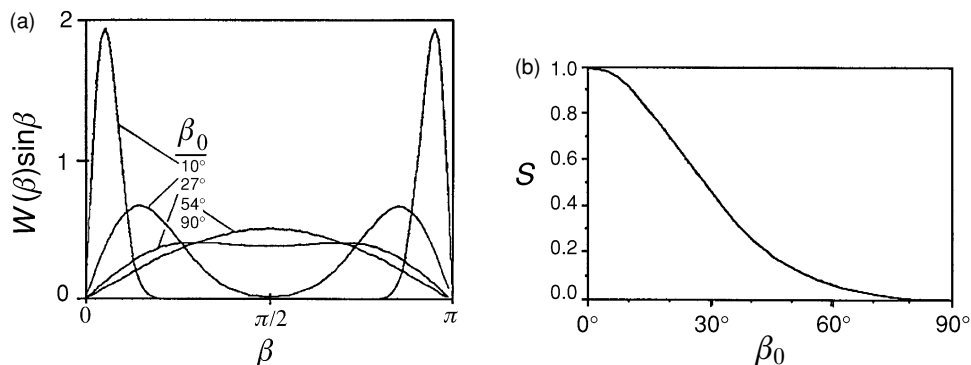


Fig. 5.13. (a) Plots of the probability density $W(\beta) \sin(\beta)$ with a Gaussian distribution versus β for differing widths β_0 (Eq. (5.3)); and (b) the computed (Eq. (5.2)) order parameter S versus the width β_0 of the Gaussian distribution.

the nematic director associated with this spread (or, for that matter, any value of β_0), is 0° . In summary, the diffraction pattern in Fig. 5.12(b) tells us that, locally, the nematic fluid has a common axis of symmetry (the director) defined by the preferred direction in which the molecular axes **I** *spontaneously* align in the liquid crystal and, moreover, the average degree of order of **I** relative to the director may be computed from $I(\chi)$. This methodology for extracting S from diffraction data is applicable both to low molecular weight and to polymer liquid crystals [43–45].

5.3.5 Anisotropic properties

For simple liquids it is straightforward to relate a bulk macroscopic property to its microscopic origins. Consider, for example, how the molecular electronic polarizability α manifests itself in the refractive index n_r of a simple liquid. The relative permittivity (the dielectric constant) ϵ_r is a simple function of α and the number density N of molecules (the number per unit volume) in the liquid:

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{N\alpha}{3\epsilon_0} \quad (5.4)$$

where ϵ_0 is the vacuum permittivity; this is the Clausius–Mossotti equation. At optical frequencies ($\sim 10^{15}$ Hz), there is a quadratic relationship between n_r and ϵ_r :

$$\frac{n_r^2 - 1}{n_r^2 + 2} = \frac{N\alpha}{3\epsilon_0} \quad (5.5)$$

Thus the relationship between the macroscopic refractive index and the microscopic polarizability is achieved without reference to the fact that the latter molecular

property is described by a second-rank tensor α , i.e. all directions in the molecule do not exhibit the same electronic response to an applied electric field. The simplicity of Eqs. (5.4) and (5.5) comes about because the average projection of α along the direction of observation, α_{zz} , is independent of the orientation of z in the liquid. This projection is a simple scalar and is related to the mean value of the diagonal elements of α ; $\alpha \equiv \alpha_{zz} \equiv \frac{1}{3} \text{Trace}(\alpha) = (\alpha_{kk} + \alpha_{ll} + \alpha_{mm})/3$. By contrast, in the nematic liquid, a nonzero order parameter has macroscopic implications; the directional dependence of the molecular polarizability tensor manifests itself when one relates macroscopic properties to microscopic properties. That is, one must explicitly account for the anisotropic part of the polarizability tensor, namely $\alpha' \equiv \alpha - \frac{1}{3} \text{Trace}(\alpha)$, when one is computing α_{zz} by recognizing that the orientation of the z axis relative to the director plays a key role in the observed macroscopic properties. The importance of the orientation of z comes about because the (directional) molecular properties are averaged in a unique way in the nematic.

Consider a small region of a nematic fluid having a uniform director field (a monodomain wherein the orientation of $\mathbf{n}$ is unchanged throughout). In this uniaxial fluid volume element, molecular properties (polarizability, magnetic susceptibility, etc.) are incompletely averaged with respect to the director; the average projections of these second-rank tensorial properties depend on Ω (the angle between $\mathbf{n}$ and the z axis of a laboratory x, y, z frame), the average orientation of the k, l, m frame relative to $\mathbf{n}$ via $\mathbf{S}$, and the intrinsic molecular anisotropy of the polarizability α' :

$$\alpha_{zz} = \alpha + \frac{2}{3} \text{Trace}(\alpha' \cdot \mathbf{S}) P_2(\cos \Omega) \quad (5.6)$$

Equation (5.6) reduces to the result for an ordinary isotropic liquid when $\mathbf{S} = 0$. In the nematic, $\mathbf{S} \neq 0$ and the projection of the polarizability takes on its extreme values, $\alpha_{||}$ and $\alpha_{\perp}$, when $\Omega = 0^\circ$ and 90° , respectively. If we consider a mesogen with cylindrical symmetry having a principal value of the polarizability along the long molecular axis, α_l ($\equiv \alpha_{ll}$), and a unique value transverse to the $\mathbf{l}$ axis, α_t ($\equiv \alpha_{kk} = \alpha_{mm}$), we find when we expand the tensor product in Eq. (5.6) and take its trace that the principal values of the polarizability of the phase are given by

$$\begin{aligned} \alpha_{||} &= \alpha + \frac{2}{3}(\alpha_l - \alpha_t)S \\ \alpha_{\perp} &= \alpha - \frac{1}{3}(\alpha_l - \alpha_t)S \end{aligned} \quad (5.7)$$

In Eq. (5.7) we have substituted S for the principal value of the order tensor S_{ll} . It should be clear from the results of Eq. (5.7) in conjunction with the relationship between the polarizability and the refractive index (Eq. (5.5), leaving aside complications associated with anisotropic internal-field corrections), that $n_{r||} \neq n_{r\perp}$. In short, a nematic liquid may be readily distinguished from an ordinary liquid because

it exhibits birefringence, $\Delta n_r \equiv n_{r\parallel} - n_{r\perp}$. Thus we have a connection between the liquid crystal and the molecular crystal: a nematic volume element is birefringent, *albeit* with differences in refractive index attenuated by molecular disorientation (accounted for by the factor S in Eq. (5.7)) relative to differences in refractive index observed in a perfectly ordered single crystal ($S = 1$). Additionally, the changing value of the refractive index as the orientation of the director meanders in a random fashion throughout the bulk sample of a nematic very effectively scatters light in a manner reminiscent of a polycrystalline powder and, together with thermally excited fluctuations of the director (fluctuations of the value of $n_{r\parallel}$), accounts for the opaque, milky appearance of the nematic fluid. The opaqueness disappears at the nematic–isotropic transition, hence the origin of the term *clearing temperature*.

In general we can expect to find anisotropy in all macroscopic properties Q of the nematic phase. This macroscopic anisotropy, denoted $\Delta Q \equiv Q_{\parallel} - Q_{\perp}$ (the difference between the value of the bulk property measured parallel to $\mathbf{n}$, $Q_{\parallel}$, and that normal to $\mathbf{n}$, $Q_{\perp}$), is simply related to the order parameter S by

$$\Delta Q = N(q_l - q_t)S \quad (5.8)$$

where $q_l - q_t \equiv \Delta q$ is the molecular anisotropy (the difference between the principal longitudinal and transverse tensorial molecular properties) and N is the number of molecules per unit volume [14, 24]. Equation (5.8) provides a very convenient measure of S if one knows Δq (e.g. from single-crystal studies) and measures experimentally ΔQ in a macroscopically aligned nematic.

5.3.6 Dichroism

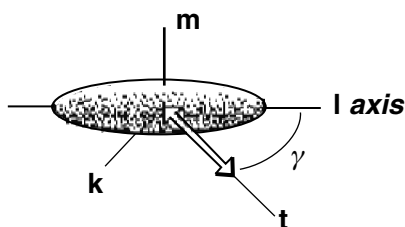
The molecular anisotropy also manifests itself in a variety of spectroscopic techniques. Dichroism, the difference in absorption coefficients of linearly polarized light measured in orthogonal directions, is another phenomenon wherein one can extract average molecular orientational order present in the nematic phase. The dichroic ratio $D \equiv A_{\parallel}/A_{\perp}$ (see Chapter 7), the ratio of the intensities of the absorption band of a characteristic transition measured with the polarized incident radiation parallel to $\mathbf{n}$, $A_{\parallel}$, relative to that with it perpendicular to $\mathbf{n}$, $A_{\perp}$, is given by

$$D = \frac{\cos^2 \gamma \langle \cos^2 \beta \rangle + \frac{1}{2} \sin^2 \gamma \langle \sin^2 \beta \rangle}{\frac{1}{2} \cos^2 \gamma \langle \sin^2 \beta \rangle + \frac{1}{2} \sin^2 \gamma \langle 1 + \cos^2 \beta \rangle} \quad (5.9)$$

where γ is the angle between the axis of symmetry of the molecule (the $\mathbf{l}$ axis) and the direction of the transition moment $\mathbf{t}$ in the molecule-fixed $\mathbf{k}$, $\mathbf{l}$, $\mathbf{m}$ frame.

The averages over the molecular orientation, e.g. $\langle \cos^2 \beta \rangle$, where β is the angle between $\mathbf{l}$ and $\mathbf{n}$, may be rewritten in terms of the order parameter S . For the case when the transition moment is parallel to $\mathbf{l}$ ($\gamma = 0^\circ$), Eq. (5.9) reduces to a simple relationship between the dichroic ratio and the order parameter:

$$D = \frac{1 + 2S}{1 - S} \quad (5.10)$$



5.3.7 Magnetic resonance

Nuclear magnetic resonance (NMR), in particular, deuterium NMR, has proven to be a valuable technique for determining the nature of molecular organization in liquid crystals. The utility of the ^2H NMR technique derives from the fact that the relevant NMR interactions are entirely intramolecular, i.e. the dominant interaction is that between the nuclear quadrupole moment of the deuteron and the local electric-field gradient (EFG) at the deuterium nucleus. The EFG tensor is a traceless, axially symmetric, second-rank tensor with its principal component along the C—D bond. In a nematic fluid rapid anisotropic reorientation incompletely averages the quadrupolar interaction tensor $\mathbf{q}$, resulting in a nonzero projection similar to the result in Eq. (5.6):

$$q_{zz} = \frac{2}{3} \text{Trace}(\mathbf{q} \cdot \mathbf{S}) P_2(\cos \Omega) \quad (5.11)$$

In a homogeneous nematic the deuterium NMR spectrum consists of a resolved pair of resonances at frequencies $\nu_{\pm}$ centered about the Larmor frequency ν_L :

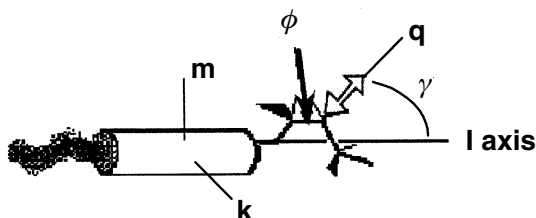
$$\nu_{\pm} = \nu_L \pm \frac{3}{4} q_{zz} P_2(\cos \Omega) \quad (5.12)$$

In an aligned nematic with $\Delta\chi_m > 0$, Ω , the angle between the magnetic field and $\mathbf{n}$, is zero and, for a molecule assumed to have cylindrical symmetry (i.e. we ignore any molecular biaxiality, $S_{kk} - S_{mm} = 0$), the separation in frequency between the two transitions in Eq. (5.12), $\Delta\nu = \nu_+ - \nu_-$ (the quadrupolar splitting), is given

simply in terms of the average orientation of the molecular long axis **l** by

$$\Delta\nu = \frac{3e^2qQ}{2h} P_2(\cos \gamma) S \quad (5.13)$$

In Eq. (5.13) we have explicitly written out the expression for the principal value of the quadrupolar interaction tensor in terms of the electrostatic charge e , the EFG at the deuterium nucleus eq , the deuteron's quadrupole moment Q , and Planck's constant h ; γ is the angle that the C—D bond (principal value of the interaction tensor **q**) makes with the molecular symmetry axis **l**, and S gives the degree of order of the **l** axis in the nematic.



When the mesogen has internal degrees of freedom (more than one conformation, i.e. a variable dihedral angle ϕ), the quadrupolar splitting is reduced, reflecting the greater averaging of the EFG brought about by isomerization – rotations of ϕ . Continuing with the over-simplified assumption of cylindrical symmetry, in the presence of internal motion we would modify Eq. (5.13) by using $\langle P_2(\cos \gamma) \rangle$, where the angular brackets signify an intramolecular average over rapid isomerization. Hence the magnitude $\Delta\nu$ is a direct measure of the efficacy of the motional averaging in the nematic, yielding the order parameter when the molecular geometry (γ) is known, and alternatively inferring information about the internal flexibility of the mesogen $\langle P_2(\cos \gamma) \rangle$ when S is determined independently. It should be emphasized that, for any real mesogen, one cannot assume that the simple symmetry implied in Eq. (5.13) applies. Additionally, the total order tensor **S** needs to be used in quantitative interpretations of NMR data. Moreover, when there are many conformations $\{\phi\}$, one needs to consider the order tensor for *each* conformer, $S\{\phi\}$ [46]. In spite of these complications, the NMR technique can be very valuable when molecular flexibility is present. For example, it has been possible to examine critically the rotational-isomeric-state approximation itself by carefully analyzing incompletely averaged NMR interactions (direct dipole–dipole couplings of pairs of protons) exhibited by normal alkanes dissolved in a nematic solvent [47].

5.3.8 Field-induced reorientation of the director

There is a further consequence of the macroscopic anisotropy exhibited by liquid crystals. In particular, the anisotropies in the electric susceptibility $\Delta\chi_e$, where $\chi_e = 3(\epsilon_r - 1)/(\epsilon_r + 2)$, and the diamagnetic susceptibility, $\Delta\chi_m$, play important roles in alignment (and reorientation) of liquid crystals by external fields. These anisotropies also have their origins in the anisotropic averaging of molecular properties with respect to the director (Eq. (5.7)). There is a difference in potential energy for the case in which the field is parallel to $\mathbf{n}$ versus the case in which the field is perpendicular to $\mathbf{n}$. Using an electric field $\mathbf{E}$ interacting with the induced dipole moment per unit volume $\mathbf{P} = \epsilon_0\chi_e\mathbf{E}$, the potential energy U is given by

$$\begin{aligned} U &= -PE \cos \theta \\ &= -\epsilon_0\chi_e\mathbf{E}^2 \end{aligned} \quad (5.14)$$

where θ ($= 0^\circ$) is the angle between the *induced* moment and the field. Since Eq. (5.7) tells us that we will find $\chi_{e\parallel}$ to be different from $\chi_{e\perp}$ in a nematic volume element, there will be a preferred low-energy orientation of the director in the applied field. For positive dielectric anisotropy ($\Delta\chi_e > 0$) Eq. (5.14) indicates that the low-energy orientation of the director occurs when $\mathbf{n} \parallel \mathbf{E}$. Consequently, in a sufficiently strong field, all volume elements will assume the same orientation of the director and a macroscopically aligned nematic results. In such an aligned sample, application of $\mathbf{E}$ normal to $\mathbf{n}$ will rapidly (on a sub-millisecond timescale) drive a 90° rotation of the director in the fluid mesophase. This basic interaction between an external electric (magnetic) field and the bulk anisotropy of the electric (magnetic) susceptibility, $\Delta\chi_e$ ($\Delta\chi_m$), in conjunction with the optical anisotropy of the nematic, Δn_r , may be exploited to reorient the director and simultaneously change the optical properties of the mesophase. This is the basis of field-generated electro-optic responses in LCD devices. Furthermore, because of molecular-structural similarities between MLCs and the monomers used in some mesogenic polymers (i.e. they have comparable molecular anisotropies), the same phenomena may be observed in polymer liquid crystals.

Field-induced reorientation of the director with attendant optical changes has recently been used in a novel application with the potential for large-area LCDs: polymer dispersed LCs (PDLCs). A PDLC is a microemulsion of MLC dispersed in a conventional transparent polymer film. In the “off” state there is a mismatch between the refractive index of the MLC and that of the host polymer film. Hence the dispersion of MLC droplets scatters light very effectively, giving an optically opaque film (Fig. 5.14, left-hand side). On application of an external electric field (across a capacitor-like transparent coating of tin oxide on both sides of the polymer film), the director assumes the same orientation in all of the microdroplets. If the

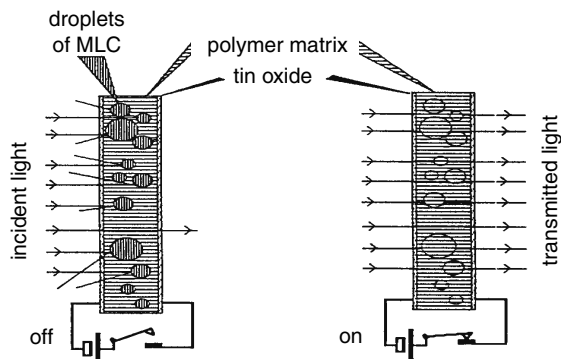


Fig. 5.14. A polymer dispersed liquid-crystal (PDLC) device consisting of a microdispersion of a low molecular weight nematic fluid (MLC) in a conventional transparent polymer host matrix sandwiched between thin coats of transparent, conducting tin oxide. On the left is shown the “off” state with a refractive-index mismatch between the dispersion and the host that scatters incident light. On the right is shown how an external electric field aligns the director of the nematic matching the refractive indices of the dispersion and the host, yielding an optically transparent medium.

refractive index along the director matches that of the host polymer film, in the “on” state the film suddenly switches from opaque to transparent (Fig. 5.14, right-hand side), giving a very economical large-area “light valve.”

5.3.9 Disclinations

In a bulk nematic the director field is not uniform unless external influences (electric, magnetic or shear fields, surface alignments, etc.) are operative. At the junction of two differently oriented director fields, there are disclinations – the analog of a dislocation in a crystal – and domain walls (“grain boundaries”). The presence of these distortions in the director field may be readily recognized and characterized with a polarizing microscope [48]. The configurations of the director field for line disclinations of strengths $+\frac{1}{2}$, $+1$, -1 , and $-\frac{1}{2}$ are illustrated in Fig. 5.15. The strength is a function of the number of “dark brushes” meeting at a point while the sample is being observed under crossed polars; the sign depends on the relative rotations of the brushes on rotating the polarizer. These patterns under crossed polars are useful for characterizing the phase type. For example, disclinations of $\pm\frac{1}{2}$ are possible in nematic phases only and may be readily identified in Fig. 5.9.

Strikingly clear visualizations of disclinations are found in transmission electron micrographs of replicas of solidified thermotropic polymer liquid crystals wherein the director field is mapped out by crystallite formation [49]. (Prolate nanoparticles when they are closely packed and floating on a liquid interface also exhibit

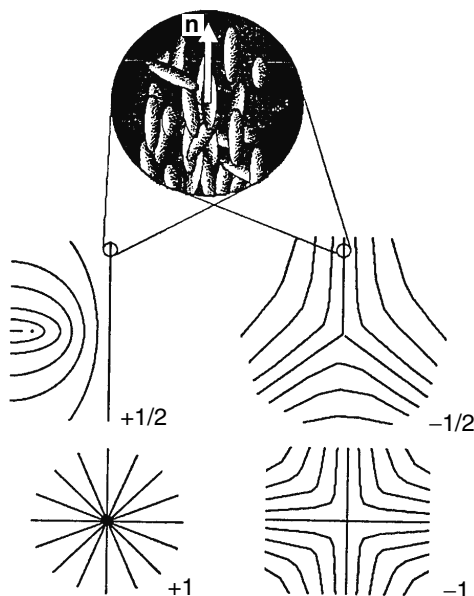


Fig. 5.15. Illustrations of the patterns that the director field assumes for disclinations of strengths $+\frac{1}{2}$, $+1$, -1 , and $-\frac{1}{2}$.

two-dimensional analogs of disclinations [50].) These textural features are exhibited both by polymer liquid crystals and by MLCs. The density of disclinations may be increased by turbulent stirring of the nematic fluid. Disclinations with equivalent strengths and opposite sign may combine and annihilate one another, restoring a uniform director field. The annihilation of disclinations or “ripening process” in MLCs has been used as an example of the temporal evolution of complex systems in models of cosmological processes [51]. Needless to say, watching the movement of disclinations and texture formation in quiescent LC polymers, fluids characterized by much larger viscosities and correspondingly smaller diffusion coefficients, is not a very exciting “spectator sport!”

Distortions and disclinations of the director field are particularly important in commercial polymer mesophases because the density of such defects is thought to play a significant role both in the LCP’s rheological properties (ease of processing) and in the ultimate mechanical properties of polymeric solids derived from mesophases.

5.3.10 Elastic properties

Deformation of the director field away from its equilibrium configuration increases the free-energy density of the mesophase. The curvature strains (and associated

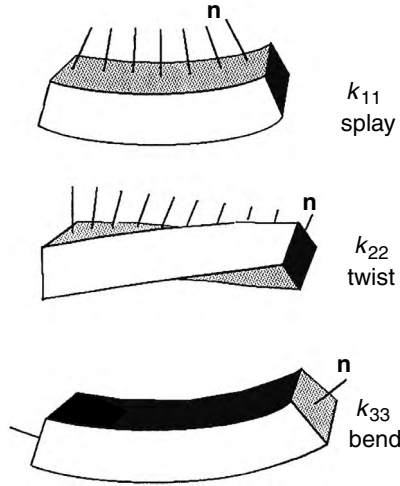


Fig. 5.16. The director-field patterns in volume elements subjected to splay, twist, and bend curvature strains.

restoring forces – the curvature stresses) are small and may be treated with continuum elasticity theory since the scale over which the director changes orientation is very large relative to molecular dimensions. In fact, a variant of Hooke's law (the stress is proportional to the strain) may be used in conjunction with three distinct kinds of curvature strains and the associated elastic constants, k_{11} , k_{22} , and k_{33} , corresponding, respectively, to splay, twist, and bend strains (Fig. 5.16). In nematic MLCs, the k_{ii} are approximately equal; splaying is relatively difficult in smectics. These materials constants are extremely small ($\sim 10^{-7} \text{ N m}^2$) relative to the elastic constants of polymer networks and rubbers ($\sim 10^{+5} \text{ N m}^2$). Note that, while these moduli would appear negligible to polymer materials scientists, they provide the delicate elastic restoration of the initial director field in electro-optic devices, i.e. the elasticity of MLCs drives the “off”-state dynamics in a typical LCD. In order to “turn on” a LCD, one has to exceed a threshold voltage in order to overcome the elastic energy associated with the initial configuration of the director field. (The initial configuration is established by a variety of proprietary surface treatments, which “anchor” the director field in LCD cells and PDLC microemulsions.) Under the influence of an external electric (magnetic) field, the two competing forces – the elastic restoring force and the torque the applied field exerts on the anisotropic electric (diamagnetic) susceptibility $\Delta\chi$ – are related to the critical or threshold field F_{crit} by

$$F_{\text{crit}} = \sqrt{\frac{k_{ii}}{\Delta\chi}} \frac{\pi}{d} \quad (5.15)$$

where d is the distance scale over which the field-induced distortion of the orientation of the director takes place. In LCDs electric fields are the usual method of switching; typical sample thicknesses are $d \sim 10^{-5}$ m and critical-field values are $F_{\text{crit}} \sim 10$ V.

5.3.11 Chiral phases

Thus far discussion has focused on the nematic phase, a translationally disordered fluid with long-range, uniaxial ordering of the molecular **I** axes. More subtle supramolecular arrangements are possible when the mesogen is chiral: a twisted nematic (cholesteric) phase forms with the local director (normal to the **z** axis in Fig. 5.17) changing its orientation systematically in the mesophase tracing out a helicoidal trajectory over a large distance scale ($\sim 10^3$ times a nominal intermolecular distance and typically in the range 1500–8000 Å). This twisted nematic organization is symbolized⁴ by N^* . Again there are dramatic macroscopic consequences that result from this twisted organization: the periodic change in the electronic polarizability (refractive index) as the director twists through the fluid establishes an optical grating when the pitch $P \approx \lambda$, the wavelength of visible light. In this case, particular wavelengths (colors) satisfying the Bragg equation will be diffracted, giving these materials a beautiful iridescent sheen when they are examined in reflected light. This is the origin of the colors reflected from the surfaces of some insects; the major constituent of a beetle's exocuticle, chitin, is an anisometric biopolymer aggregate, and it is deposited in a lyotropic cholesteric fluid form before the exocuticle congeals [52].

The “reflected” color from cholesterics is remarkable: the reflected light is circularly polarized with the same sense (right- or left-handed) as that of the N^* helicoidal organization. (The light with polarization of opposite sense passes through the N^* structure). The strength of this *supramolecular* optical rotation of the reflected light is many times larger ($\sim 10^4$ degrees) than that of optical rotations that chiral molecules exhibit in dilute solutions ($\sim 10^\circ$). Since the pitch P is established by a thermal average in the fluid N^* phase, it will change with temperature, changing the wavelength (color) of the selectively reflected light from the cholesteric phase and thereby yielding an efficient temperature sensor. We emphasize again the extremely subtle forces underlying this phenomenon: in the cholesteric fluid the (motionally averaged) intermolecular forces between the members of a pair of chiral molecules are slightly asymmetric, prejudicing the quasiparallel alignment of molecular axes. That is, chirality causes a very small (minutes of arc) average twist of the molecular **I** axis relative to its neighbor in the same sense (right- or

⁴ With the symbol N^* we establish contact with the chemical convention indicating a chiral center within a molecule by appending an asterisk to the chiral atomic site.

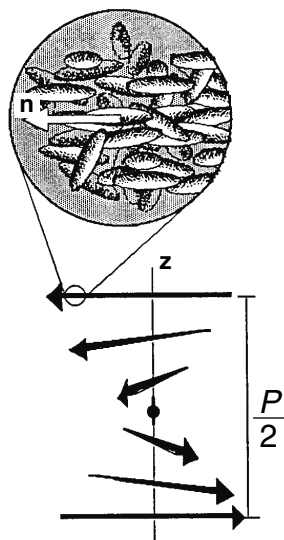


Fig. 5.17. The helicoidal director field of the twisted nematic (cholesteric) organization is illustrated. The very small unidirectional twist from chiral mesogen to chiral mesogen causes the spiral supramolecular organization of the director that turns through 180° after traversing a distance $P/2$ (half of the cholesteric pitch).

left-handed, depending on the chiral center in the mesogen), which is manifested on a supramolecular scale as a unidirectional twist of the director $\mathbf{n}$, thereby giving the structure shown diagrammatically⁵ in Fig. 5.17. Cholesterics with opposite twist-handedness are obtained from L and D isomers of the mesogen, respectively; a racemic mixture of chiral mesogens yields a *compensated* (untwisted) N^* phase. One may also compensate cholesterics with external fields. For susceptibilities having positive anisotropy ($\Delta\chi > 0$), a sufficiently strong external field will untwist the helicoidal arrangement of the director, eventually aligning $\mathbf{n}$ parallel to the field. On the other hand, for $\Delta\chi < 0$, the spatial average of the susceptibility (over the helicoidal cholesteric arrangement) makes the low-energy arrangement one in which the cholesteric structure remains intact with the cholesteric z axis oriented parallel to the external field.

Molecular chirality also manifests itself in the technologically important class of chiral S_C^* phases. Recall that, in the S_C phase, in addition to segregation of the molecules into smectic layers, the molecular $\mathbf{l}$ axis is on average tilted with respect to the layer normal (Figure 5.2(c)). A more realistic representation of the S_C organization is shown in Fig. 5.18. In this arrangement, if we represent the mean direction of alignment by the local director $\mathbf{n}$, the magnitude of this unit vector $\mathbf{n}$ may be

⁵ Frequently the helicoidal structure is illustrated with a stack of planes each with a rotated orientation of $\mathbf{n}$ and this has given the false impression that cholesteric phases possess a stratified supramolecular structure.

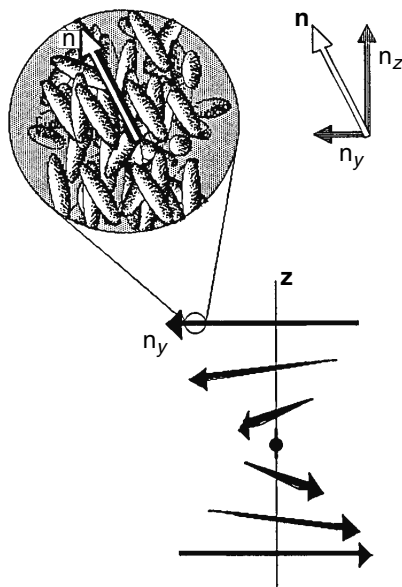


Fig. 5.18. The chiral smectic C phase (S_C^*) has the molecular axes on average tilted with respect to the layer normal of the smectic, and the in-plane component of the local director n_y , the so-called *tilt director*, traces out a helicoidal path in the mesophase.

decomposed into two components: n_z along the layer normal and n_y , the component in the layer plane (the *tilt director*). In a chiral smectic C (S_C^*), the tilt exhibits a unidirectional twist as one moves from smectic layer to smectic layer: n_y traces out a helicoidal path in the S_C^* phase (Fig. 5.18). Phenomenological descriptions of the electrostatic implications of chiral mesogens in the tilted smectic typically read as follows. The molecular chirality breaks the local uniaxial symmetry about $\mathbf{n}$; hence transverse molecular electric dipoles μ_i will be incompletely averaged by molecular rotations about the molecular long axis $\mathbf{l}$. Consequently, within a single S_C^* layer, there is a net residual electric polarization oriented at right angles to the “tilt plane,” the plane defined by n_z and n_y . This local polarization is averaged by the twist of n_y to give a nonpolar bulk material. However, a ferroelectric monodomain S_C^* can be created, for example, by cooling into this phase in the presence of a strong magnetic field, which has $\mathbf{n}$ (n_y) uniformly oriented throughout the bulk sample (Fig. 5.19). The process of compensating for the natural twist of S_C^* yields a fluid with macroscopic polarization $\mathbf{P}$ – a ferroelectric smectic liquid crystal. When the compensated twist of the S_C^* is stabilized by surface treatments (that anchor the director field to give a monodomain sample), one has the “surface-stabilized ferroelectric liquid crystal” (SSFLC) [53], which exhibits very fast electro-optic switching (within $\sim 10^{-6}$ s) and bistability – two states i and ii corresponding to

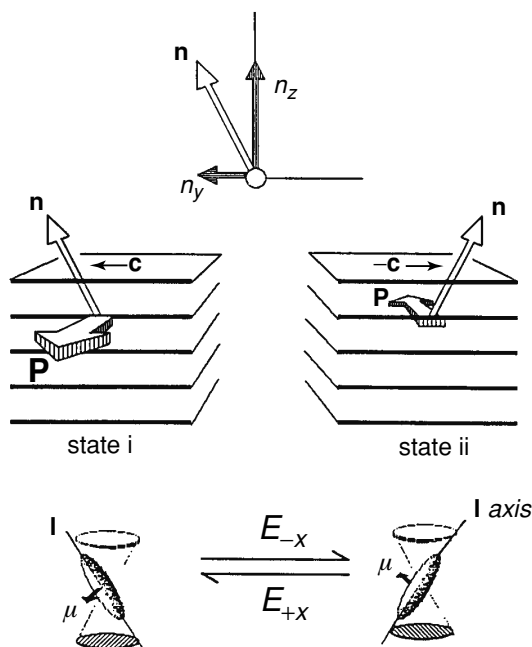


Fig. 5.19. A surface-stabilized S_C^* phase adopts a bistable (state i or state ii) monodomain ferroelectric organization with a net polarization $\mathbf{P}$ (indicated by the three-dimensional arrow) derived from incompletely averaged transverse molecular dipoles. Application of an electric field antiparallel to $\mathbf{P}$ (E_{-x}) results in a reorientation of the director (and polarization) from state i to state ii by efficient rotation of the $\mathbf{l}$ axis of the molecule over the surface of a cone (bottom illustration).

the two orientations of $\mathbf{P}$ shown in Fig. 5.19. This fast switching is a consequence of the fact that one need not reorient the director $\mathbf{n}$ but must only reorient the n_y component with an external electric field. When $\mathbf{E}$ is antiparallel to the polarization $\mathbf{P}$, the reorientation of $\mathbf{P}$ is readily accomplished merely by letting $\mathbf{l}$ travel on the surface of a cone to the new low-potential-energy orientation in the presence of the field E_{-x} (see the bottom of Fig. 5.19). It appears that this desirable rapid switching can also be realized in polymeric mesophases, e.g. when S_C^* mesogens are incorporated into polymers as side chains [54]. That this is so is undoubtedly a consequence of the very local nature of the motions required to reorient $\mathbf{P}$.

Development of molecular descriptions of spontaneous polarization, $\mathbf{P}$, in the S_C^* phase was retarded by a failure of early researchers to recognize the role of *indigenous polarity* in simple tilted smectics [55]. The tilt in the S_C phase singles out a unique direction about the normal to the smectic layer, $\mathbf{z}$. This direction is sometimes referred to as the $\mathbf{c}$ director, the projection n_y of the local director $\mathbf{n}$ onto the layer plane (Fig. 5.19), with $\mathbf{c}$ and $-\mathbf{c}$ describing the physically distinct states i and ii. The tilt pseudovector, $\mathbf{t} = (\mathbf{z} \times \mathbf{n})(\mathbf{z} \cdot \mathbf{n})$, is an alternative to the $\mathbf{c}$ director;

$\mathbf{t}$ is normal to the tilt plane and $\mathbf{t}$ and $-\mathbf{t}$ describe the opposite tilt states, i and ii, and $\mathbf{t}$ represents the direction of the indigenous polarity in the achiral (or chiral) tilted smectics. The averaged (over internal and extramolecular reorientations) projection of the molecule's bond dipole moments, μ_i , onto $\mathbf{t}$ gives rise to the observed $\mathbf{P}$, and quantitative understanding of how molecular structure determines the spontaneous polarization exhibited by the S_C^* phase can be achieved [56].

Also it is worth remarking on potential uses of the intrinsic *noncentrosymmetry* of the S_C^* phase. This symmetry is important for certain nonlinear-optical (NLO) [57] applications such as *second-harmonic generation* (SHG) – doubling the frequency of incident laser light. Consequently, this phase is being considered as a host for hyperpolarizable, organic (NLO-active) chromophore guest molecules. In many cases the molecular structural attributes of NLO-active chromophores for SHG – linear, hyperpolarizable molecules – are similar to those of calamitic mesogens themselves. Often only small structural modifications (e.g. appending a sufficiently long alkyl chain) will convert such hyperpolarizable molecules into a mesogen. Hence, if glassy liquid-crystal textures with uniform alignment (homeotropic or planar) can be prepared (to minimize scattering of light), mesogenic, NLO-active chromophores may be ideal materials for fabricating stable, organic (polymeric), opto-electronic devices requiring special local symmetries [58]. Lastly, we conclude this section on chiral phases by recalling that achiral nonlinear mesogens can form chiral supramolecular arrangements in tilted smectics (see Fig. 5.5).

5.3.12 Dynamics and transport properties

Molecular dynamics and transport phenomena in isotropic liquids are reasonably well understood. In the case of small prolate, ellipsoidal molecules, the rotational diffusion of molecules is very fast. The rotational correlation time τ corresponding to rates of diffusion about the ellipsoid's major axes is in the range 10^{-9} – 10^{-11} s. Intramolecular transitions among conformers – isomers formed by rotating dihedral angles defined by three consecutive chemical bonds within flexible molecules – are also very fast (conformer lifetimes of 10^{-10} s). Center-of-mass translational diffusion is isotropic and characterized by a self-diffusion coefficient $D_{\text{cm}} \sim 10^{-10} \text{ m}^2 \text{ s}^{-1}$.

In the nematic phase, the same timescales are operative. Although conformer probabilities are slightly shifted from the distribution in the isotropic liquid (more anisometric conformers are favored in the nematic), intramolecular isomerization rates are not influenced by the long-range orientational order. Incoherent, quasi-elastic neutron scattering gives the typically fast rotational diffusion about the principal axis $\mathbf{l}$, $\tau_{||} \sim 10^{-10}$ – 10^{-11} s. Reorientational flipping of the $\mathbf{l}$ axis is itself

slower ($\tau_{\perp} \sim 10^{-7}$ – 10^{-10} s) than the mean value for τ in the isotropic state. Thus the long-range order retards large-scale reorientations of mesogens which require cooperative movement of neighboring molecules. These differences between $\tau_{\parallel}$ and $\tau_{\perp}$ are greater in fluid smectic phases. Nevertheless, these correlation times are indicative of a fluid phase wherein molecules execute rapid rotational diffusion. Self-diffusion in liquid-crystalline phases is anisotropic: diffusion along the nematic director $D_{\text{cm}}^{\parallel}$ is more facile than is diffusion in the transverse direction and diffusion coefficients differ by about a factor of two ($D_{\text{cm}}^{\parallel} \sim 2D_{\text{cm}}^{\perp}$). Such anisotropy may reverse sign ($D_{\text{cm}}^{\perp} > D_{\text{cm}}^{\parallel}$) in smectic phases, especially for smectics with good layer definition, wherein diffusion within a layer is easier than is translation of the mesogen from one layer to another. In general, the magnitude of D_{cm} in MLC mesophases is about a factor of 10–100 times smaller than that observed for molecules of similar size in the isotropic liquid state.

The macroscopic properties of polymer solutions and melts are fundamentally different from those of low molecular weight materials even though the local dynamics (isomerization and libration) operate on roughly the same timescales as for small molecules. Transport properties (D_{cm}) and viscosity are dramatically different in polymer fluids. These characteristic similarities and differences between polymers and small molecules carry over on comparing MLCs and polymer LCs. D_{cm} for a polymer may be many orders of magnitude smaller than those observed in MLCs; hence, it takes longer for textures to develop, disclinations to annihilate, director fields to respond to externally applied fields, etc. However, aside from the more sluggish response, coarsely speaking, the dynamic and transport phenomena in polymer mesophases parallel those observed in low molecular weight materials. In the next section we begin to delineate some of the unique properties of macromolecular mesogens.

5.4 Macromolecular mesomorphism

For the purpose of discussing mesophase formation in polymers it is convenient to partition the polymers into two categories and introduce abbreviations that refer to these categories. *Polymerized* liquid crystals, here abbreviated PLCs, are derived from known, low molecular weight *monomer* liquid crystals (MLCs) that contain polymerizable functionality (e.g. vinyl units). We designate *liquid-crystalline polymers* (LCPs) to be semiflexible, linear polymers that are structurally related to conventional engineering thermoplastics, i.e. polymers derived from poly(ester)s, poly(amide)s, poly(imide)s, etc. We will examine the attributes of polymerized liquid crystals first, stressing the similarities between their properties and those of MLCs.

5.4.1 Polymerized liquid crystals (PLCs)

When we incorporate MLC secondary structures of the type shown in Fig. 5.1 into polymers, three general types of topologies readily come to mind: *linear* or *main-chain* polymers (MCPLCs) having the mesogenic cores covalently concatenated (Fig. 5.20(a)), *side-chain* polymers (SCPLCs) with the mesogenic cores attached covalently as side chains on a polymer backbone (Fig. 5.20(b)), and *dendritic* or *hyperbranched* polymers (Fig. 5.20(c)). In these types of PLCs, the core is linked to the polymer via a flexible “*spacer chain*” (usually an alkyl, siloxane, or ethylene glycol chain). It is obvious even from the limited number of secondary structures shown in Fig. 5.20 that a large number of variations on the topologies is possible (e.g. the combination of MCPLCs and SCPLCs) [59]. All of these polymers merely exploit the intrinsic tendency of the core to form spontaneously a thermotropic mesophase. The only difference between these high molecular weights PLCs and low molecular weights MLCs lies in the variable topological constraints that result from covalently embedding the cores into a macromolecule. In fact, if we consider these polymers in terms of their idealized shapes (Fig. 5.1), we lose sight of the covalent linkages. In other words, at that extreme level of abstraction, we can predict behavior that is nearly the same as that exhibited by MLCs, and we may view the polymer backbone and linkages as insubstantial diluents in an otherwise-conventional MLC. This extreme picture is worthy of some consideration because all of the static, equilibrium properties of thermotropic (lyotropic) MLCs may be realized in PLCs simply by polymerizing the appropriate mesogenic core and heating (dissolving) the polymer into the mesophase ($T_m < T < T_{cl}$). This is

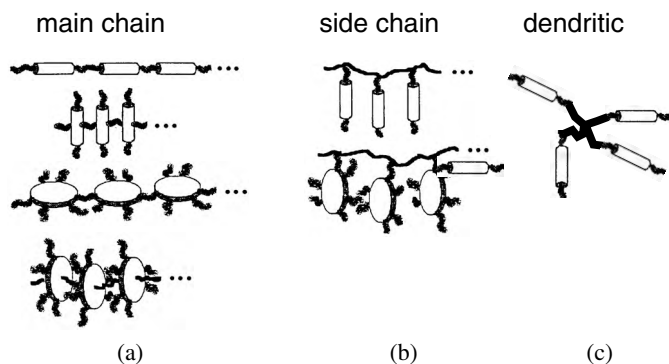


Fig. 5.20. Some simple topologies of polymer liquid crystals (PLCs) derived from calamitic and discotic mesogenic cores: main-chain PLCs, copolymers with core and flexible spacer alternating; side-chain PLCs with mesogenic cores attached by flexible spacers to the main chain of a conventional polymer; and dendritic (or star-shaped) structures with mesogens emanating from a central core via flexible spacers.

particularly so in SCPLCs when the spacer linkage is very flexible and sufficiently long to “*decouple*” the behavior of the core from that of the polymer chain [13].

Inserting a spacer chain into the backbone of a MCPLC yields a regular alternating copolymer: *...core-spacer-core-spacer...* This MCPLC topology exhibits additional features that require consideration of the resulting secondary structure: spacer-chain parity (an *even* versus an *odd* number of atoms in the spacer chain) and spacer-chain length may make one type of mesophase more stable than another (e.g. nematic versus smectic). These features and others introduced below obviously cannot be accounted for if we restrict our discussion to the idealized mesogenic cores. For example, nematic (or N^*) and smectic phases are readily formed both by main-chain and by side-chain topologies. X-ray diffraction from the nematic phase of a PLC is in many ways indistinguishable from that of MLCs. At the same time, however, the constraint of having to accommodate the polymer backbone in the mesophase of SCPLCs leads one to a rich variety of structures (and quasiperiodic defects) that can be discerned by X-ray diffraction, especially in smectic phases of SCPLCs [60].

The magnitude of the order parameter for a SCPLC core and consequently the size of the anisotropy in physical properties are comparable to those observed for MLCs. There are some notable exceptions to this finding for MCPLCs, however. Differences between MLCs and the polymerized, linear analogs (MCPLCs) show up in the thermodynamics: linear MCPLCs, for example, exhibit transition temperatures that depend strongly on the degrees of polymerization at low degrees of polymerization [61]. Asymptotic values of T_m and T_{cl} are generally reached for a degree of polymerization of 10. Within a homologous series of MLCs having terminal alkyl tails of successively longer lengths, transition temperatures and thermodynamic quantities exhibit magnitudes oscillating with the number of methylene units in the alkyl tails. This odd–even oscillation with spacer-chain parity is exaggerated in linear oligomers and MCPLCs because the connectivity of the cores in the polymer backbone reinforces core-orientational correlations between successive cores for even spacer chains whereas conformer geometries of odd spacer chains discourage such correlations (Fig. 5.21(a)). Such spacer-chain-parity effects are apparent in the order parameters exhibited by the mesogenic cores. Figure 5.21(b) shows the dramatic influence of dimerization and spacer-chain parity on mesogenic core-orientational order as delineated by deuterium NMR [62]. Odd spacer-chain parity yields values of S that are *lower* than observed for MLCs whereas even spacer-chain parity *enhances* the core-order parameter. (Note that, on the scale employed in Fig. 5.21(b), terminal chain parity has only marginal effects on ordering in MLCs.) Thus the connectivity of mesogenic cores in MCPLCs does manifest itself by influencing the degree of order of the core and, in turn, it influences the magnitudes of the anisotropies of bulk properties (via Eq. (5.7)). In addition, this

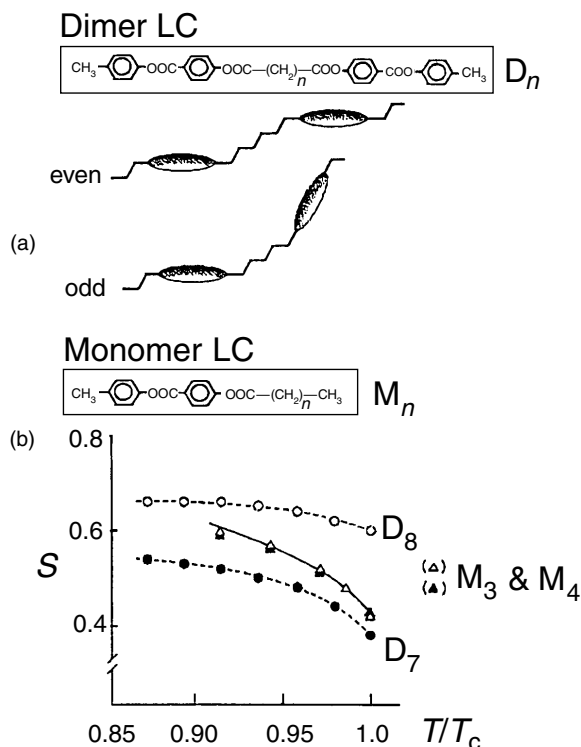


Fig. 5.21. (a) A schematic illustration of relative core orientations in members of a covalently connected pair of mesogenic cores for even and odd spacer-chain parities (all-*trans* conformation); and (b) dimer (D_n) versus monomer (M_n) LC core order parameters in the nematic phase (from [62]).

important role of the spacer chain in MCPLCS was dramatically illustrated by the discovery of a tilted smectic C phase having its tilt alternate from layer to layer [63]. This *anticlinic* mesogen stacking results because the secondary structure (for odd parity of the spacer chain) dictates an alternation in the orientation of successive mesogenic cores along the polymer chain.

Another example of the role of covalent connectivity of cores is suggested by the fact that the temperature range of mesophase stability for a particular mesogen can be increased by incorporating it into a polymer. There are even instances in which a particular core that does not exhibit mesomorphism as a monomer will become mesomorphic when it is polymerized [64]. Presumably in such situations the spatial restrictions imposed on such nonmesogenic cores when they are covalently linked together in the polymer allow them to achieve the required relative orientations for mesomorphism over some temperature range.

Polymerization of MLCs introduces covalent connectivity between mesogens and thereby introduces orientational and translational restrictions into the

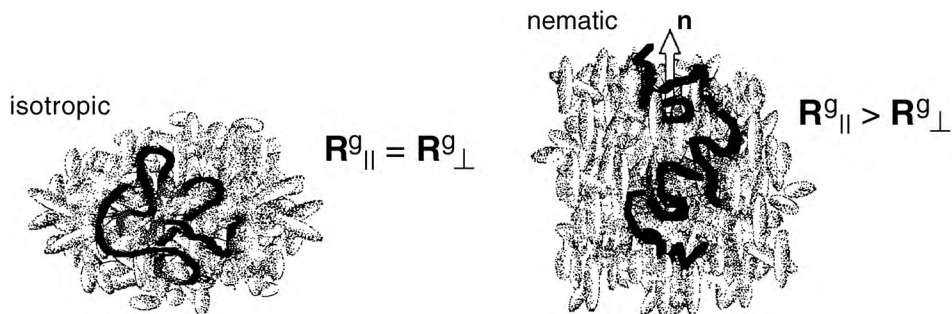


Fig. 5.22. Schematic illustrations of the trajectory of a polymer solute chain in isotropic solvent and in a nematic solvent; relative magnitudes of the parallel and perpendicular (to the vertical direction and $\mathbf{n}$, respectively) components of the radius-of-gyration tensor $\mathbf{R}^g$ are indicated.

mesophase of PLCs. Simultaneously, the director field generated by the spontaneously aligned mesogenic cores will in turn impose configurational constraints on the polymer chain's trajectory. One can begin to appreciate the constraints in this highly coupled system by considering the behavior of a flexible polymer chain *dissolved* in a liquid-crystalline solvent. Neutron scattering in conjunction with isotopic labeling can give insights into the overall shape of the solute chain in an anisotropic fluid. Results from studies of such solute–solvent systems suggest that the solute chain's radius-of-gyration tensor $\mathbf{R}^g$ conforms to the core organization in the MLC solvent (Fig. 5.22). In nematic phases $R_{||}^g > R_{\perp}^g$, where $R_{||}^g$ is the radius of gyration along the nematic director. However, since there is a severe entropic cost for deformation of the chain, the anisotropy ($R_{||}^g - R_{\perp}^g$) is rather small.

When the polymer chain is covalently linked to prolate mesogenic cores to form a SCPLC, the influence of the director field, to which we have alluded for the case of a free solute chain in a nematic, may be overwhelmed by the covalent topological constraints in the SCPLC. For the simple SCPLC wherein the mesogenic core is connected to the backbone with a flexible spacer, both prolate and oblate chain trajectories have been observed. Oblate radii of gyration ($R_{||}^g < R_{\perp}^g$) are observed in SCPLC nematics with a tendency for “smectic fluctuations” (nematics with a lower temperature smectic phase) [65]; in this situation the chain trajectory persists in a plane normal to the director (Fig. 5.23) and is denoted a nematic N_I phase by Warner [66]. A prolate trajectory (designated N_{III}) with the polymer backbone parallel to the director is also conceivable for SCPLCs. In smectic phases of SCPLCs, the polymer backbone assumes an oblate trajectory ($R_{||}^g < R_{\perp}^g$). However, the anisotropy in the radius of gyration is small ($R_{||}^g \sim R_{\perp}^g$), indicating that the backbone is *not* confined to the narrow interface between smectic layers. The backbone chain apparently traverses (ill-defined) layers in order to avoid a severe entropic penalty associated with confinement between smectic layers. Below we explicitly look at entropic

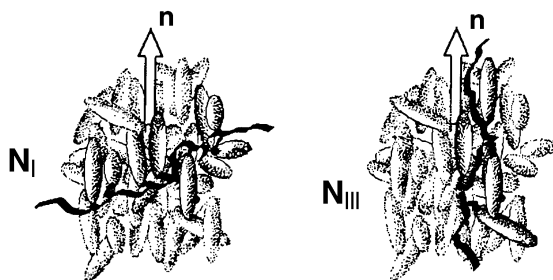


Fig. 5.23. Two possible configurations of the polymer backbone relative to its mesogenic side chains are illustrated, N_I and N_{III} (after [66]).

consequences in PLCs – namely, the rubber elastic properties of liquid-crystalline polymer networks after we very briefly consider the solid state of PLCs.

One very striking attribute of the polymeric mesogens is glass formation. While there are only a few MLC examples for which it is possible on vitrification to retain in the solid state the molecular organization present in the mesophase, this is a very common phenomenon in PLCs. The nematic or smectic glass thereby becomes a valuable solid host medium for orienting and exploiting optical properties of selected guest molecules. Moreover, the polymer becomes a vehicle for covalently including substantial numbers⁶ of guest molecules in the mesophase and oriented solid state [67]. The same rationale for glass formation as that in ordinary (isotropic) polymers applies also to PLCs – restriction of reorientational mobility on cooling the (LC) melt traps non-equilibrium configurations and prevents crystallization. In Fig. 5.24 we show a generic DSC trace for PLCs. After the first heating, a supercooled nematic glass is formed on cooling; this glass may transform directly into the nematic fluid on subsequent heating runs above the *glass-transition temperature*, T_g . In addition to the T_g , for sufficiently long spacer chains there may also be a T_m (not shown in Fig. 5.24) that is associated with melting of crystalline spacer chains.

Viscoelasticity is perhaps the most ubiquitous characteristic of high molecular weight polymers at temperatures above T_g . Here we consider the implications of coupling rubber elasticity and mesomorphism via synthesizing covalent networks from conventional elastomers (siloxanes, isoprenes, etc.) and typical MLC mesogenic cores; such networks are thermotropic PLCs. At low levels of cross-link densities in the PLC network, there is no appreciable change in the transition temperatures (T_g , T_{cl} , etc.) from those of the uncross-linked PLC (and its ancestral MLC) [68]. Below T_{cl} , rather modest mechanical deformations (extension ratio $\lambda < 1.5$) may convert an initial random and disclination-ridden texture into a

⁶ Only limited amounts of a nonmesogenic guest (10 mol%) can be accommodated by a MLC without depressing the mesophase; levels of ~40% of an anisometric guest can readily be tolerated in PLCs if the guest (comonomer) is covalently incorporated into a PLC.

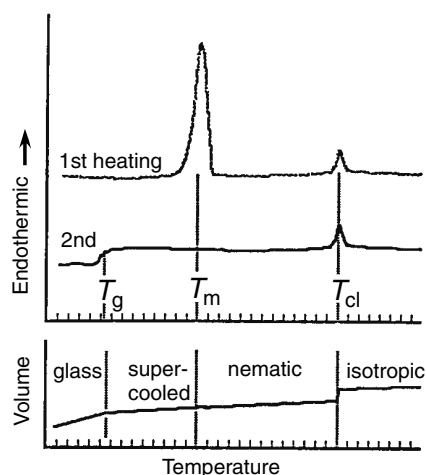


Fig. 5.24. Schematic representations of the DSC trace and change in volume on heating a thermotropic polymer liquid crystal. After the first heating, the mesophase supercools and vitrifies; on subsequent heatings (lower curves) the DSC trace and change in volume reveal transformations from glass to mesophase at T_g ; the mesophase goes isotropic at T_{cl} .

macroscopically uniform director field – a single liquid-crystal network [69]. In the isotropic melt of such an elastic network, application of a mechanical deformation will generate a stress field that will bias orientational alignment of the mesogenic cores. On lowering the temperature such orientational biasing will predispose the melt for spontaneous mesophase formation. As described in more detail in Section 5.5, a mechanical deformation can effectively increase T_{cl} , thereby inducing a phase transition ($I \rightarrow N$) at a temperature T'_{cl} that is higher than the zero-stress T_{cl} (intermediate dotted curve in Fig. 5.25). The order parameters at the clearing temperatures (S_{cl}) are indicated. The temperature dependence of the order parameter is illustrated in Fig. 5.25 for three situations: zero external stress (thick curve), an intermediate stress level (dotted curve), and at the critical stress level (thin line). The latter applies above some critical stress level (deformation ratio λ_{crit}); in this case the orientational order in the isotropic melt should increase continuously as the temperature is lowered, i.e. no first-order phase transition is observed as one lowers the temperature through T_{crit} if the sample is deformed above λ_{crit} (thin line in Fig. 5.25).

Coupling mesophase transitions and director reorientations to mechanical deformation lends itself to some novel applications. Mechano-optical sensors/switches may be fabricated. At low strains, chiral elastomeric mesophases exhibit unique electromechanical phenomena that originate from the change in electric polarization caused by a mechanical deformation. The opposite interaction – a change in

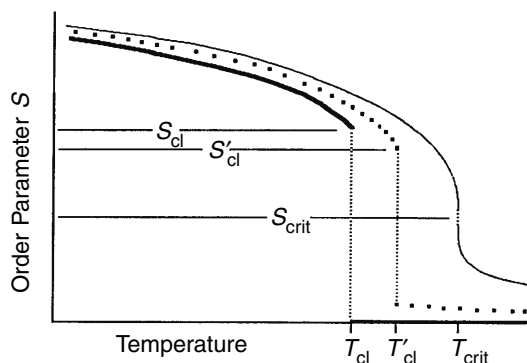


Fig. 5.25. The order parameter of an elastomeric liquid-crystalline polymer versus temperature in the absence (bold solid line, Maier–Saupe-like theory) and presence of external stress (dotted line and thin line). As the stress is increased, the first-order transition temperature (T_{cl}) increases (dotted line); above some critical stress (thin line) there is a continuous increase in S as the temperature is lowered.

the elastomers' dimensions – may be induced by applying an external electric field. The former piezoelectric effect may also be accompanied by pyroelectric and flexoelectric effects, namely induction of surface changes by changes in temperature and distortions of the director field, respectively [70, 71]. Chiral-monomer-based elastomeric PLCs that form N^* and S_C^* polydomain textures can be converted into single-domain samples at low deformations ($\lambda \sim 1.3$); the supramolecular twist may even be compensated at high deformations ($\lambda > 3$) to yield, for example, a compensated N^* or S_C^* phase [68]. Photonic phenomena in such mesogenic networks have also been reported. Spatially localized deformations can induce uniform director fields (homogeneous nematic optical anisotropy) and thereby delineate waveguide pathways in nematic elastomers [72]. New soft elastic deformation modes have been observed in nematic elastomers [73] as well as photonic band structure in cholesteric elastomers that varies sensitively and extensively with strain, displaying brilliantly colored reflections and lasing [74]. All of these phenomena suggest that practical realizations of PLCs will soon be demonstrated.

5.4.2 Block copolymers

Macroscopic anisotropy is observed in fluid phases – microphase-separated melts and solvent-swollen gels – of block copolymers [75]. In analogy with the hydrophobic–hydrophilic-driven aggregation of amphiphiles, diblock and triblock copolymers wherein the chemically different blocks exhibit differential solubility in conventional solvents also exhibit mesomorphism. (Hydrophobic interactions may also be exploited in mesophases of block copolymers [76].) The insoluble block will aggregate at high polymer concentrations (Fig. 5.26) and these aggregates

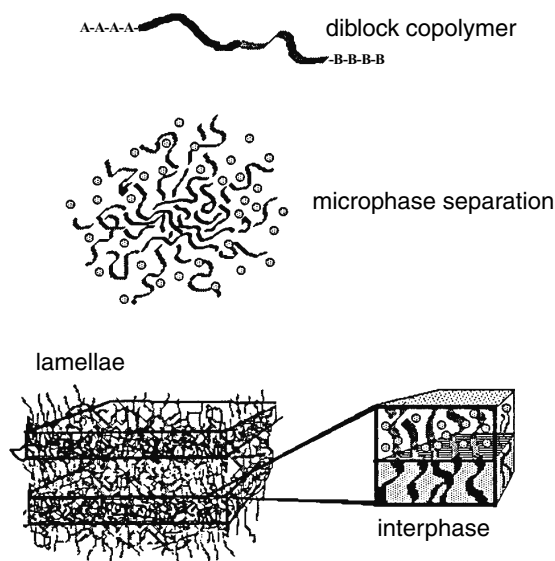


Fig. 5.26. A linear (AB) block copolymer with preferential solvation of the B block (top), an “inverted micelle” (middle), and a swollen lamellar morphology (bottom). The magnified view at the bottom shows the chain trajectories in the *interphase* near the A–B interface in the fluid microphase-separated morphology.

(with the swollen block on the periphery of the aggregate) will pack in the excess solvent in a variety of regular morphologies (cubic, hexagonal, lamellar, etc.). The long-range positional order in neat or swollen microphase-separated block copolymers confers anisotropic macroscopic properties (e.g. birefringence) on these fluid (gel-like) systems. However, the nature of the molecular (monomer) orientational order in such mesophases departs from that typically associated with MLCs. Generally the chain trajectory in each block will be random; the system will try to maintain maximum-entropy configurations in the spatially distinct phases. At the same time, the fact that the chain trajectory begins with the chain contour normal to the interface separating the incompatible blocks requires “brush-like” configurations [77] wherein the trajectory is extended in the direction normal to the interface. Similar kinds of biased chain trajectories would occur in semicrystalline polymers at the crystal–amorphous interface. However, the orientational anisotropy of the monomer for these intrinsically nonmesogenic systems is rather small ($S \sim 10^{-3}$ in deformed elastomers, for example) and leads to some confusion when terminology such as “nematic order” (implying that $S \sim 0.5$) is used to describe the biased chain trajectories. More recently, the term *interphase* has been introduced to acknowledge the departure of the polymer chains from a totally relaxed, equilibrium configuration near the interfaces in these systems (*interphase* in Fig. 5.26). It is on a global (i.e. supra-aggregate) scale that mesomorphic phenomena are encountered in block

copolymers and, consequently, mesomorphism is not dependent on anisometric monomer geometry, but rather on specific solvent-driven aggregation.

5.4.3 Liquid-crystalline polymers

The acronym LCP is used here to signify industrially important lyotropic and thermotropic polymers derived from conventional commercially relevant monomers. These polymers are not simply based on idealized, monomeric structures having an obvious tendency toward mesomorphism as was the case for PLCs. In LCPs mesomorphism derives from high-persistence-length chain contours. The requisite chain stiffness is exhibited by known classes of conventional monomers that have desirable end uses (thermal stability, solvent resistance, high strength, etc.). That is, the liquid-crystalline polymers have the requisite secondary structural rigidity/anisotropy to form ordered fluid phases spontaneously – if they can be solubilized or melted! Some characteristic structures are shown in Fig. 5.27. The first three entries in Fig 5.27 form lyotropic mesophases and, apart from the helical polypeptide (the first entry), these polymers require very aggressive acid solvents in order to solubilize the polymers at the sufficiently high concentrations needed for liquid-crystal formation, especially the poly(benzbisoxazole)s and poly(benzbisthiazole)s (the second entry with X = oxygen and sulfur, respectively). Poly(arylamide)s (the third entry) from DuPont and Akzo dominate the industrially important lyotropic LCPs.

The remaining entries in Fig 5.27 are thermotropic LCPs. Generally these polymers are of the “semiflexible” type with variable persistence lengths. Often the primary structure can be decomposed into mesogenic, core-like subunits (e.g. a couple of aromatic rings linked by an ester unit) that may be structurally related to known MLCs. Essentially all of the industrially important thermotropic LCPs are copolyesters with more than two comonomers, and, in such copolyester thermotropics, there is the distinct possibility of primary structural heterogeneity. Authors of a few studies have addressed the impact of structural heterogeneity of polyesters (brought about by interchange of esters in the melt) on mesophase properties [78]. Heterogeneity (in the molecular weight distribution as well as the primary structure) could cause nanophase separation – microscopic volume elements of isotropic melt dispersed in the mesophase – and, correspondingly, the possibility of a single chain traversing both isotropic and liquid-crystal phases. This possibility suggests that the usage of the phrase *degree of liquid crystallinity*, in analogy with *degree of crystallinity* in semicrystalline polymers, might be appropriate. Since polyesters are multicomponent systems (with a mixture of chain lengths and compositional heterogeneity), according to the phase rule these LCPs invariably exhibit large “two-phase” regimes (isotropic plus mesophase) when they are heated to near the

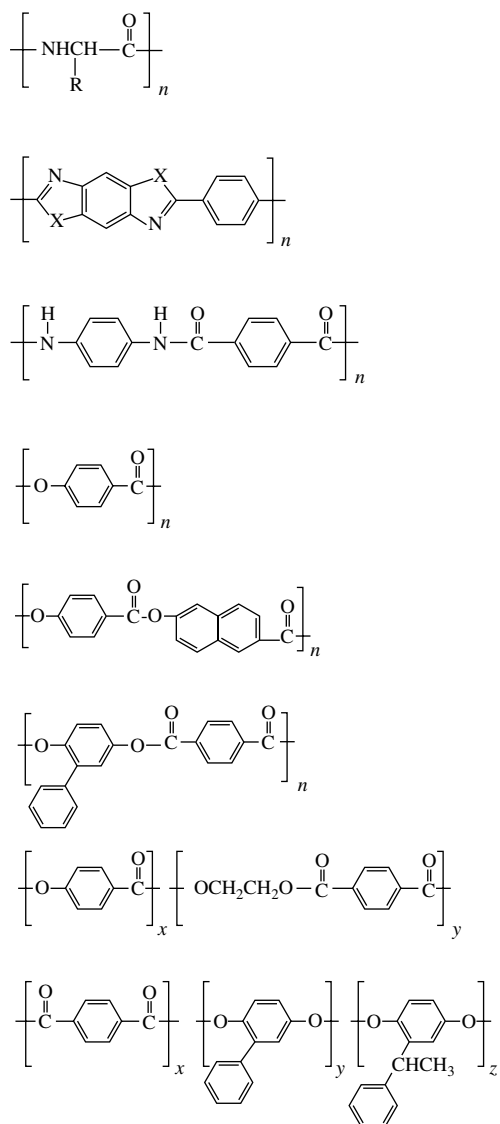


Fig. 5.27. Structures.

clearing temperature. The significance of phase equilibria in thermotropic LCPs has prompted heated discussions [79] in the literature, which have not been satisfactorily resolved. More importantly, although sample homogeneity is critical to ultimate physical properties of thermotropic LCPs, little systematic work on this topic with thermally stable LCPs has been published in the open literature.

Structural defects (bent or kinked monomers, e.g. 1,3-phenylenes and 2,6-naphthalenes, respectively) have deliberately been introduced into the backbones

of polyesters in an effort to make thermotropic LCPs more thermally tractable. New monomers of intermediate tortuosity (e.g. 2,5-thiophene [80] and oxadiazole [81]) would appear to have an important role to play in this respect.

5.5 Theories of mesomorphism

Four principal theories describing the transformation of the isotropic fluid into a spontaneously organized nematic fluid, the $I \rightarrow N$ transition, have been developed: (1) Onsager's density expansion of the free energy of anisometric particles, (2) Flory's estimate of the insertion probability for a rod-like (multisite) solute into a lattice, (3) Maier and Saupe's construction of a potential of mean torque experienced by mesogens (or solutes) in a nematic environment, and (4) de Gennes' transposition of Landau theory to the $I \rightarrow N$ transition. We briefly examine each of these in reverse chronological order because each is relevant to more-recent theoretical descriptions of polymer mesophases.

5.5.1 Landau molecular-field theory

The Landau molecular-field theory as applied to LC phase transitions by de Gennes [24] assumes that the Gibbs free-energy density $g(P, T, S)$ is an analytic function of the order parameter S . Expanding the nematic component of the free-energy density $g_{\text{nem}} \equiv g - g_{\text{iso}}$ in a power series (assuming that S is small) yields

$$g_{\text{nem}} = \frac{1}{3}AS^2 - \frac{2}{27}BS^3 + \frac{1}{9}CS^4 \quad (5.16)$$

where the coefficients A , B , and C are in general functions of P and T . Equation (5.16) predicts a phase transition in the vicinity of the temperature T^* where A vanishes; A is assumed to have the form

$$A = A'(T - T^*) \quad (5.17)$$

The discontinuous first-order phase transition occurs at a temperature T_c that is slightly higher than T^* (T^* is a second-order transition temperature). The first-order nature of the $I \rightarrow N$ transition is due to the presence of the odd-order power of S . The associated temperature T_c (equivalent to T_{cl} used earlier and in Fig. 5.25) and the order parameter at the $I \rightarrow N$ transition S_c may be obtained by minimizing g with respect to S (setting $(\partial g / \partial S) = 0$):

$$T = T^* + \frac{1}{27} \frac{B^2}{A'C} \quad S_c = \frac{B}{3C} \quad (5.18)$$

As suggested by the thick solid curve in Fig. 5.25, the order parameter changes discontinuously from $S = 0$ to a finite value S_c on lowering the temperature. If one considers the influence of an external field F interacting with the anisotropic molecular susceptibility $\Delta\chi$, an additional term $-\frac{1}{2}(N\Delta\chi)SF^2$ must be added to the expression for g [24, 26]. This external alignment influence shows up as a shift in T_{cl} to higher temperatures (the dotted curve in Fig. 5.25).

The general Landau theory, which was developed by de Gennes to describe critical phenomena in MLCs, has been applied to elastic networks comprised of PLCs [66]. The Landau formalism also allows one to make contact with the theory used to describe conventional orientation phenomena in *nonmesogenic* polymer networks. In particular, a mechanical deformation via its associated stress field σ influences g (and therefore T_c and S_c) analogously to external magnetic or electric fields. For a small (uniaxial) extension ratio $\lambda = e - 1$, where e is the strain, the form of g in Eq. (5.16) is modified by the additional terms as follows:

$$g = g_{iso} + g_{nem} - USe + \frac{1}{2}\mu e^2 - \sigma e \quad (5.19)$$

where $-USe$ describes the coupling of strain to the nematic order and μ is the modulus (U and μ would, for example, depend on the cross-link density). These extra terms have remarkable consequences. Even in the absence of an external stress field ($\sigma = 0$), a spontaneous change in the macroscopic dimensions of a network cross-linked in the nematic state can occur as the free energy is minimized at the strain value $e_{min} = US/\mu$. The resulting form for $g(e_{min})$ yields a higher transition temperature $T'_c = T_c + U^2/(2\mu A)$. The elastic PLC network will exhibit an $I \rightarrow N$ transition that occurs more readily than it would in the absence of cross-links, and T'_c will increase with increasing stress (the dotted curve in Fig. 5.25). Above some critical stress level σ_{crit} , on lowering the temperature the network will pass continuously from isotropic to mesophase at a critical temperature T_{crit} (the thin curve in Fig. 5.25). This regime cannot be realized in low molecular weights mesogens with electric or magnetic stresses. However, the coupling between the mechanical stress field and the anisotropic excluded volume of the mesogenic cores is much stronger than the coupling between electric (magnetic) fields and anisotropic susceptibilities $\Delta\chi$ of mesogens. Hence mechanical strains yield dramatic results in elastic PLC networks and allow one to achieve regimes that are not accessible in MLCs. Pre-transition phenomena driven by the stress field (e.g. the increase in birefringence as the nematic phase is approached from $T > T_{cl}$) have been reported [82]. The field-induced birefringence, $\Delta n_r \propto \Delta\chi F^2/A$, diverges as $T \rightarrow T_{cl}$ according to the definition of A in Eq. (5.17). That is, the principal source of temperature dependence in the expression for g_{nem} results in $\Delta n_r \propto A^{-1} \sim (T - T^*)^{-1}$.

These observations with PLC networks have reopened an old question in conventional elastic rubber networks (those composed of nonmesogenic monomers such as isoprenes, butadienes, and siloxanes), which are treated classically in Chapter 1. *Are orientational correlations (excluded-volume effects) among ordinary chain segments significant, and might there be coupling of segment orientation to the stress field in conventional elastic networks (“nematic-like interactions”)?* Recent theoretical work has suggested that deviations of experimental stress–strain data from classical descriptions of rubber elasticity could be accounted for by considering nematic-like interactions in such materials [83]. These ideas have also been implicated in stress-relaxation mechanisms for “isotropic” polymer melts [84].

5.5.2 Maier–Saupe theory

The Maier–Saupe theory [85] posits a simple potential of mean torque that originates from an average over the interactions a given mesogen experiences because of its (oriented) neighbors – the mean field:

$$V(\beta) = -wSP_2(\cos \beta) \quad (5.20)$$

It satisfies the symmetry conditions of the apolar nematic fluid with its simple $P_2(\cos \beta)$ angular dependence (here β is the polar angle between the molecular **I** axis of the mesogen and the director **n**), increases in importance with increasing orientational ordering S , and is parameterized by the coupling constant w – a measure of the strength of the influence of the nematic mean field on the mesogen. Since $V(\beta)$ vanishes in the isotropic liquid, where $S = 0$, $V(\beta)$ represents anisotropic interactions over and above those encountered in ordinary liquids. A self-consistent definition of the order parameter (S appears on both sides of Eq. (5.21) since $V(\beta)$ is a function of S) follows:

$$S = \frac{\int_0^1 P_2(\cos \beta) \exp\left(-\frac{V(\beta)}{k_B T}\right) d(\cos \beta)}{\int_0^1 \exp\left(-\frac{V(\beta)}{k_B T}\right) d(\cos \beta)} \quad (5.21)$$

Equation (5.21) may be solved numerically to give the temperature dependence of the order parameter (the thick solid curve in Fig. 5.25). Conventional statistical-mechanical manipulations of the partition function show that a first-order phase transition is predicted at T_c (T_{cl}). Other quantities are $S_c = 0.43$ and $T_c = 0.22w/k_B$ at the I $\rightarrow$ N phase transition.

This theory has been used by Warner [66] and others to suggest that there is more than one type of nematic phase in SCPLCs, depending on the relative magnitude (and signs) of the coupling constants w_{core} and w_{backbone} representing the respective interactions of the side chain and the backbone with the mean field (see Fig. 5.23). With the exception of SCPLCs, the Maier–Saupe theory makes an appearance only as a supplement to the athermal excluded-volume interaction in the Flory lattice theory (see below). However, it should be stressed that, although w was identified with anisotropic attractive interactions (dispersion forces) in the original theory, Gelbart [86] and Cotter [87] have shown that averaging *isotropic* attractive interactions over an anisotropic space (arising from excluded-volume considerations regarding rod-like mesogenic cores) leads to the same form for $V(\beta)$. That is, an apparent anisotropic attractive potential of mean torque may be generated from purely isotropic attractions when shape anisotropy is correctly factored into the averaged intermolecular interactions. Such local (effective) anisotropy derived from excluded-volume considerations may also underlie the physics of linear thermotropic LCPs having semiflexible mainchains.

5.5.3 The Flory lattice model

The Flory lattice model [88] for polymeric LCs has received the most attention, although it lay dormant for more than a decade after it had been introduced in 1956. It is ideally suited for lyotropic LCs consisting of solvent and rigid rods, although it has been considered (with modifications) in the context of semiflexible linear polymers and thermotropic monomer LCs more recently. The crux of this model is the derivation of the partition function Z corresponding to the insertion of n_p rod-like solute particles (each comprised of x segments) into a lattice with n_0 sites; all sites are filled in the solution by inserting $n_s = n_0 - xn_p$ solvent particles. Z is the product of two components: a combinatorial part,

$$Z_c = \left(\frac{1}{n_p!} \right) \prod_{j=1}^{n_p} v_j \quad (5.22)$$

and an orientational part,

$$Z_0 = \prod_y (n_p \sin \beta_y / n_{py})^{n_{py}} \approx \left(\frac{\bar{y}}{x} \right)^{2n_p} \quad (5.23)$$

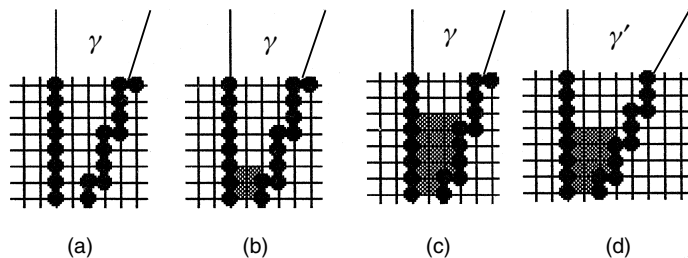
In Z_c , v_j is the insertion probability for the j th solute rod; it is a function of $y = x \sin \beta_y$, where β_y is the inclination of the rod from the local director. (The variable y may also be viewed as the number of “sub-rods” comprising a particle at inclination β_y ;

this deconstruction of the particle into sub-rods is a natural consequence of inserting the entire rod into a discrete lattice.) v_j and thus Z_c increase with increasing y and have maximum values for perfect order ($y = 1$). Thus Z_c behaves oppositely to Z_0 , which is a maximum for isotropic configurations of the n_p particles on the lattice (n_{py} is the number of particles with inclination y). In this model the length of the particle, x , divided by its width (one lattice site) is the aspect ratio of the solute rods ($x = L/d$). For small axial ratio x and/or small concentration of rods n_p , Z_0 dominates and complete disorder ($y = x$) is the most stable state of the system of rods and solvent. For large x and/or n_p , Z_c can compensate Z_0 , yielding a regime of free energy $-\ln Z$ where partially ordered mixtures of rods and solvent are stabilized. The critical volume fraction ϕ_1 signaling the appearance of the LC phase is simply a function of solute geometry (aspect ratio x):

$$\phi_1 \approx \frac{8}{x} \left(1 - \frac{2}{x} \right) \quad (5.24)$$

The general predictions of Eq. (5.14) are in agreement with experiment for a variety of lyotropic LCPs [88]. One consequence of this theory for a system of polydisperse rods (a distribution of x values) is the possibility of fractionation [89]: longer rods would distribute themselves into the anisotropic LC phase while short ones would be relegated to the isotropic phase in the two-phase regime. The theory can also be extended [90] to make predictions about ternary mixtures – rods, random coils, and solvent – and is in agreement with experimental observations [91] that indicate the strong incompatibility of the two kinds of polymers. It has been adapted to treat semiflexible polymers also.

Before concluding this section, we briefly consider efforts to treat MLCs with the Flory lattice theory by adding *anisotropic* attractive interactions of the type given by Maier and Saupe (Eq. (5.20)) [92]. The necessity for adding intrinsically anisotropic attractive interactions would appear to this author to be an artifact of the way attractive interactions are handled in the lattice model itself: only nearest-neighbor lattice-site interactions are independently summed. Consequently, anisotropic attraction can be observed only if one adds *intrinsic (site) anisotropy*. However, if, in addition to nearest-neighbor site interactions, second-, third-, etc. nearest-neighbor interactions were also incorporated into the lattice sums, then *anisotropic* attraction would naturally result from *isotropic (site) interactions*. The magnitude of the total attractive interaction between a pair of rods (sequentially occupied sites) would be, in a longer-ranged lattice-summation scheme, a function of the relative angular orientation of a pair of rods (assuming that the interaction between two solute-occupied sites has a magnitude that differs from that between a solute-occupied site and a site occupied by solvent). This phenomenon is readily illustrated in the two-dimensional square lattice fragments below.



In (a), nearest-neighbor interactions only are considered and, in the fragment shown, no nearest-neighbor sites are occupied for the rod fragments oriented at an angle γ ; in (b) and (c), second- and third-nearest-neighbor interactions, respectively, are illustrated with shaded regions. When γ is increased to γ' in (d), the number of third-nearest-neighbor interactions decreases (from 13 in (c) to 11 in (d)), which is indicative of an angle-dependent attractive interaction. This kind of angle-dependent attraction is derived from excluded-volume considerations in a manner reminiscent of the modeling of Cotter and Gelbart for MLCs [86, 87], without resorting to intrinsic anisotropy at the sites occupied by the rod-like polymer.

5.5.4 Onsager's virial expansion

Onsager's virial expansion [93] was the first correct model of an athermal I $\rightarrow$ N phase transition. Its formulation was motivated by lyotropic mesomorphism in solutions of the rod-like TMV particles. Other colloidal particles with anisotropic shapes were identified as mesomorphic in the 1920s – inorganic V_2O_5 particles [94], liquid-crystalline dispersions of polytetrafluoroethylene “whiskers” [95], and inorganic nanoparticles [50] are contemporary examples of this phenomenon. In the Onsager model the Helmholtz free energy of n_p polymer rods (axis ratio $x = L/d$) in a volume V is given by

$$\frac{\Delta F}{n_p kT} \approx \frac{\mu^o}{kT} + \ln\left(\frac{n_p}{V}\right) - 1 + \int f(\Omega) \ln[4\pi f(\Omega)] d\Omega + \rho B_2 + \dots \quad (5.25)$$

where the distribution function $f(\Omega)$ gives the probability of finding a rod at orientation Ω . The second virial coefficient B_2 is given in terms of the cluster integral

$$B_2 = -\frac{1}{2} \iint B(\Omega, \Omega') f(\Omega) f(\Omega') d\Omega d\Omega' \quad (5.26)$$

Onsager approximated $f(\Omega)$ by

$$f(\beta) = \frac{\alpha}{4\pi \sinh \alpha} \cosh(\alpha \cos \beta) \quad (5.27)$$

Table 5.1. Critical parameters from various trial functions $f(\Omega)$

xc_I	xc_N	S_{crit}	$f(\Omega)$
3.340	4.486	0.848	Onsager trial function
3.450	5.120	0.910	Gaussian function
3.290	4.191	0.792	Numerical iteration

where $d\Omega = 2\pi \sin\beta d\beta$ and α is a variational parameter determined by minimizing $\Delta F/(n_p kT)$; Onsager approximated the mutually excluded volume of a pair of cylinders (length L , diameter d , and relative orientation γ) by

$$-B(\Omega, \Omega') \approx 2dL^2 |\sin \gamma| \quad (5.28)$$

and computed the coexistence of nematic and isotropic phases by equating the concentration-dependent osmotic pressures and chemical potentials in these two phases,

$$\Pi_I(c_I) = \Pi_N(c_N) \quad \mu_I(c_I) = \mu_N(c_N) \quad (5.29)$$

The results – the onset of liquid crystallinity (the product of c_I and the axial ratio x), the concentration when the entire system is nematic (xc_N), and S_{crit} , the critical order parameter – are given in Table 5.1 for various trial functions $f(\Omega)$.

The critical concentrations and order parameters are obviously sensitive to the nature of the orientational distribution of the rods. The Onsager description has largely been ignored by the polymer community; truncation at the second virial coefficient was thought to be too unrealistic for rod densities needed to obtain liquid crystals. Methods for decoupling translational and orientational degrees of freedom have extended the range of validity of the virial expansion to higher concentrations (and smaller axial ratios x) [96]. This decoupling also allows one to introduce rod flexibility into the model in a simple way. (Flory and Matheson [97] considered rod flexibility in the lattice model contemporaneously with Khokhlov and Semenov's [98] consideration of this phenomenon in the context of Onsager's model.) Defining the chains' persistence length to be R_x , a rigid rod exists when $L/R_x \ll 1$. The dependences of c_I and c_N on the flexibility L/R_x have been simulated by DuPre and Yang [99]; as the flexibility L/R_x increases the necessity for larger polymer concentrations before one finds mesomorphism is apparent (Fig. 5.28). Excellent fits to experimental data for macromolecules exhibiting various inherent flexibilities are obtained on introducing the (additional) L/R_x parameter [99]. The revival of interest in the seminal work of Onsager (with flexibility incorporated, as introduced by Khokhlov and Semenov [98] and Odijk [100]) is the subject of a comprehensive review by Vroege and Lekkerkerker [101].

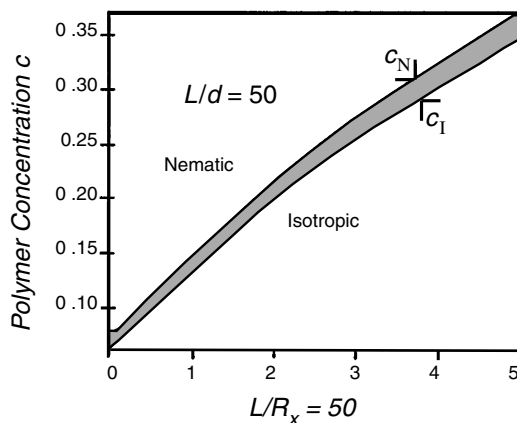


Fig. 5.28. The variation in the phase boundaries c_I and c_N with the rod flexibility L/R_x ; the dark area is the two-phase regime (after [99]).

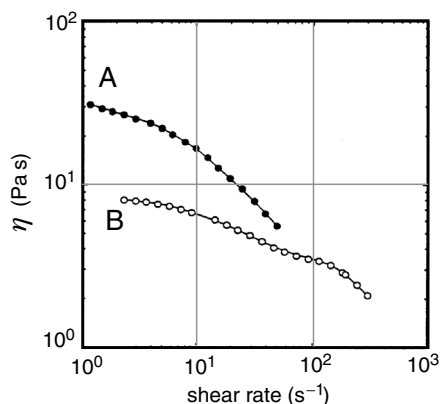


Fig. 5.29. The dependence of the shear rate on polymer concentration for solutions of PBLG (polybenzyl-L-glutamate) solutions: (A) $c < c_I$ (isotropic solution) and (B) $c > c_N$ (mesomorphic solution), from [104].

5.5.5 Rheology

When anisotropy is present in the fluid state, the phenomenon described in Chapter 3 becomes more complex. We attempt to illustrate this complexity with a few aspects of viscoelastic behavior taken from the literature on lyotropic polypeptide LCPs (rod-like α -helical macromolecules in helicogenic solvents). For example, when $c < c_I$, conventional viscosity-versus-shear-rate behavior is observed (see Chapter 3). Contrary to intuition, however, Fig. 5.29 shows that, at any given shear rate, the viscosity decreases with increasing concentration of polymer when the polypeptide concentration c exceeds that required for uniform LC formation,

$c > c_N$. Superficially, when rigid rod-like polymers are added to a solution, there is an extremely strong dependence of the viscosity η on the rod concentration ϕ .⁷ Below the $I \rightarrow N$ transition η increases dramatically with ϕ ; the viscosity exhibits a maximum in the two-phase regime ($\phi_I < \phi < \phi_N$) and then η decreases for $\phi > \phi_N$. Doi [102] has successfully described these qualitative observations using a rheological constitutive equation based on a molecular-kinetic equation wherein the role of mutual ordering of the rod-like solute is included; in his model $\phi_I = 8\phi^*/9$ and $\phi_N = \phi^*$. The reduced steady-state viscosity η/η^* is dependent on the reduced concentration ϕ/ϕ^* and the degree of orientational order of the rods S :

$$\frac{\eta}{\eta^*} = \left(\frac{\phi}{\phi^*}\right)^3 \frac{(1-S)^4(1+S)^2(1+2S)(1+3S/2)}{(1+S/2)^2} \quad (5.30)$$

S in turn depends on the density of rods in the anisotropic phase:

$$S = \begin{cases} 0 & \phi < \phi^* \\ \frac{1}{4} + \frac{3}{4}[1 - 8\phi^*/(9\phi)]^{1/2} & \phi > 8\phi^*/9 \end{cases} \quad (5.31)$$

A plot of Eq. (5.30) shows the rise and fall of η/η^* in the isotropic and nematic phases, respectively (Fig. 5.30(a)). The inset, Fig. 5.30(b), is an estimate of the behavior of the viscosity in the two-phase regime ($8\phi^*/9 < \phi < \phi^*$ where a mixture of isotropic and anisotropic phases is present. The plotted behavior is computed with the Taylor formula for a mixture of two immiscible fluids,

$$\frac{\eta}{\eta_0} = 1 + f \left(\frac{5\eta_1/\eta_0 + 2}{2(\eta_1/\eta_0 + 1)} \right) \quad (5.32)$$

where f is the fraction of anisotropic phase in the mixture and η_0 and η_1 are the viscosities of the “host” and “guest” phases, respectively. When $f < 0.5$, the Doi values of the isotropic and anisotropic reduced viscosities are used for η_0 and η_1 ; these are interchanged when $f > 0.5$ (it is assumed that f changes linearly with the reduced volume fraction in the two-phase regime – from $f = 0$ at ϕ_I to $f = 1.0$ at ϕ_N). Thus the Taylor formula predicts [103] a maximum in η/η^* within the two-phase region, in agreement with experiments.

Larson and co-workers [104] have carefully studied the rheology of lyotropic polypeptide liquid crystals. The shear-rate dependence of η has been examined for isotropic and anisotropic (liquid-crystalline) solutions (Fig. 5.29). Additionally, the first and second normal-stress differences N_1 and N_2 have been shown to exhibit very unusual behaviors; e.g. N_2 is an oscillatory function of the shear rate (Fig. 5.31). The observations are in qualitative agreement with extensions of Doi’s theory. (In a disclination-ridden mesophase it is necessary to average over

⁷ In order to facilitate contact with the original literature we use the rod’s aspect ratio to transform from the number concentration c to the volume fraction of rods $\phi = (p/4)cd^2L$.

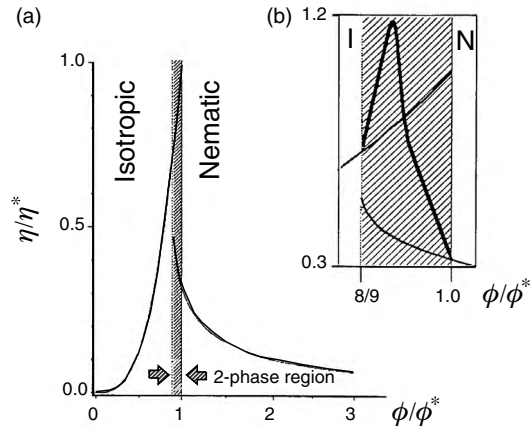


Fig. 5.30. (a) The predicted reduced viscosity versus reduced concentration for rigid rods according to Doi (Eq. (5.20)). (b) In the two-phase regime ($c_I > c < c_N$) the reduced viscosity is expected to reach a maximum according to the classical behavior of two immiscible fluid phases [103].

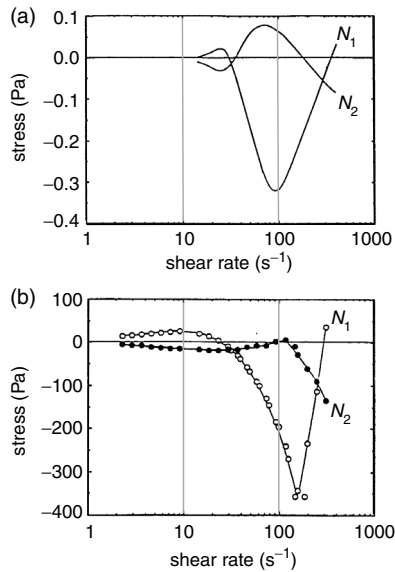


Fig. 5.31. Calculated (a) and experimental (b) dependences of the first and second normal stress differences (N_1 and N_2) on the shear rate (PBLG mesophase $c < c_N$). The calculated values are dimensionless and are based on the extended version of the Doi theory; from Magda [104].

domain orientations since the Doi theory pertains to monodomain samples, i.e. a macroscopically uniform director field.) In recent theoretical work Marrucci [105] explicitly considers the “tumbling regime” of the nematic fluid – the rotational motion of the director and the resulting polydomain texture – at low shear rates. (At high shear rates, a monodomain with a uniform director field exists.) The theory is in accord with experimentally observed [106] damped oscillations of the transient stress response to step strains.

We conclude the discussion on LCP rheology by drawing attention to the phenomenon of *band formation* – a “serpentine” distortion of the director field caused by shearing [107]. Although the mechanism is not fully understood (two orthogonal deformations of the director field appear [108] to be necessary: simple shear and perhaps Frank elasticity orthogonal to the shear direction), it would appear to be very important in processing LCPs. A periodic orientational distortion reminiscent of the banded texture is observed in monofilaments that are spun from lyotropic LCPs, and its influence on the ultimate mechanical properties of the fiber has been discussed (see below).

5.5.6 Elasticity

In rigid-rod mesophases where interactions are dominated by excluded-volume interactions, the contributions of elasticity to the free energy are entropic in nature. The elastic constants k_{ii} are proportional to $\phi^2(L/d)^2$ and order-parameter-dependent factors; bend (k_{33}) is more important than splay (k_{11}), which is three times the twist elastic constant (k_{22}) [109]. On the other hand, consideration of a semiflexible polymer with a chain contour that could follow local distortions of the director field suggests that there would be different relationships among the k_{ii} . For example k_{33} should be linear in ϕ and independent of the chain length L . Meyer [110] suggested that k_{ii} is linear in L/d and ϕ and that $k_{11} > k_{33}$ for long chains; splay is thought to be dominated by changes in entropy associated with the chain ends. Lee and Meyer [111] have delineated the distinctions between rigid and semiflexible LCPs using the lyotropic polypeptide mesophase. They see a crossover from rigid-rod behavior $L/d < R_x$ to semiflexible behavior $L/d > R_x$ with increasing molecular weight of the polypeptide. They observe that bending distortions of the chain’s contour play a significant part in determining the viscoelastic properties of LCPs and confirm the validity of some of the geometric arguments used to model the elasticity of LCPs.

5.5.7 Solid-state morphology and properties

Generally speaking, the morphological features of the solid state of LCPs are derived from the forms of macromolecular organization exhibited by mesomorphic

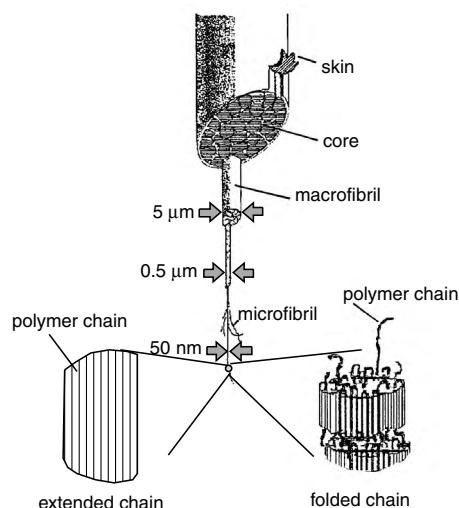


Fig. 5.32. The hierarchical morphology exhibited by fibers [11]. In the case in which rigid, rectilinear polymers are drawn from mesophases, an extended-chain crystal habit is adopted, with the chains running parallel to the fiber axis (left inset). In conventional flexible polymers, the semicrystalline folded-chain crystal habit exists (right inset).

melts and solutions. A striking example of this is the nature of the hierarchical morphology found in fibers (Fig. 5.32). Until the microscopic levels of this hierarchy are reached, the features of fiber morphology in fibers obtained from conventional flexible polymers and from LCPs are similar. In the former polymers a two-phase morphology is present at the molecular level: a chain-folded crystal habit coexists with amorphous connecting chains (lower right in Fig. 5.32; also see Chapter 4). In LCPs the chain persists for its entire length in an extended-chain crystal that is essentially continuous along the length of the fiber (lower left in Fig. 5.32). There are correspondingly large differences in the physical properties of these otherwise very similar morphologies. These differences may be readily appreciated by contrasting the ultimate tensile moduli of polyethylene (PE) in fibers with the folded-chain habit (fcPE) with those having the extended-chain crystal (ecPE). The ecPE habit may be produced in polyethylene by gel-spinning [112] or solid-state extrusion [113]. In fcPE the average modulus is ~ 80 GPa; it is found by summing, in series, contributions from the amorphous component (~ 6 GPa) and estimates of the crystal contribution (~ 300 GPa). In ecPE a value of 220 GPa is observed for the tensile modulus; the theoretical maximum estimated for PE is 320 GPa [114]. In fibers from lyotropic semiflexible polyaramides, one finds moduli around 185 GPa; for the more rigid poly(benzbisoxazole), moduli of 365 GPa are reported.

In the fibers produced from lyotropic spinning dopes, there still appear to be limitations on the ultimate physical properties due to higher-order morphological defects (the periodic director-orientation distortions alluded to earlier) [115]. In this context, much experimental and theoretical work remains to be done to delineate those parameters that control disclination textures and director patterns created by complex shear fields encountered in processing LCPs. As is typically the case, there are natural systems wherein these difficulties appear to have been optimally minimized: spiders spin nearly defect-free fibers from a mesomorphic form of silk [116]. Consequently, efforts to analyze the spinning process – the spinner draw-down geometry and its associated shear field – used by arachnids are under way.

In melts and solutions of semiflexible LCPs rheologically induced stress fields probably couple with conformational changes of the polymer; this additional complication needs to be investigated in order to resolve the origins of the hierarchical “skin-core” morphologies observed in the solid state of LCPs. Another important issue is the development of defect structures in flow fields [117]. These kinds of supramolecular considerations undoubtedly play a key role in determining the ultimate physical properties of high-performance LC polymers. In fact, lack of understanding of the processing of LCPs is one limitation of the utility of this class of materials [11, 118]; current costs of the monomers are also a significant consideration. Nevertheless, there remains general agreement in the polymer-science community that the role of LCPs – in specialized applications that exploit anisotropy, in blends and (self-reinforcing) composites, and as processing aids – will be a very important one, and, at the same time, a technologically challenging one.

Acknowledgment

The author's research program concerning liquid crystals has been supported primarily by the National Science Foundation, Division of Materials Research.

References

- [1] M. Baron and R. F. T. Stepto, *Pure Appl. Chem.*, **74** (2002), 493; M. Baron, *Pure Appl. Chem.*, **73** (2001), 845.
- [2] D. A. Dunmur, A. Fukuda, and G. R. Luckhurst (eds.), *Liquid Crystals: Nematics* (INSPEC, London, 2001).
- [3] S. Kumar (ed.), *Liquid Crystals: Experimental Study of Physical Properties and Phase Transitions* (Cambridge University Press, Cambridge, 2000).
- [4] R. G. Larson, *The Structure and Rheology of Complex Fluids* (Oxford University Press, Oxford, 1999).

- [5] P. J. Collings and M. Hird, *Introduction to Liquid Crystals, Chemistry and Physics* (Taylor and Francis, Bristol, 1997).
- [6] D. Acierno and A. A. Collyer, *Rheology and Processing of Liquid Crystal Polymers* (Chapman & Hall, London, 1996).
- [7] N. A. Plate (ed.), *Liquid Crystalline Polymers* (Plenum Press, New York, 1993).
- [8] A. A. Collyer (ed.), *Liquid Crystal Polymers: From Structures to Applications* (Elsevier Applied Science Publishers, London, 1992).
- [9] A. M. Donald and A. H. Windle, *Liquid Crystalline Polymers* (Cambridge University Press, Cambridge, 1991).
- [10] A. Ciferri (ed.), *Liquid Crystallinity in Polymers* (Cambridge University Press, Cambridge, 1991).
- [11] E. T. Samulski, *Liquid Crystalline Polymers* (National Academy Press, Washington, 1990).
- [12] R. A. Weiss and C. K. Ober (eds.), *Liquid Crystalline Polymers* (American Chemical Society, New York, 1990).
- [13] C. B. McArdle (ed.), *Side Chain Liquid Crystal Polymers* (Blackie and Son, London, 1989).
- [14] G. Vertogen and W. H. deJeu, *Thermotropic Liquid Crystals, Fundamentals* (Springer-Verlag, Berlin, 1988).
- [15] G. W. Gray (ed.), *Thermotropic Liquid Crystals* (John Wiley & Sons, New York, 1987).
- [16] L. L. Chapoy (ed.), *Recent Advances in Liquid Crystalline Polymers* (Elsevier Applied Science Publishers, Amsterdam, 1985).
- [17] A. Blumstein (ed.), *Polymeric Liquid Crystals* (Plenum Press, New York, 1985).
- [18] *Polymer Liquid Crystals*, Faraday Discussion of the Chemical Society No. 79 (Royal Chemical Society, London, 1985).
- [19] M. Gordon (ed.), *Liquid Crystal Polymers*, vols. I, II, and III (Springer-Verlag, Berlin, 1984).
- [20] A. Ciferri, W. R. Krigbaum, and R. B. Meyer (eds.), *Polymer Liquid Crystals* (Academic Press, London, 1982).
- [21] H. Kelker and R. Hatz, *Handbook of Liquid Crystals* (Verlag Chemie, Berlin, 1980).
- [22] A. Blumstein (ed.), *Liquid Crystalline Order in Polymers* (Academic Press, New York, 1978).
- [23] S. Chandrasekhar, *Liquid Crystals* (Cambridge University Press, Cambridge, 1977); 2nd edition (1992).
- [24] P. G. de Gennes, *The Physics of Liquid Crystals* (Oxford University Press, Oxford, 1974); 2nd edition (1993).
- [25] E. B. Priestly, P. J. Wojtowicz, and P. Sheng (eds.), *Introduction to Liquid Crystals* (Plenum Press, New York, 1974).
- [26] M. J. Stephen and J. P. Straley, *Rev. Mod. Phys.*, **46** (1974), 617.
- [27] D. Vorländer, *Z. Phys. Chem.*, **449** (1927), 126.
- [28] G. W. Gray and J. W. Goodby, *Smectic Liquid Crystals: Textures and Structures* (Leonard Hill, London, 1984).
- [29] M. J. Freiser, *Phys. Rev. Lett.*, **24** (1970), 1041.
- [30] T. Niori, *et al.*, *J. Mater. Chem.* **6** (1996), 1231; D. R. Link, *et al.*, *Science*, **278** (1997), 1924; G. Heppke, *et al.*, *Phys. Rev. E*, **60** (1999), 5575.
- [31] R. H. Hurt and Z.-Y. Chen, *Phys. Today*, **53** (2000), 39.
- [32] E. Nishikawa and E. T. Samulski, *Liq. Cryst.*, **27** (2000), 1463.
- [33] R. Cai and E. T. Samulski, *Liq. Cryst.*, **9** (1991), 617.

- [34] H. Shi, S. H. Chen, M. E. DeRosa, T. J. Bunning, and W. W. Adams, *Liq. Cryst.*, **20** (1996), 277.
- [35] D. Demus and H. Zasehke, *Flüssige Kristalle in Tabellen* (VETS Deutscher Verlag für Grundstoffindustrie, Leipzig, 1984).
- [36] X. Wen and R. B. Meyer, *Phys. Rev. Lett.*, **59** (1987), 1325.
- [37] I. C. Lewis and C. A. Kovac, *Mol. Cryst. Liq. Cryst.*, **51** (1979), 173.
- [38] E. T. Samulski, *Israel J. Chem.*, **23** (1983), 329.
- [39] X. H. Cheng, *et al.*, *Langmuir*, **18** (2002), 6521.
- [40] C. A. Vieth, E. T. Samulski, and N. S. Murthy, *Liq. Cryst.*, **19** (1995), 557.
- [41] T. J. Dingemans and E. T. Samulski, in preparation (2003).
- [42] D. Chandler, J. D. Weeks, and H. C. Anderson, *Science*, **220** (1983), 787.
- [43] B. K. Vainshtein, *Diffraction of X-rays by Chain Molecules* (Elsevier, Amsterdam, 1966).
- [44] R. Oldenbourg, X. Wen, R. B. Meyer, and D. L. D. Caspar, *Phys. Rev. Lett.*, **61** (1988), 1851.
- [45] S. N. Murthy, J. R. Knox, and E. T. Samulski, *J. Chem. Phys.*, **65** (1978), 4835.
- [46] E. T. Samulski, *NMR in Orientationally Ordered Liquids*, edited by C. A. de Lange and E. Burnell (Kluwer, Dordrecht, 2003), chapter 13, p. 285.
- [47] D. J. Photinos, B. J. Poliks, E. T. Samulski, A. F. Terzis, and H. Toriumi, *Molec. Phys.*, **72** (1991), 333.
- [48] C. Viney and C. M. Daniels, *Molec. Cryst. Liq. Cryst.*, **196** (1991), 133 and references therein.
- [49] B. A. Wood and E. L. Thomas, *Nature*, **324** (1986), 655.
- [50] F. Kim, S. Kwan, J. Akana, and P. Yang, *J. Am. Chem. Soc.*, **123** (2001), 4360.
- [51] I. Chuang, R. Durrer, N. Turok, and B. Yurke, *Science*, **251** (1991), 1336.
- [52] A. C. Neville and S. Caveney, *Biol. Rev.*, **44** (1969), 531.
- [53] N. A. Clark and S. T. Lagerwall, *Appl. Phys. Lett.*, **36** (1980), 899; B. O. Myrvold, *Molec. Cryst. Liq. Cryst.*, **202** (1991), 123.
- [54] J. Naciri, S. Pfeifer, and R. Shashidhar, *Liq. Cryst.*, **10** (1991), 585.
- [55] D. J. Photinos and E. T. Samulski, *Science*, **270** (1995), 783.
- [56] A. F. Terzis, D. J. Photinos, and E. T. Samulski, *J. Chem. Phys.*, **107** (1997), 4061.
- [57] P. N. Prasaël and D. J. Williams, *Introduction to Nonlinear Optical Effects in Molecules and Polymers* (John Wiley & Sons, Inc., New York 1991); see also G. R. Mohlman and C. P. J. M. van der Vorst, in *Side Chain Liquid Crystal Polymers* (Blackie and Son, London, 1989), chapter 12.
- [58] I-C. Koo and S-T. Wu, *Optics and Nonlinear Optics of Liquid Crystals* (World Scientific, Singapore, 1993).
- [59] W. Brostow, *Polymer*, **31** (1990), 979.
- [60] P. Davidson and A. M. Levelut, *Liq. Cryst.*, **11** (1992), 469.
- [61] C. K. Ober, J. Jin, and R. W. Lenz, in *Liquid Crystal Polymers*, vol. I, edited by M. Gordon (Springer-Verlag, Berlin, 1984) p. 104.
- [62] H. Toriumi, H. Furuya, and A. Abe, *Polym. J.*, **17** (1985), 895.
- [63] J. Watanabe and M. Hayashi, *Macromolecules*, **22** (1989), 4083.
- [64] R. B. Blumstein and E. M. Stickles, *Molec. Cryst. Liq. Cryst.*, **82** (1982), 151.
- [65] P. Davidson, L. Noirez, J. P. Cotton, and P. Keller, *Liq. Cryst.*, **10** (1991), 111 and references therein.
- [66] M. Warner, in *Side Chain Liquid Crystal Polymers*, edited by C. B. McArdle (Blackie and Son, London, 1989) chapter 2.
- [67] H.-W. Schmidt, *Angew. Chem. Adv. Mater.*, **101** (1989), 964.
- [68] R. Zentel, *Angew. Chem. Int. Ed. Engl. Adv. Mater.*, **28** (1989), 1407.

- [69] G. R. Mitchell, F. J. Davis, and A. Ashman, *Polymer*, **28** (1987), 639.
- [70] J. H. Wendorff, *Angew. Chem. Int. Ed. Engl.*, **30** (1991), 405.
- [71] W. Meier and H. Finkelmann, *Makromol. Chem. Rapid Commun.*, **11** (1990), 599.
- [72] H. Finkelmann, *Angew. Chem. Int. Ed. Engl.*, **27** (1988), 987.
- [73] M. Warner and S. Kutter, *Phys. Rev. E*, **65** (2002), 51 707.
- [74] P. A. Bermel and M. Warner, *Phys. Rev. E*, **65** (2002), 56 614.
- [75] A. Skoulios, *Adv. Liq. Cryst.*, **1** (1975), 169.
- [76] J. Yang and G. Wegner, *Macromolecules*, **25** (1992), 1786; see also B. M. Discher, *et al.*, *Science*, **284** (1999), 1143.
- [77] S. T. Milner, *Science*, **251** (1991), 905.
- [78] D. G. Martin and S. I. Stupp, *Macromolecules*, **21** (1988), 1222; see also J.-I. Jin, in *Liquid Crystalline Polymers*, edited by R. A. Weiss and C. K. Ober (American Chemical Society, New York, 1990), chapter 3; J. Economy, R. D. Johnson, J. R. Lyerla, and A. Mutelebach, in *Liquid Crystalline Polymers*, edited by R. A. Weiss and C. K. Ober (American Chemical Society, New York, 1990), chapter 10.
- [79] General discussion in *Faraday Discuss. Chem. Soc.*, **79** (1985), 89.
- [80] R. Cai, J. Preston, and E. T. Samulski, *Macromolecules*, **25** (1992), 563; S. Stompel, *et al.*, *High Perform. Polym.*, **9** (1997), 229.
- [81] T. J. Dingemans, Ph.D. Dissertation, University of North Carolina, Chapel Hill (1999).
- [82] W. Gleim and H. Finkelmann, in *Side Chain Liquid Crystal Polymers*, edited by C. B. McArdle (Blackie and Son, London, 1989), chapter 10.
- [83] M. Warner and X. J. Wang, *Macromolecules*, **24** (1991), 4932 and references therein.
- [84] M. Doi, D. Pearson, J. Kornfeld, and G. Fuller, *Macromolecules*, **22** (1989), 1488.
- [85] W. Maier and A. Saupe, *Z. Naturf.*, **A13** (1958), 564; *Z. Naturf.*, **A14** (1959), 1909; *Z. Naturf.*, **A15** (1960), 282.
- [86] W. M. Gelbart, *J. Phys. Chem.*, **86** (1982), 4298.
- [87] M. A. Cotter, *Phil. Trans. R. Soc., London, A*, **309** (1983), 127.
- [88] P. J. Flory, *Proc. R. Soc., London, A*, **234** (1956), 73.
- [89] P. J. Flory and R. S. Frost, *Macromolecules*, **11** (1978), 1126.
- [90] P. J. Flory, *Macromolecules*, **15** (1982), 1286.
- [91] S. M. Aharoni, *Polymer*, **21** (1980), 21; E. Bianchi, A. Ciferri, and A. Tealdi, *Macromolecules*, **15** (1982), 1268.
- [92] P. J. Flory and G. Ronca, *Molec. Cryst. Liq. Cryst.*, **54** (1979), 311.
- [93] L. Onsager, *Ann. N. Y. Acad. Sci.*, **51** (1949), 627.
- [94] H. Zocher, *Anorg. Chem.*, **186** (1925), 75.
- [95] T. Folda, H. Hoffman, H. Canzy, and P. Smith, *Nature*, **333** (1988), 55.
- [96] S.-D. Lee, *J. Chem. Phys.*, **87** (1987), 4972.
- [97] R. R. Matheson and P. J. Flory, *Macromolecules*, **14** (1981), 954; P. J. Flory, *Macromolecules*, **11** (1978), 1141.
- [98] A. R. Khokhlov and A. N. Semenov, *Physica*, **108A** (1981), 546; *Macromolecules* **17** (1984), 2678; A. R. Khokhlov, *Phys. Lett.*, **68A** (1978), 135.
- [99] D. B. DuPre and S.-J. Yang, *J. Chem Phys.*, **94** (1991), 7466.
- [100] T. Odijk, *Macromolecules*, **19** (1986), 2313.
- [101] G. J. Vroege and H. N. W. Lekkerkerker, *Rep. Prog. Phys.*, **55** (1992), 1241.
- [102] M. Doi, *J. Polym. Sci.: Polym. Phys. Ed.*, **19** (1981), 229.
- [103] E. T. Samulski, *Phys. Today*, **35** (1982), 40; private communication to P. J. Flory (July 2, 1982).

- [104] J. J. Magda, S.-G. Baek, K. L. DeVries, and R. G. Larson, *Macromolecules*, **24** (1991), 4460 and [4].
 - [105] G. Marrucci, *Macromolecules*, **24** (1991), 4176; G. Marrucci and P. L. Maffettone, *Macromolecules*, **22** (1989), 4076.
 - [106] J. Mewis and P. Moldenaars, *Molec. Cryst. Liq. Cryst.*, **153** (1987), 291.
 - [107] C. Viney and A. H. Windle, *Polymer*, **27** (1986), 1325; P. Navard and A. E. Zachariades, *J. Polym. Sci. Pt B: Polym. Phys.*, **25** (1987), 1089.
 - [108] P. L. Maffettone, N. Grizzuti, and G. Marrucci, *Liq. Cryst.*, **4** (1989), 385.
 - [109] S.-D. Lee and R. B. Meyer, *J. Chem. Phys.*, **84** (1986), 3443.
 - [110] R. B. Meyer, in *Polymer Liquid Crystals*, edited by A. Ciferri, W. R. Krigbaum, and R. B. Meyer (Academic Press, New York 1982), chapter 6.
 - [111] S.-D. Lee and R. B. Meyer, *Phys. Rev. Lett.*, **61** (1988), 2217.
 - [112] A. J. Pennings, C. J. H. Schouteten, and A. M. Kiel, *J. Polym. Sci.*, **C38** (1972), 167.
 - [113] T. Kanamoto, A. Tsuruta, K. Tanaka, M. Takeda, and R. Porter, *Polym. J.*, **15** (1983), 327.
 - [114] W. W. Adams and R. K. Eby, *Mater. Res. Soc. Bull.*, **22** (1987).
 - [115] M. G. Northolt and D. J. Sikkema, *Adv. Polym. Sci.*, **98** (1990), 115.
 - [116] K. Kerkam, C. Viney, D. Kaplan, and S. Lombardi, *Nature*, **349** (1991), 596.
 - [117] M. G. Forest, Q. Wang, and H. Zhou, *Physica D*, **152** (2001), 288.
 - [118] J. Economy, *Angew. Chem. Int. Ed. Engl.*, **29** (1990), 1256.
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Part II

Some characterization techniques

6

The application of molecular spectroscopy to characterization of polymers

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6.1 Introduction

Molecular spectroscopy has made a lasting impact on polymer chemistry and technology by providing direct methods to study polymer structures and their mutual interactions. Polymer scientists have found great utility in the commercially available spectroscopic instrumentation which is becoming increasingly widely available and easily applied to day-to-day polymer-characterization problems. In addition, there continues to be a wealth of new and evolving spectroscopic technologies that enhance the utility of molecular spectroscopy for the determination of the molecular architecture of synthetic polymers.

Most polymers are complex mixtures of materials of various sizes (relative molecular masses) and chemical compositions and with various end groups and molecular architectures. Thus, synthetic and biological polymers present a particularly difficult problem for molecular characterization due to the multicomponent nature of the systems. In practice, no single spectroscopic or analytic technique is sufficient for the complete determination of all of these structures and distributions.

The molecular architectures of synthetic polymers are determined by composition and composition distribution along the chain, functionality and functional-group distribution (block, random, blend), and chain length and chain-length distribution. Additionally, the main-chain structure of the polymer is controlled by the nature of the regiochemical (head-to-tail, tail-to-tail, head-to-head) and stereochemical (isotactic, syndiotactic, atactic) monomer insertion. Topological structures including cyclics, branched, dendritic, and cross-linked systems have been prepared, which are finding uses in polymer applications and require molecular characterization as well.

The purpose of this chapter will be to indicate the molecular-spectroscopic methods and approaches required for the determination of the chemical structure of the

repeat unit of the polymer as well as the microstructures arising from the nature and distribution of chemical defects. Although nearly all spectroscopic techniques have been used for characterization of polymers at one time or another and for examination of specific classes of polymers, here we will discuss only the principal methods of vibrational (infrared and Raman), nuclear (nuclear magnetic resonance), and mass spectroscopy.

6.2 Vibrational techniques

Vibrational spectroscopy, which encompasses infrared and Raman spectroscopy, is one of the most versatile and powerful analytic tools and considerable success has been achieved in enhancing their sensitivity and selectivity.

A vibrational (infrared or Raman) spectrum of a molecule consists of vibrational modes (resulting from the interaction of two or more different vibrations of neighboring bonds). These absorption (IR) or scattering (Raman) modes provide information about features such as the chemical nature (e.g. bond types and functional groups) and molecular conformation (e.g. *trans* and *gauche*). They also provide information about the individual molecular bonds (intramolecular interactions) and the interactions between molecules (intermolecular effects).

The advantages of the vibrational methods are that they are nondestructive, fast, and easy to use, and that remote measurement can be achieved through use of optic-fiber technology. Vibrational spectroscopic techniques provide methods of determining the chemical structure of a polymer and have the advantage that the methods are applicable to all polymers regardless of the phase or state of order in the system. The complete analysis of any type or shape of a polymer sample, from raw material via intermediate to final product, is possible on an “as it is basis” in the majority of cases.

6.2.1 Selection rules for FTIR and Raman spectroscopy

The selection rules for IR arise from changes in the dipole moment, μ_k ,

$$\mu_k = -\partial V / \partial E_k$$

and those for Raman spectroscopy from changes in the polarizability, α_{jk} ,

$$\alpha_{jk} = -\partial^2 V / (\partial E_j \partial E_k)$$

where V is the potential energy and E is the applied electric field of the radiation. The expansion of the potential energy with respect to electric field and vibrational

coordinates is given as

$$\begin{aligned}
 V = V_0 + \frac{1}{2} \sum_p \omega_p^2 + Q_p^2 \cdots \\
 - \sum_k \left(\mu_k + \sum_p \frac{\partial \mu_k}{\partial Q_p} Q_p + \frac{1}{2} \sum_{p,r} \frac{\partial^2 \mu_k}{\partial Q_p \partial Q_r} Q_p Q_r + \cdots \right) E_k \\
 - \sum_{i,k} \left(\alpha_k + \sum_p \frac{\partial \alpha_{ik}}{\partial Q_p} Q_p + \frac{1}{2} \sum_{p,r} \frac{\partial^2 \alpha_{ik}}{\partial Q_p \partial Q_r} Q_p Q_r + \cdots \right) E_j E_k
 \end{aligned}$$

where Q_p is the p th normal vibrational mode of a given molecule and ω_p is the vibrational angular frequency of the p th mode. When E_k is the electric field of the radiation, the term $\partial \mu_k / \partial Q_p$ gives rise to absorption or emission of light accompanied by a vibrational transition of one quantum, and the term containing the term $\partial \alpha_{ik} / \partial Q_p$ gives rise to Raman scattering.

To the first order in the external electric field, and neglecting the higher-order derivatives of the dipole moment, the vibrational displacement is expressed as follows:

$$\delta Q_p = \frac{1}{\omega_p^2} \sum_k \frac{\partial \mu_k}{\partial Q_p} E_k$$

Because of this displacement, the molecule is polarized according to

$$\delta_i \mu_i = \sum_p \frac{\partial \mu_i}{\partial Q_p} \delta Q_p$$

The larger the value of $\delta_i \mu_i$ the greater the intensity of the i th mode in IR absorbance. Similar considerations apply to the intensity of Raman spectral lines, for the change in polarization dictates the intensities of the Raman lines.

6.2.2 Characteristic group frequencies in vibrational spectroscopy

While *ab initio* interpretation of vibrational spectra, as independent entities, is a tedious and subjective task, direct comparison of the experimentally observed molecular spectra with cataloged spectra reveals an amazing correlation between vibrational frequencies and chemical groups in the molecule, which facilitates interpretation [1]. Certain chemical groups have been found empirically to absorb or scatter at very nearly the same frequencies regardless of the molecules in which they are found. Such absorptions are called “group frequencies” and often provide a rapid, unambiguous means of confirming the presence or absence of the chemical moiety responsible for the absorption. Although it has been found that there are slight shifts in the observed frequencies, the group frequencies usually vary only

within a sufficiently small frequency range for them to be identifiable for many of the chemical groups.

Attempts to justify these empirical observations have been made. To a first approximation, the frequency of a two-atom system in a molecule is

$$\nu = \frac{1}{2\pi} \left(\frac{k}{\mu} \right)^{1/2}$$

where ν is the vibrational frequency, k is the force constant of the connecting chemical bond, and μ is the reduced mass of the functional pair. The primary variable is the force constant. If one assumes that the two-atom functional group is “decoupled” (i.e. not harmonically interacting with the remainder of the molecule), the determining factor for the observed vibrational frequency is the force constant, which is a measure of the “stiffness” of the chemical bond.

For example, consider the case of a light atom, such as hydrogen, vibrating against a heavier atom, such as carbon, as in a C—H stretching vibration. The displacement motion, in this case, is primarily the lighter atom “stretching,” i.e. moving back and forth against the carbon, and the carbon is constrained to considerably less displacement of the motion. Because of the large differences in energy between the C—H bonds and the other bonds, i.e. C—C and C—O, the motion is largely localized to the C—H bonds, so a “characteristic group frequency” is observed for the C—H bond under these circumstances.

Similar types of group frequencies are observed when the atoms involved are of similar masses, but the vibrations couple only very weakly to the rest of the molecule. Examples of this situation are found in the multiple-bond frequencies such as $>\text{C}=\text{O}$ and $\text{C}\equiv\text{N}$ stretching modes.

Since the environments of the chemical bonds (uncoupled from the rest of the molecule) are very similar, to a first approximation, one could imagine that the force constants are very similar, giving rise to the empirically observed frequencies in a narrow region, i.e. characteristic frequencies.

A strict interpretation of the group frequencies in terms of molecular mechanics is difficult. However, one can accept that the frequencies of similar chemical entities should be similar and slight differences in bond lengths and in polarity, direction, and strength (stiffness) of the bonds could lead to small differences in the empirical frequencies. Factors that directly influence small shifts of group frequencies include changes in atomic mass, vibrational coupling, resonance, inductive and field effects, conjugation, hydrogen bonding, and bond-angle strain.

Group frequencies having approximately the same magnitude and occurring in adjoining portions of the molecule sometimes interact to give a mixed vibration in which both groups take part. In this case, this coupling results in a shifting of the frequencies of the modes apart from each other.

Since the molecular vibrations are influenced by intermolecular interactions, adsorption bands in mixtures change in relation to those of pure substances. Usually intermolecular interactions such as hydrogen bonding are very weak and can be broken by increasing the temperature. Consequently, the vibrational spectrum will change due to these changes in temperature. An increase in temperature for pure water results in an increase in intensity, a shift of the peak toward lower wavelengths, and band narrowing. The increase in temperature results in a decrease in the number of hydroxyl groups involved in hydrogen bonding, and, consequently, the absorption band of “free” hydroxyl increases.

6.3 Infrared spectroscopy

Traditionally, IR spectroscopy has been one of the most popular physical methods in the polymer-characterization laboratory since it is useful in the elucidation of structures and the identification of organic and inorganic systems alike. The quantitative analysis of samples down to picogram quantities is straightforward for systems for which the spectra of the pure compounds are available. Yet, the most attractive advantage of the method is the potential for a rapid multicomponent analysis to be carried out from a single measurement (spectrum), once the methodology has been calibrated.

IR spectroscopy is used extensively to investigate hydrogen bonding because the positions of the peaks for the X—H stretching mode are very sensitive to the extent of association. The unbonded X—H stretch gives rise to a relatively sharp peak, whereas, on formation of a hydrogen bond, X—H···Y (where Y is the acceptor atom), the peak shifts to a lower wavenumber and becomes much broader. The downward shift is caused by the lengthening of the X—H bond, which results from the formation of hydrogen bonds. Hence formation of a stronger hydrogen bond will lengthen the X—H bond more and produce a shift to a lower wave number. Furthermore, a relationship between the position of the peak for the X—H group and the X—H···Y bond distance (determined from crystallographic data) has been observed, whereby a lower frequency for the peak correlates with a shorter hydrogen-bond distance (i.e. a stronger hydrogen bond and a longer X—H bond) [2]. IR spectroscopy can be used to measure the fraction of hydrogen-bonded groups present as a function of composition and temperature.

6.3.1 IR instrumentation

IR spectrometers are compact, rugged, and relatively inexpensive. The user does not have to be a highly trained individual in order to operate the instruments or interpret the spectra. IR-spectroscopic analysis can be carried out on gases, liquids,

and homogeneous or inhomogeneous solid samples. The presence of inorganic fillers (except the totally absorbing carbon black) can be monitored together with the polymer-matrix component. As a result, IR methodology is useful not only in the laboratory, but also in the plant for process control by in-line or off-line methods. Field studies in which instruments are taken to the sample for real-world measurements such as forensics can be performed. Since no reagents or other consumables (such as electrodes) are required, IR spectroscopy has a low operational cost.

IR-absorbance spectra have traditionally been recorded using dispersive (prism or grating) monochromator instruments, but, since 1970, Fourier-transform infrared (FTIR) instruments that are capable of collecting high-quality spectra in a fraction of the time previously required with enhanced signal-to-noise ratio and wavenumber accuracy have been available. The primary difference between dispersive IR and FTIR is that FTIR systems use an interferometer, rather than a monochromator. Because of this difference, FTIR systems can simultaneously analyze the entire spectrum of frequencies, rather than analyzing wavelengths sequentially. FTIR spectroscopy can analyze a sample in less than a second, whereas a dispersive system takes 10–15 min. The key component of FTIR spectrometers is a Michelson interferometer, which operates on the principle of amplitude division of the incoming light. Commercial FTIR instruments come in a variety of sizes and price ranges.

At present there are six different useful variations of FTIR instrumentation: a traditional laboratory spectrometer, a portable on-site instrument, and microscopic, near-IR (NIR), hyphenated, and dynamic FTIR imaging. The traditional laboratory FTIR is widely used in the polymer laboratory, particularly for determination of molecular orientations by measuring dichroic ratios. The portable on-site instruments allow the measurements to be made in the field (forensic purposes) and in the plant. In other words, one brings the instrument to the sample rather than bringing the sample to the laboratory. The microscopic mapping instruments have the ability to extract chemical information from small areas or small samples (microanalysis). NIR instruments have special utility because sampling is easier with them (thicker samples can be analyzed). FTIR systems can be linked to liquid-chromatography (LC) and gas-chromatography (GC) instruments and to thermogravimetric-analysis (TGA) systems as detectors, yielding the hyphenated GC-FTIR, LC-FTIR, and TGA-FTIR methods for analyzing chromatographically (or thermally) separated components of the sample. The FTIR dynamic-imaging instruments use focal-array detectors (FPAs) to acquire information on diffusion, degradation, and dissolution of polymers rapidly.

FTIR has emerged as one of the most important analytic tools for noncontact and nondestructive evaluation/analysis of polymers, irrespective of their type, nature,

and morphology. One of the problem areas for FTIR is the strong absorbance of polar polymers, which requires the use of extremely thin ($\sim 10\ \mu\text{m}$) films in order to have the absorbances measured in transmittance mode be in the linear region ($<1\ \text{au}$), which is required for accurate quantitative analysis. However, the availability of a number of new sample-handling techniques (for example IR microscope techniques, the diffuse-reflectance IR Fourier transform (DRIFT), and photoacoustic (PAS) methods) has further expanded the utility and applications of FTIR.

6.3.2 Infrared sampling methods

The IR sampling techniques used depend on a number of parameters, including the geometry of the sample (thin films or bulk samples), the angle of incidence of radiation (normal or low angle of incidence), and the relative transparency of the sample, which depends on the optical constants of the sample. The methods used are shown in Fig. 6.1. They include transmission methods (which require thin films of thickness $3\text{--}50\ \mu\text{m}$), reflection–adsorbance (for which the samples are on a reflecting substrate, i.e. metal or a smooth surface), diffuse reflectance (which is used for highly scattering samples such as filler-filled polymers), and external reflectance (which is used for samples with mirror-like surfaces). Attenuated total reflectance (ATR) (which is used for highly absorbing samples) involves varying the angle of incidence through the critical angle of incidence.

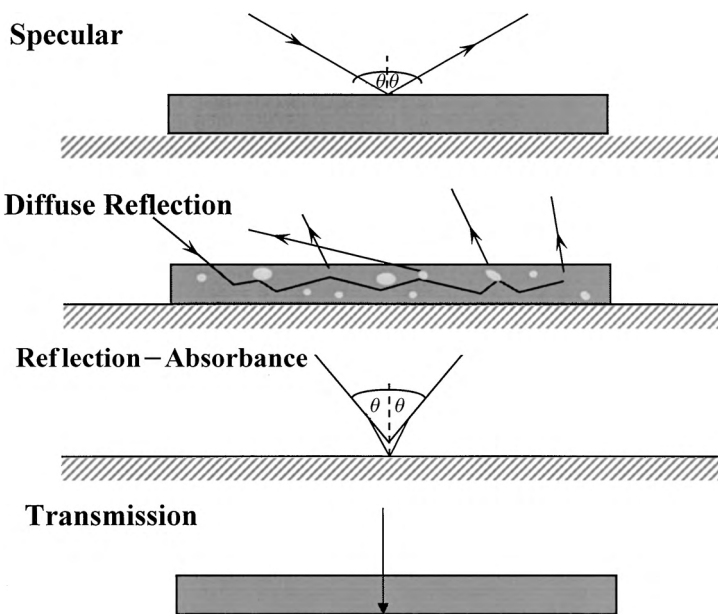


Fig. 6.1. Sampling methods for IR.

6.3.3 *The basis of spectral identification*

IR spectroscopy is one of the simplest and fastest methods for the identification of unknown compounds when the spectra of the reference compounds are in an IR database. The idea underlying IR identification is that the IR spectra provide a pattern of frequencies corresponding to a “fingerprint” of the molecule and a unique pattern of frequencies can be recognized when an IR-spectral database containing the spectrum of the unknown molecule is searched. Today, molecular identification is carried out by computer algorithms. In general, these computer algorithms are called upon to find the identity of the spectrum by comparing the unknown spectra with those within a database. Identification is performed by calculating a matching score for the spectra of the unknown and an IR spectrum of a known compound in the database. Additional spectra from molecules of similar structure in the database are ranked according to the computed matching score and the spectroscopists must make a final determination (since the match is never perfect due to contributions of noise in the reference and unknown spectra) based on their knowledge of the properties of the unknown sample relative to those of the chemicals with high matching scores.

Raman spectroscopy can be used in the same fashion as IR for identification using catalogs of Raman spectra in a database.

6.3.4 *Determination of conformations of polymers*

One of the most useful applications of FTIR is the determination of the conformation of polymer chains. This is a result of the high sensitivity of the IR spectra to rotations around chemical groups. This is illustrated in Fig. 6.2, which shows the IR spectrum of the *trans* and *gauche* structures for the ethylene glycol portion of the polyethylene terephthalate (PET) chain. From these spectra, it is possible to determine the conformational composition for PET as a function of crystallization, annealing, and processing conditions.

6.3.5 *Quantitative IR measurements of the composition and structure of polymers*

FTIR provides chemical structural information on polymers that is not only suitable for qualitative identification, but also can be used for quantitative structural analysis. A quantitative analysis of the composition of a copolymer by FTIR spectroscopy is not a difficult task if a well-resolved absorption peak for each component can be found in the composite spectrum of the copolymer. Conventional quantitative analysis of a polymeric sample uses a single spectrophotometric measurement at

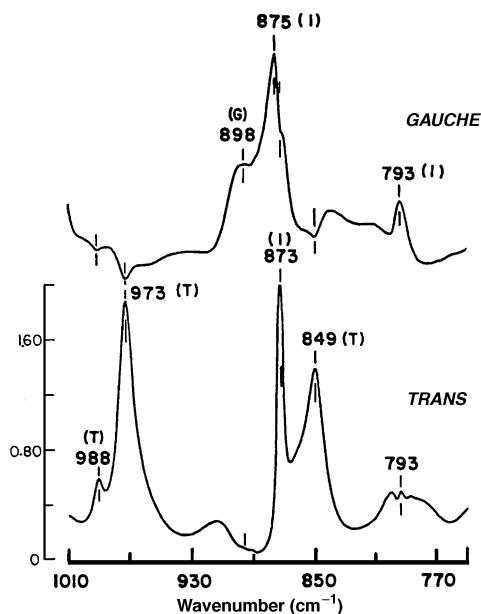


Fig. 6.2. Infrared spectra of the *gauche* and *trans* isomers of the ethylene glycol portion of the PET chain.

discrete wavelengths at which one component, but not the other, absorbs. However, for copolymers with more structural entities and greater spectral overlap, the use of this conventional approach for quantitative analysis becomes more difficult. Quantitative analysis from IR spectra has been improved greatly by the use of a variety of multivariate statistical methods. These methods include classical least squares (CLS), inverse least squares (ILS), partial least squares (PLS), and principal-component regression (PCR). In general, the mathematical robustness of these methods can allow reliable analytic information to be obtained (Table 6.1). The choice of the optimal linear multivariate calibration technique depends upon the extent of the calibration data [3].

6.3.6 IR measurements of orientation in polymer systems

The molecular orientation induced during the processing of polymers by the preferential alignment of macromolecular chains or segments has an impact on the macroscopic physical properties. FTIR methods have been developed in order to measure this induced orientation. The FTIR technique determines the orientation-distribution function, $f(\theta)$, which, in the case of a uniaxially drawn sample, relates the number of chain elements lying in one direction to the angle they make with respect to the draw direction.

Table 6.1. *Calibration*

Information available	Number of components	Method
Full set of pure spectra	Known	Ordinary least squares
Spectra from mixtures with known concentrations	Known	Classical least squares
Only the concentration of one species is known	Unknown	Partial least squares or principal-component analysis followed by principal-component regression

IR absorption is caused by the interaction between the IR electric-field vector and the molecular dipole-transition moments (i.e. molecular vectors) related to the molecular vibrations. Absorption is at a maximum when the electric-field vector and the dipole-transition moment are parallel to each other. In the case of perpendicular orientation, the absorption is zero. Directional absorptions $A_{\perp}$ and $A_{\parallel}$ are measured using polarized light. The terms parallel and perpendicular refer to the orientation of the polarized beam with respect to a reference axis. For deformation studies, the reference axis corresponds to the direction of stretching.

The dichroic ratio may be considered to be characteristic of the directional orientation of the segments of the molecule. For a polymer whose molecular axis is oriented parallel to the sampling plane of the spectrometer, the dichroic ratio, R , is defined as

$$R = \frac{A_{\parallel}}{A_{\perp}}$$

where $A_{\parallel}$ is the absorbance parallel to the chain axis, and $A_{\perp}$ is the absorbance perpendicular to the chain axis. For highly oriented samples, the dichroic ratio may approach either infinity or zero, depending on the alignment of the transition-moment vector with respect to the molecular chain axis. The alignment of the chain segments can be determined from dichroic-ratio measurements if the inherent polarizations are known [4]. In general, $A_{\parallel}$ and $A_{\perp}$ are determined successively by using a polarizer that is aligned first parallel and then perpendicular to the direction of stretching. For samples that have a low level of orientation, the magnitude of the dichroic ratio is close to 1. In these cases of minimal orientation, it is better to measure the difference $A_{\parallel} - A_{\perp}$ because it is a more sensitive measurement under these conditions. One of the advantages of using IR for orientation measurements, compared with X-ray diffraction, for example, is that the alignments both of the amorphous and of the crystalline chains can be determined by IR whereas only the crystalline phase is measured with X-rays.

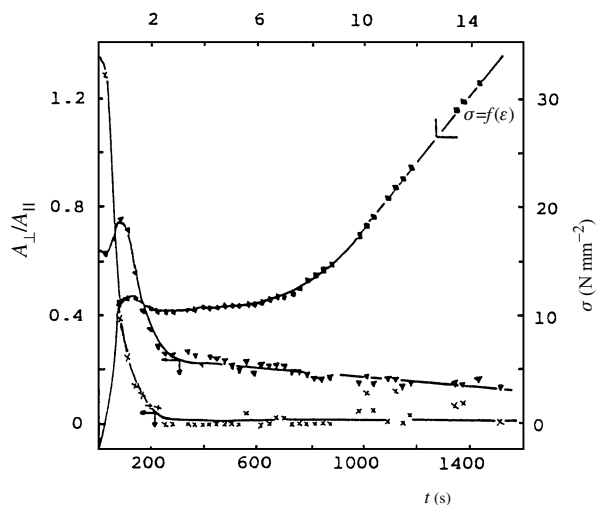


Fig. 6.3. Dichroic ratios and stress as functions of strain and time (stretching velocity) for polyethylene for the CH_2 rocking modes at 730 cm^{-1} ($\times$) and 720 cm^{-1} ($\blacktriangledown$). The stress-strain diagram is given by ($\blacksquare$). From K. Holland-Mortiz and K. van Werden, *Makromol. Chem.*, **182** (1981), 651. (Reproduced with permission. Copyright 1981 Hüthig & Wepf Verlag.)

Because IR spectra can be obtained rapidly by using modern FTIR equipment, the deformation process can be studied while the polymer is being stretched [5]. The dichroic ratio and stress as a function of strain and time for the CH_2 rocking bands between 736 and 726 cm^{-1} and between 726 and 710 cm^{-1} are shown in Fig. 6.3. The CH_2 rocking band between 736 and 726 cm^{-1} has a transition moment that is parallel to the a crystal axis, and the CH_2 rocking band between 726 and 710 cm^{-1} has a transition moment that is perpendicular to the a crystal axis. Before the stretching process, the 730-cm^{-1} band exhibits parallel dichroism, indicating that the preferred initial orientation of the a crystal axis is along the stretching direction. For small strains, the degree of the original orientation increases slightly. With the beginning of the necking process, the dichroic ratio shows the occurrence of a small rotation of the b crystal axis into the direction of stretching and an opposite movement of the a axis. There is a rotation of the a and b axes into directions perpendicular to the direction of stretching when the strain corresponds to draw ratios between 1 and 3.

6.3.7 IR microspectroscopic imaging

To examine small samples or small regions of larger samples, a microscope is usually required. Microspectroscopic imaging is achieved when the microscope

can be used for observation of the microsample or selection of an area on a larger sample and is coupled to the FTIR spectrometer for making the spectroscopic measurements. The coupling of the microscope, spectrometer, and computer has generated a new “hyperdiscipline” that can be termed *molecular spectroscopic imaging* (MSI). The MSI method has allowed microanalysis of small samples and spatially resolved measurements of larger samples. With the appropriate software to analyze, assemble, and display images, MSI brings a new range of possibilities in characterization of materials.

The coupling of vibrational spectroscopy with microscopy allows the chemical identification of species in small or microscopically heterogeneous samples. Furthermore, vibrational imaging techniques allow the determination of the spatial distribution of such species, with unique capabilities in terms of chemical contrast and specificity. Molecular microspectroscopy can look at thin transparent samples by transmission or at thick samples using reflection methods, so a wide range of samples can be studied.

Molecular microspectroscopy is the ideal platform for locating phases and/or subtle features in heterodispersed samples. One can use the color (different frequencies), shape (geometry), and contrast (intensities) to detect and measure morphological objects.

6.3.8 FTIR microscopic mapping

The conventional mid-FTIR apparatus uses a standard FTIR bench coupled to a microscope equipped with reflective optics such as a Cassegrain objective and condenser, to focus the IR light onto the sample and collect the transmitted light for delivery to the detector (Fig. 6.4) [6].

Variable apertures are used to select a specific area of the sample to be measured. For the generation of an IR image, a spectrum is collected from the sample area with the apertures set to the desired size; the sample is then translated in x and y incrementally using a computer-controlled stage, and successive spectra are collected. Plotting intensities at a specific wavelength (or some higher-order function) versus x and y generates the map. This process is time consuming, particularly if the apertures are small, necessitating long-duration signal averaging to acquire a sufficient signal-to-noise ratio. Collection of data for one experiment can require up to several hours even for a small 10×10 map.

The ultimate limit to the spatial resolution for conventional microscopy is determined by diffraction of the interrogating light ($\sim \lambda/2$); however, in practice, the maximum spatial resolution obtained in IR microscopy is $\sim 2\lambda$ (5–20 μm for the mid-IR range) due to throughput deficiencies and various optical aberrations.

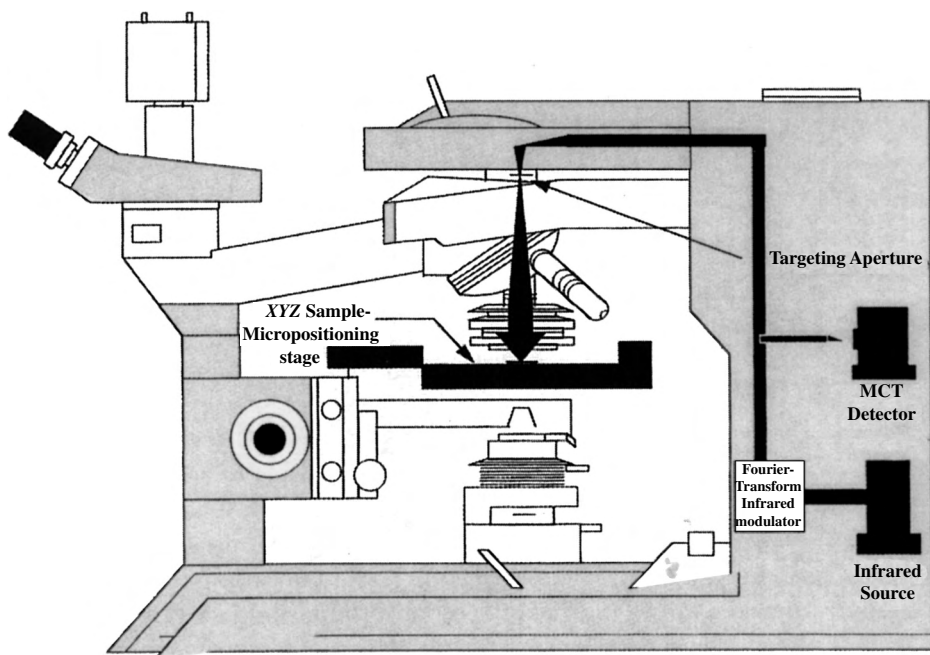


Fig. 6.4. An optical diagram of an infrared microscope.

6.3.9 FTIR imaging using focal-plane-array detectors

It is now widely accepted that the most promising FTIR microspectroscopic instrumentation today utilizes focal-plane-array (FPA) detection of radiation from an FTIR spectrometer [7, 8]. The use of focal-array detectors is an example of parallel measurements of a signal. FPA systems consist of a rectangular array of detectors on a single substrate much like the CCD chip in a video camera. All of the information from the sample is collected in parallel by all of the detector elements at the same time. This advantage of having multichannel detection results in a significant decrease in data-acquisition time, since the improvement in the set of measurements consisting of N resolution elements arises from sampling each element N times, thus raising the signal by a factor of N . A supporting computer system capable of real-time capture of data at rates of $>25 \text{ Mbytes s}^{-1}$ is required. The system must also be able to process and manage individual files $>250 \text{ Mbytes}$ in size.

In contrast to point-by-point examination of the sample area, this technique renders “snapshots” or images consisting of information collected from all areas at the same time. Hence, the technique has been termed “FTIR imaging.” The data-acquisition time is reduced by at least two orders of magnitude compared with the FTIR mapping experiment. One useful configuration of the FTIR imaging

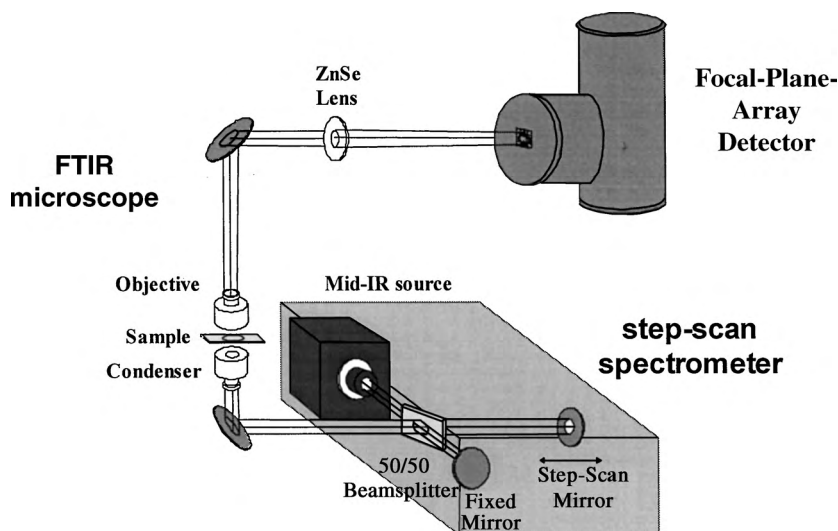


Fig. 6.5. A schematic diagram of a FTIR imaging-spectrometer system.

microspectrometer (shown in Fig. 6.5) is a combination of a step-scan spectrometer and FPA mounted onto an attached microscope accessory [9]. An electric synchronization board between the spectrometer and the FPA completes the coupling.

FPA detectors consist of a large number of small detectors laid out in a grid pattern. Thus, each individual detector in the grid (pixel) is capable of simultaneously collecting data from a specific sample area in the field of view. Similarly to other FTIR instrumentation, the whole field of view is illuminated by a single source. Hence, a large area is imaged simultaneously using the multichannel-detection elements to provide spatial specificity. Depending on the array and collection parameters, thousands of moderate-resolution spectra can be acquired at near-diffraction-limited spatial resolution in a few minutes.

The material composition of the FPAs determines the detectable IR-spectral frequency range. Many types of detectors are available, ranging from the commonly used indium antimonide (InSb) for near IR and mercury cadmium telluride (HgCdTe, MCT) for the mid IR to the more exotic silicon arsenide (Si:As) [10] and uncooled barium strontium titanium (BST) [11]. Mid-IR imaging using MCT FPAs [12] has been the most popular in terms of the number of studies performed, due to its ability to provide access to the molecular-fingerprint region.

In principle, measurements with FTIR microspectroscopic imaging systems using FPA detectors are performed in the same way as with a conventional FTIR microscope [13]. Sample and background interferogram files are acquired, Fourier-transformed, and ratioed, in order to calculate a file of absorbance spectra. When the imaging system uses a FPA, each element is used to generate simultaneously

an interferogram and spectrum corresponding to a separate location of the sample. Thus, FTIR imaging with FPAs can be used to study dynamic processes in polymers, such as diffusion, dissolution, degradation, and phase separation.

6.3.10 Near-field FTIR microscopy

Near-field microscopy makes use of a radiation source that is subwavelength in size, and often formed from a tapered light tube with a subwavelength-sized aperture at the narrow end. The tip must approach the sample to within the dimension of the aperture (i.e. sub-micrometer), requiring accurate z -axis control. The efficiency of transmission through the aperture can be extremely poor (10^{-7} for $\lambda/10$) and thus one requires an intense light source such as laser- or synchrotron-generated IR.

A near-field IR imaging instrument was developed using an IR microscope. It includes a broadly tunable IR light source producing ultrafast pulses with a FWHM bandwidth of 150 cm^{-1} , an IR FPA-based spectrometer that allows parallel detection of the entire pulse bandwidth with 8-cm^{-1} resolution, and a single-mode fluoride glass-fiber probe that supports transmission from 2200 to 4500 cm^{-1} [14, 15]. This instrument was demonstrated to provide spatial resolution of $\lambda/8$ at 2900 cm^{-1} , in the absence of artifacts due to topology. Initial applications of this technique have been focused on measuring lateral variations in chemical composition for thin organic films such as polystyrene (PS)/polyethylacrylate (PEA) polymer blends, a model system for the study of degradation and corrosion of organic coatings [16].

A tunable CO_2 laser has been combined with an atomic-force-microscopy (AFM) microscope to form an apertureless near-field-imaging system [17]. This technique can produce spatial resolution of up to $\lambda/100$ with high throughput; however, the tunable range of the CO_2 laser is limited to a region of the IR spectrum that is not particularly informative for most IR chromophores (2300 cm^{-1}).

6.4 Raman spectroscopy

Raman spectroscopy is a complementary technique to IR. Both IR and Raman spectra arise from the vibrational energy levels of the molecules. The difference in the information content of the two vibrational methods arises from differences in selection rules. In the simplest terms, IR absorption arises from vibrational modes that give rise to changes in the dipole moments of the bonds and consequently is most sensitive to polar bonds. Raman absorption arises from changes in the “induced” polarity of bonds and is most sensitive to nonpolar bonds. For polymers, IR absorption is sensitive to substituents on the backbone of the chain, i.e. C—H, C=O, C—OH, etc., whereas Raman absorption is sensitive to the C—C backbone

itself. In this sense, IR and Raman techniques are complementary but some of the vibrational modes will be common, i.e. appear at the same frequency, in IR and Raman spectroscopies.

The Raman effect occurs when a sample is irradiated by intense monochromatic light such as that from a laser, causing a small fraction of the scattered radiation to exhibit shifted frequencies that correspond to the sample's vibrational transitions. Lines shifted to energies lower than that of the source are produced by ground-state molecules, whereas the slightly weaker lines at higher frequencies are due to molecules in excited vibrational states. These new lines, the result of the inelastic scattering of light by the sample, are called Stokes and anti-Stokes lines, respectively. Elastic photon collisions result in Rayleigh scattering and appear as the much-more-intense, unshifted component of the scattered light.

In normal Raman scattering, a molecule is excited to a virtual state, which corresponds to a quantum level related to the electron-cloud distortion created by the electric field of the incident light. A virtual state does not correspond to a real eigenstate (vibrational or electronic energy level) of the molecule, but rather is a sum over all eigenstates of the molecule.

Raman scattering is envisaged as the process of reirradiation of scattered light by dipoles induced in the molecules by the incident light and modulated by the vibrations of the molecules. In normal Raman scattering by molecules in isotropic media, the dipoles are simply those which result from the action of the electric-field component E of the incident light on the molecules.

When a beam of light is incident upon a molecule, it can be either absorbed or scattered. Scattering can be either *elastic* or *inelastic*. The electric field of the incident light induces a dipole moment, P , in the molecule, given by

$$P = \alpha E$$

where E is the electric field, and α is the polarizability of the molecule. Because the electric field oscillates as it passes through the molecule, the induced dipole moment in the molecule also oscillates.

6.4.1 Raman instrumentation and sampling

The Raman spectrum is given by the detection of the intensity of the scattered, frequency-shifted light by a photoelectric system. The resulting signal of the detector is amplified and converted into a form appropriate for plotting as a function of frequency. Raman spectroscopy is a scattering technique rather than an absorbance method and so does not require special sampling techniques. All materials – fluids as well as solids – can be measured by scattering methods with no sample preparation.

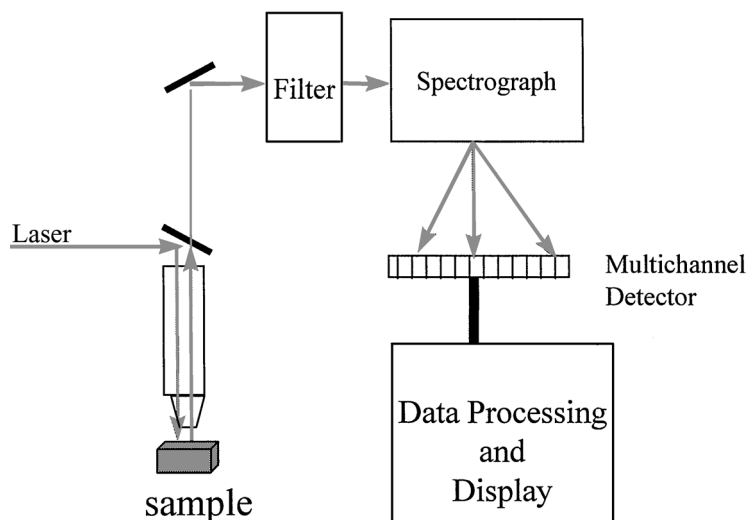


Fig. 6.6. The optical configuration of a Raman spectrophotometer.

For sample cells, quartz can be used as the optical material for measurements with fiber-optic probes.

The configuration of a Raman spectrometer basically consists of five parts (laser, sample, dispersing element, detector, and computer). A monochromatic laser beam (excitation radiation) is focused onto the sample. The scattered light from the sample is focused onto the entrance slit of a monochromator and dispersed. The dispersion element discriminates between the strong elastic scattering (Rayleigh scattering) and the weak inelastically scattered light (Raman scattering) with different frequencies. Typical single monochromators provide stray-light rejections of 10^{-5} – 10^{-6} (as a fraction of the Rayleigh light that enters the spectrometer), limited by the imperfections on the optical surfaces such as gratings. Double and triple monochromators are often required in order to obtain adequate stray-light rejection. The ideal Raman spectrometer would consist of a high-dispersion, low-stray-light single monochromator with a multichannel detector (Fig. 6.6).

In the new generation of Raman instruments, a polychromator or spectrograph and a multichannel detector are used instead of the monochromator and photomultiplier described above. The entire spectrum is collected simultaneously, using an array of detectors in which each element of the multichannel detector is of comparable sensitivity to a single photomultiplier. The assumption is that all light incident on the detector is correctly positioned with a single wavelength incident upon each single detector. In this way the time needed to record a spectrum is reduced markedly. Additionally, the simultaneous detection of the spectrum increases the accuracy of intensity measurements of different Raman bands and avoids errors

in interpreting accidental changes in the background due to laser fluctuations as Raman bands. Furthermore, multichannel detectors offer new possibilities for investigation of photolabile systems and for time-resolved experiments.

However, when a multichannel detector is used, only a limited wavelength range can be observed at any one time. This range is determined by the size of the detector, the position (or wavelength) of the spectrometer, and the linear dispersion of the grating at the detector.

6.4.2 Raman sampling

The sampling techniques used in Raman spectroscopy are shown in Fig. 6.7. A sample in any state can be examined without difficulty by using Raman spectroscopy.

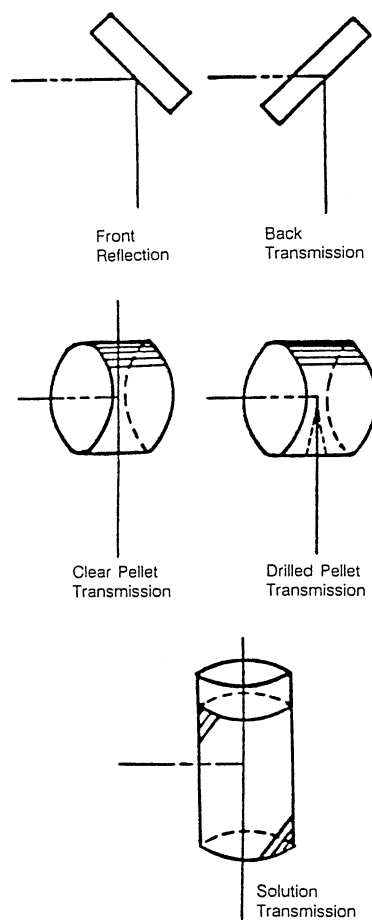


Fig. 6.7. Raman sampling techniques for polymers.

The laser beam is narrow, collimated, and unidirectional, so it can be manipulated in a variety of ways, depending on the configuration of the sample.

For liquids, a cylindrical cell of glass or quartz with an optically flat bottom is positioned vertically in the laser beam. For solids, the particular method used depends on the transparency of the sample. For clear pellets or samples, right-angle scattering is used. With translucent samples, it is helpful to drill a hole in the sample pellet. Powdered samples can be analyzed by using front-surface reflection from a sample holder consisting of a hole in the surface of a metal block inclined at 90° with respect to the beam. Injection-molded pieces, pipes, and tubing, blown films, cast sheets, and monofilaments can be examined directly. One of the advantages of Raman sampling is that glass containers, which can be sealed if desired, can be used.

Raman spectroscopy can be used to examine samples contained inside polymeric packages. The pharmaceutical industry takes advantage of this Raman internal-package analysis in order to examine pills that are mixtures in which the active component is distributed in an excipient. Analysis of samples directly in gel capsules is possible. For forensic purposes, drugs can be examined without opening the evidence bags. Samples such as sugars and artificial sweeteners can be identified in paper packets.

6.4.3 Raman intensities

Raman spectroscopy measures the weak inelastic scattering created by interaction between the incoming light and the vibration levels in molecules. The intensity of Raman signals is directly proportional to the concentration of the scattering group, and is described by the equation

$$I_s \sim I_0 \nu_s^4 c$$

where I_0 is the intensity of the incoming laser intensity, ν_s is the frequency of the scattered light, and c is the concentration of the scattering group.

Raman scattering is a two-photon process of intrinsically low efficiency in terms of the number of photons scattered per exciting photon irradiating the sample. Typical nonresonant Raman cross-sections are of the order of 10^{-30} cm² per molecule. With conventional instrumentation, this condition means that a signal-to-noise ratio usually below 10^4 is obtained. The Raman-scattered signal, which is usually less than 1 ppm of the incident light, from a given sample is proportional to

- (1) the number of particles per unit volume,
- (2) the total volume of sample uniformly illuminated,
- (3) the excitation-laser irradiance per unit area, and
- (4) the Raman-scattering cross-section of the material.

The intensity of a line in the Raman spectrum of any compound is given by

$$I_{\text{Raman}} \sim \sigma_{\nu} I_{\text{laser}} \nu_{\text{laser}} (\nu_{\text{laser}} - \nu_{\text{vib}})$$

where σ_{ν} is the Raman-scattering cross-section for a particular vibration, I_{laser} is the power of the laser, ν_{laser} is the wavenumber of the laser, ν_{vib} is the wavenumber of the vibrational transition, and $\nu_{\text{laser}} - \nu_{\text{vib}}$ is the absolute wavenumber of the Raman band. Because $\nu_{\text{laser}} \gg \nu_{\text{vib}}$ the term $(\nu_{\text{laser}} - \nu_{\text{vib}})$ is often approximated as ν_{laser} [4].

The generally low cross-sections for Raman scattering lead to very weak signals for most samples. Since Raman spectroscopy is effectively an emission phenomenon, the effect of background is not as serious. There is no theoretical bound on line intensities that can be effectively subtracted away as long as the band shape and frequency are stable. Therefore, in the Raman experiment greater signal intensity is always advantageous.

Unlike absorbance spectroscopy, Raman spectroscopy is a single-beam method. Thus the intensities of the peaks are proportional not only to the concentration of analyte but also to the intensity of the excitation source.

The experimental intensities of the sample peaks (I_{SP}) are given by

$$I_{\text{SP}} = R(\nu)[1/A(\nu)]\nu^4 I_0 J(\nu) C_{\text{SP}}$$

where C is the concentration, $R(\nu)$ is the overall response of the spectrometer, $A(\nu)$ is the absorption of the medium, ν is the frequency of the scattered light, I_0 is the intensity of the exciting light, and $J(\nu)$ is a molar scattering parameter. For quantitative Raman measurements, line-intensity ratios are used.

6.4.4 Interfering fluorescence

If the exciting line is partially absorbed by the sample, it can be reemitted as fluorescence. Fluorescence by the sample has been a factor prohibiting the widespread use of Raman spectroscopy as an analytic technique for a broad range of samples and applications. When it occurs, it often overwhelms the weaker Raman signal and renders the result useless. Because fluorescence relies on excited electronic states and fewer samples have chromophores excitable by light of longer wavelength, it is often less problematic when longer-wavelength lasers are used. It is largely for this reason that lasers of near-infrared wavelengths are commonly employed in commercial Raman instruments, despite the disadvantage that the Raman intensity also drops off as the excitation wavelength increases. Currently, 785-nm semiconductor lasers for dispersive instruments and 1064-nm Nd:YAG lasers for FT-Raman are the most popular choices for excitation.

6.4.5 Raman microscopy and imaging

The range of applications of Raman spectroscopy has also been extended by several important recent developments, such as Raman microscopy, which makes it possible to study extremely small samples. One can also analyze the surface of an extended inhomogeneous sample to obtain very high spatial resolution, or scan across a surface using fiber optics. It is also possible to use specially developed interference filters or holographic notch filters in certain applications as an alternative to a dispersing spectrometer, provided that one suppresses the fluorescence that would otherwise interfere with the measurements.

In contrast to conventional micro-Raman spectroscopy, in which the entire field of view is uniformly illuminated and observed, the confocal arrangement uses an adjustable pinhole, placed in a back image plane of the objective of the microscope in order to block any light from outside the focal plane. The confocal aperture is designed to collect the Raman scattering only from distinct focal volumes within the diffraction limit. Thus, the Raman signal from a small volume element in the sample can be selected and separated from signals originating outside the selected volume. In this manner, depth-profiling information can be obtained by adjusting the pinhole and hence the sampled volume. Confocal Raman spectroscopy is used to obtain information from thin layers when discrimination in depth is required.

6.4.6 Raman-depolarization measurements

In the usual Raman experiment, the observations are made perpendicular to the direction of the incident beam, which is plane polarized. The “depolarization ratio” is defined as the intensity ratio of the two polarized components of the scattered light which are parallel and perpendicular to the direction of propagation of the (polarized) incident light. The polarization of the incident beam is perpendicular to the plane of propagation and observation (Fig. 6.8).

For this geometry, the depolarization ratio is defined as the intensity ratio:

$$\rho = V_H / V_V$$

for the right-angle-scattering experiment, V is perpendicular to the scattering plane and H is in the scattering plane. An alternative notation expressed in terms of the laboratory coordinate system is

$$A(BC)D$$

where A is the direction of travel of the incident beam, B and C are the polarizations of the incident and scattered light, respectively, and D is the direction in which the Raman-scattered light is observed. Generally, the incoming beam is along the X

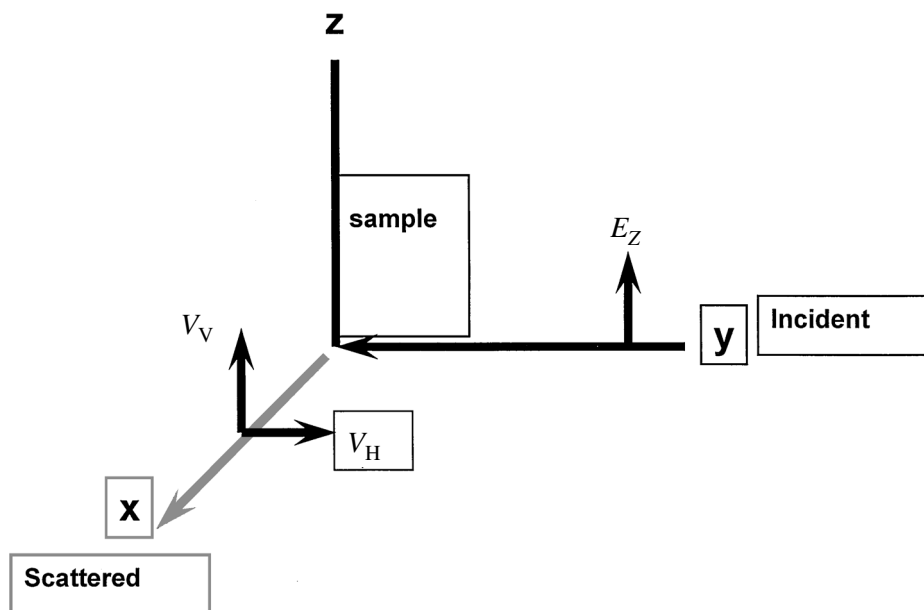


Fig. 6.8. An optical diagram for measurement of the depolarization ratio.

axis, the scattered beam is along the Z axis, and the Y axis is perpendicular to the plane of scattering.

Theoretically, the depolarization ratio can have values ranging from zero to $\frac{3}{4}$, depending on the nature and symmetry of the vibrations. Nonsymmetric vibrations give depolarization ratios of $\frac{3}{4}$. Symmetric vibrations have depolarization ratios ranging from 0 to $\frac{3}{4}$, depending on the changes in polarizability and on the symmetry of the bonds in the molecule. Accurate values of the depolarization ratio are valuable for determining the assignments of Raman lines, and, in conjunction with dichroic measurements in the IR, they constitute a powerful structural tool for examining polymers. Since the laser beam is inherently polarized and highly directional, polarization measurements can be made easily. Raman polarization measurements are also valuable for determining the orientations of polymer systems, particularly for fibers.

6.4.7 Raman spectroscopy for determining the chemical structure and composition of polymers

The choice of Raman spectroscopy for analysis of chemical composition and structure is based on the high specificity and sensitivity of the Raman effect for certain nonpolar chemical groups. In polymers, these groups are primarily the nearly homonuclear single and multiple C—C bonds, signals from which are weak or

absent in the IR spectra. The characteristic group frequencies for Raman spectroscopy have been tabulated [18]. Raman spectroscopy can differentiate between internal and external bonds as well as *cis* and *trans* isomerism and conjugation in compounds with ethylenic linkages. The type of unsaturation in butadiene and isoprene rubbers can be determined from the intense Raman scattering of the C=C stretching modes. The *trans*- and *cis*-1,4-polybutadiene structures scatter at 1664 and 1650 cm^{-1} , respectively. The 1,2-vinyl structure of polybutadiene scatters at 1639 cm^{-1} , and this scattering is well resolved from that of the 1,4-polybutadiene structures. For polyisoprene, a slightly different situation prevails. The *cis*- and *trans*-1,4-polyisoprene structures are not resolved, and they scatter at 1662 cm^{-1} , but the 3,4-polyisoprene structure scatters at 1641 cm^{-1} , and the 1,2-vinyl structure scatters at 1639 cm^{-1} .

6.4.8 Conformation of polymer chains in the solid state

For polymers with C—C backbones, the Raman spectra are dominated by the strong lines arising from the C—C skeletal modes. These skeletal modes are sensitive to the conformation because they are highly coupled, and any change in the conformation will vary the coupling and shift the frequencies accordingly.

When polymers possess helical symmetry, this symmetry changes the types of vibrational modes that can be observed in the IR and Raman spectra in a specific manner that can be used to determine the chain conformation (Fig. 6.9). Thus, for the planar 2_1 and 3_1 helices, differences in selection rules for Raman and IR spectra allow a direct determination of the conformation. For helical conformations with pitches greater than that of a 3_1 helix, the selection rules do not change but the frequencies shift.

When a polymer chain coils into a helix, characteristic splittings of nearly all of the IR and Raman modes are observed. Theory offers an explanation of these observations. All monosubstituted vinyl helical polymers have $[p, \pi]$ vibrational modes, which are termed the A modes, and $[d, \sigma]$ modes, which are termed the E modes. Theoretically there are two different E modes for each helix, but they are degenerate in frequency and do not appear separately. The frequencies of the helical A and E modes depend on the helix angle. Thus, for a polymer with the same chemical repeat units, differences in conformations will be reflected in the A modes because the different helical conformations will depend only on energy considerations, and the phase-angle difference is the same. The E-mode shifts from one helical form to another depend on the differences in energy and on differences corresponding to the different helix angles. The helical modes should be slightly more sensitive to the changes in conformation. Generally, the observed spectra will have modes that have the same frequency (characteristic modes) regardless of the type of helix, as

Structure	Symmetry	Optical Activity		Examples
	Raman	p p d d	p d 0 0	
	Infrared	π σ π σ	0 0 π σ	
Center of Symmetry	D_{2h}		✓ ✓ ✓ ✓	PE, PES
Atactic		✓ ✓ ✓ ✓		PVF
Syndiotactic				
Helix $> 3_1$	D_n		✓ ✓ ✓	PEO
Helix 3_1	D_3		✓	
Helix 2_1	D_2	✓	✓	
Planar	C_{2v}		✓ ✓ ✓	
Isotactic				
Helix $> 3_1$	C_n	✓	✓	Polybutene
Helix 3_1	C_3	✓	✓	PP
Planar	C_2		✓ ✓	

Fig. 6.9. Differences in selection rules for symmetric polymer systems.

well as modes that have different frequency positions because of the form of the helix. The latter modes are useful for characterizing the helical conformation of a polymer in the solid state.

Raman-spectroscopic studies of polymers in solution are of interest primarily to relate the structure in solution to other solution properties. In many cases, the conformation of the polymer changes upon dissolution or melting, or undergoes transformation with changes in the pH, ionic strength, or salt content of the solution. The preferred solvent for Raman spectroscopy is water because the scattering of water is very weak except for the regions of 1650 and 3600 cm^{-1} . As a consequence, Raman spectroscopy is quite useful for studying the secondary and tertiary structures of biological molecules, including carbohydrates, proteins, and nucleic acids. For synthetic polymers, the spectral results are less dramatic but nevertheless revealing.

6.5 Nuclear-magnetic-resonance spectroscopy

Nuclear-magnetic-resonance (NMR) spectroscopy is probably the single most powerful technique for confirmation of structural elucidations of unknown compounds. Additionally, NMR can be used to determine the type and frequencies of molecular

motions of polymer chains. Furthermore, the relatively low measurement times and the facility for automation contribute to its usefulness and industrial interest.

Understanding the structure–property relationships of materials requires analysis of the structure and macroscopic properties. NMR spectroscopy contributes to the analysis through the dependence of the NMR parameters on the local structure. NMR spectroscopy has become one of the most important analytic techniques used in the characterization of materials. In the field of macromolecules, its use extends from monomer characterization, through polymerization kinetics and mechanisms, to direct observation of the chemical structures of polymeric materials [19]. NMR provides information on polymer structures, including main-chain microstructures (conformation, geometric isomerization, spatial distances, etc.), comonomer composition and sequence, end- and side-group analysis, branching and cross-linking, abnormal structures (cyclic and isomerized structures), bonding, regio-enchainment, and tacticity.

One advantage of NMR spectroscopy is that it can be employed on almost all polymeric phases through either solid-state or solution NMR methods. However, the techniques and degrees of resolution of the two methods are radically different. For example, the proton NMR spectrum of water is sharp and narrow with a bandwidth of 1 Hz, whereas the proton NMR spectrum of ice is extremely broad, with a bandwidth of 20 kHz. The differences between the NMR spectra of solids and those of liquids are due to motional averaging of interactions [20, 21]. In liquids and solutions, local interacting fields are averaged to zero by the rapid isotropic motions of the nuclei (termed incoherent averaging), resulting in narrow linewidths.

Anisotropic interactions, such as dipolar and quadrupolar interactions and chemical-shift anisotropy, are averaged to zero by the molecular motions, effectively preventing them from broadening the resonances in the observed spectra. In solution NMR, because of the lower-frequency motions of polymers, incomplete averaging of anisotropic effects is observed to a certain extent, resulting in some peak broadening. In solids, however, this effect is highly magnified. Because there is not sufficient motion to average out the anisotropic interactions, extremely broad lines are present, often encompassing much of the entire spectrum. Because the incoherent averaging (molecular motion) does not narrow the NMR lines, coherent-averaging techniques such as dipolar decoupling and magic-angle spinning (MAS) must be used in order to produce narrow line widths [22].

NMR determinations do not usually require elaborate sample preparation, particularly in the case of solid-state NMR. The great utility of NMR lies in its unique selectivity, which is due to the differentiation of chemically distinct sites on the basis of the chemical shift. Indeed, solution-state NMR spectroscopy has developed into an indispensable method for characterizing polymer molecules: currently, one can even determine the complete three-dimensional structure of proteins.

Unfortunately, NMR has a number of limitations, including low sensitivity. Typically, 10^{16} – 10^{17} of each type of spin are needed for one to observe a NMR signal. This amounts to a millimolar concentration in solution. The sensitivity can be increased by signal averaging by addition of scans. The noise increases in proportion to the square root of the number of scans. An improvement in the signal-to-noise ratio by a factor of two requires a four-fold-prolonged acquisition time. The ultimate limit depends on the stability of the system, the level of rejection of small unwanted interference signals, and other factors.

6.5.1 *The basis of NMR spectroscopy*

When a sample is placed in a strong magnetic field, the spinning motion (angular momentum) of some nuclei, such as the hydrogen atom, gives rise to two energy levels or spin states. NMR exploits the fact that the energy-level spacings are a sensitive function of the nature of the intramolecular bonds, yielding characteristic chemical shifts and selective scalar couplings. The energy levels are also sensitive to intramolecular structure through dipolar interactions but these interactions are generally considered as a nuisance to be eliminated, although recent developments have made them an important part of determining three-dimensional structures.

Modern NMR spectrometry uses the pulsed Fourier method, in which a carefully shaped pulse of radio-frequency energy, tuned to the characteristic NMR frequency called the Larmor frequency (ω), is pumped into the sample. The sample then responds by sending out a very much weaker signal called a free-induction decay (FID). This FID signal appears at the same Larmor resonance frequency but with an amplitude that decays approximately as a decreasing exponential. Depending on a number of experimental parameters, the FID time constant may range from milliseconds to seconds.

The accuracy of the NMR experiment is governed primarily by the relative saturation of the peaks used to quantify the structure. Traditionally, when one is selecting experimental conditions for quantitative NMR measurements, one aims for the highest possible accuracy. This results in very long delays between radio-frequency pulses. Studies of progressive saturation are required in order to give a constant intensity ratio for sampling delays. Implementing increases in sampling delay in order to achieve an accuracy close to 100% may lengthen the analysis time by a factor of up to ten.

With the advent of Fourier-transform methods in the 1980s, NMR spectrometers with an increased dynamic receiver range became available. Thus registration of signals from samples diluted by as much as 1 : 10 000 in protonated solvents became possible.

The limit of detection in NMR experiments depends on a variety of parameters. The signal corresponds to the number of protons within the detection cell and

therefore increases with the cell volume at a constant concentration of the analyte. The signal-to-noise ratio improves by a power of $\frac{3}{2}$ with increasing magnetic-field strength, so optimum performance is obtained with modern high-field superconducting magnets.

6.5.2 Determination of molecular composition by NMR

What makes NMR useful to polymer scientists is the fact that each spinning nucleus responds to the local magnetic field. This phenomenon is expressed by the following equation:

$$B_i = B_0 + B_H + B_e + B_S + B_J$$

where B_i is the local magnetic-field intensity at the position of the i th nucleus, B_0 is the applied magnetic-field intensity; B_H is the correction for non-uniformities in the magnetic field, B_e is the perturbation to the field due to motions of the electrons surrounding the i th nucleus, B_S is the perturbation caused by direct interaction with the magnetic dipole moments of the other nuclei surrounding the i th nucleus, and B_J is indirect interaction with surrounding nuclei mediated through electrons in the intervening chemical bonds. With a well-shimmed magnet, the non-uniformities are negligible in comparison with other effects such as chemical shift, dipole coupling, and J coupling.

The chemical composition of a polymer is determined by a measurement of the chemical shifts. The effect of the electrons surrounding the nucleus is called the chemical shift. These electrons respond to the magnetic field by adjusting their orbits in a way that reduces the magnetic field at the position of the nucleus. The absolute magnitude of B_e depends linearly on the magnetic-field strength, so NMR spectroscopists generally specify the chemical shift as a ratio to the magnetic-field intensity. The chemical shift causes a small change in the Larmor frequency of each nucleus, depending on the average distance from the nucleus of its electrons in their orbits. It is called a chemical shift because the orbits of valence electrons depend on the bonds with other atoms in which they take part.

The Larmor equation

$$\omega = \gamma B_{\text{eff}}$$

describes the relationship among the Larmor precession (resonance) frequency of a magnetic nucleus, ω , the gyromagnetic ratio of the nucleus, γ , and the strength of the effective magnetic field surrounding the nucleus, B_{eff} . The field of interest, the local field in which the nucleus is immersed, is different from the field caused by the magnet alone, B_0 . This difference is caused by nearby nuclei and electrons having associated magnetic fields that contribute to the total field surrounding the nucleus of interest. Since surrounding electrons have associated magnetic fields that

give rise to diamagnetic effects (i.e. they generate opposing magnetic fields), their effect is an apparent shielding of the nucleus from the applied magnetic field. Thus, a particular nucleus of a given isotope (which has a characteristic gyromagnetic ratio) placed in a known magnetic field can have different resonance frequencies, depending on its chemical environment. This property allows the observation of a spectrum of resonance frequencies for a given molecule, which is the basis of NMR spectroscopy.

Several databases exist today, containing hundreds of thousands of chemical-shift values, in particular for the ^1H , ^{13}C , and ^{19}F nuclei useful for polymer analysis and the shift information about the chemical environments of these individual nuclei. These data are an excellent basis for computer-assisted structure determination [23].

Databases of ^{13}C NMR spectra are suitable for three applications.

- The prediction of NMR parameters for any molecular structure.
- The verification of existing assignments (including the simultaneous assignment of individual NMR signals to the respective carbon of a known structure).
- The determination of one or more possible molecular structures corresponding to a ^{13}C NMR spectrum.

6.5.3 Determination of polymer conformations

NMR is sensitive not only to the constitution of a molecule but also to its local geometry. NMR, as a local method, is insensitive to long-range order and is therefore useful for investigation of local structure. The influence of the conformational environment on NMR spectra has long been known under the name of the γ -*gauche* effect.

Conformationally related chemical-shift variations in polymers are generally reflected through two effects: the γ -*gauche* effect and the vicinal *gauche* effect. In a model with three conformations for each bond, there are two magnetically distinguishable γ positions, the *trans* (or anti) position and the *gauche* position. Replacement of a *trans* by a *gauche* position in the polymer conformation results in an upfield chemical shift. The magnitude of the shift depends on the type and number of carbons involved and the relative orientations of the substituents.

6.5.4 Measurement of J coupling constants for structure determination

Neighboring nuclear dipole moments also affect the orbits of valence electrons participating in chemical bonds with the i th nucleus. These changes again modify the local magnetic environment. This effect, known as scalar coupling, or J coupling, is distinct from the chemical shift and is independent of the magnetic-field strength. J coupling does not depend on bond orientation, so it works in the same way in

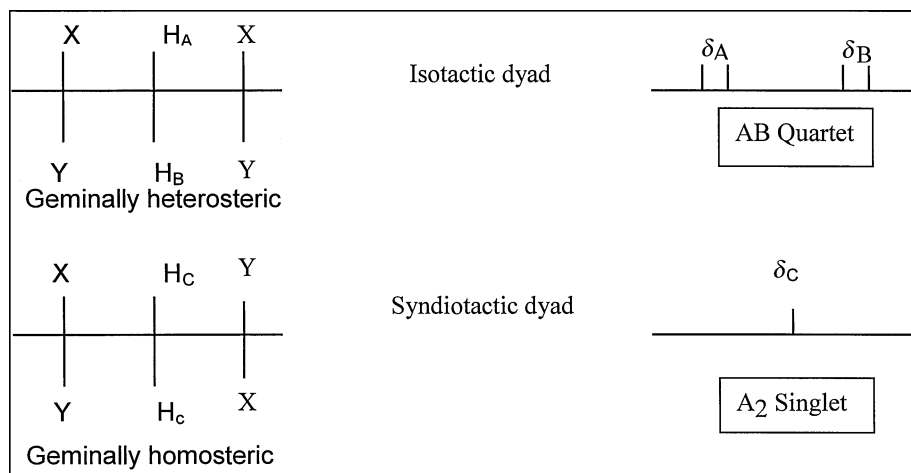


Fig. 6.10. The effect of J coupling on stereoregularity in NMR.

solids and liquids. Its effect is, again, to split the FID spectrum. The magnitude of the shift depends on the neighbor's dipole moment and the orbit of the intervening electrons.

The nuclear spin–spin coupling, J , is mediated by electrons in a process involving spin polarization of the bonding orbitals. The value of J is a function both of the character and of the polarizability of the bonding orbitals. The sign of the coupling constant $J(I - S)$ depends on the relative energies of configurations in which the nuclear spins I and J (each with a spin $\frac{1}{2}$) are aligned either in the same direction ($\uparrow\uparrow$ or $\downarrow\downarrow$) or opposed ($\uparrow\downarrow$ or $\downarrow\uparrow$). Where the configuration with spins opposed is stabilizing (i.e. shielding) $J(I - S)$ has a positive sign and where it is destabilizing $J(I - S)$ has a negative sign. In general, the one-dimensional NMR spectrum does not provide information about the signs of coupling constants; therefore a direct determination of the sign of $J(I - S)$ is not a straightforward process. The theory of J coupling is complex but the couplings are related to the extent of orbital overlap between atoms. The magnitude of a J coupling is dependent on the degree of orbital overlap in a bond. J couplings have long been used to obtain information about covalent bonds. As shown in Fig. 6.10, the J couplings can be used to differentiate between isotactic and syndiotactic dyads because the isotactic generates an AB quartet whereas the isotactic generates only a singlet.

6.5.5 ^{13}C NMR spectroscopy

^{13}C NMR spectroscopy provides complementary structural information to that obtainable from ^1H NMR spectroscopy while reducing the problems of overlap that

are often found in ^1H NMR spectra of complex mixtures, since the range of chemical shifts for ^{13}C is ~ 20 times that for ^1H . In addition, all scalar couplings are usually removed by ^1H decoupling, thus simplifying the spectrum to a single line for each chemically non-equivalent carbon. Of particular advantage for the study of biological polymer systems is the absence of a water resonance, and, hence, effective suppression of signal from the solvent. The fact that the T_1 values for ^{13}C nuclei are longer than those for ^1H nuclei can also necessitate the use of longer recycle delays, but useful ^{13}C NMR spectra can be acquired in reasonable times without the need for methods to shorten T_1 , such as addition of paramagnetic relaxation agents.

Despite enhancement by techniques such as use of the nuclear Overhauser effect, the low natural abundance ($\sim 1.1\%$) and low gyromagnetic ratio of ^{13}C nuclei ($\sim 25\%$ that of ^1H) means that, for typical concentrations in polymer mixtures, ^{13}C NMR spectra suffer from poor sensitivity and the need for long acquisition times.

NMR signal-to-noise ratios can be significantly improved by cooling the NMR radio-frequency detector and preamplifier. The noise figure is reduced approximately by a factor proportional to the square root of the temperature ratio in degrees kelvin, and thus cooling both the coil and the preamplifier from room temperature to $\sim 20\text{ K}$ reduces the thermal noise by approximately a factor of four. This gives a corresponding gain in signal-to-noise ratio per scan or, for the same signal-to-noise ratio, a reduction in acquisition time by approximately a factor of 16. This improvement in sensitivity for ^{13}C nuclei is such that cryogenic probes allow one to attain good signal-to-noise ratios with reasonable acquisition times using polymer samples. Two-dimensional NMR experiments such as ^{13}C DEPT and ^1H – ^{13}C HSQC also become easier to perform, facilitating spectral assignment. There still remains the problem that ^{13}C nuclei with long T_1 relaxation times, such as carbonyl groups, still give reduced signal intensities, and hence quantification can be problematic. Nevertheless, for polymer studies in which all the samples are measured under identical conditions, such quantization is less necessary, because it is the overall pattern of response which can be interpreted.

6.5.6 Solid-state NMR spectroscopy

In solid-state NMR, the fast isotropic molecular tumbling that leads to the observation of inherently high-resolution solution-state spectra is absent, and anisotropic interactions, e.g. the chemical-shift anisotropy (CSA), and the dipolar and quadrupolar couplings, lead to a broadening of the resonances. On the one hand, these anisotropic interactions have the significant disadvantage of hindering the resolution of distinct sites, but, on the other hand, they contain valuable structural and dynamic information.

Since the pioneering demonstration that cross-polarization ^{13}C NMR spectra can be recorded, solid-state NMR spectroscopy has advanced rapidly and is now being used to study the structure and dynamics of a variety of polymer systems. Much of the success of solid-state NMR spectroscopy is due to the evolution of a variety of techniques for studying internuclear distances, anisotropy, torsion angles, atomic orientations, spin diffusion, molecular dynamics, and exchange processes, while maintaining the high resolution and sensitivity necessary for practically useful NMR experiments in polymers.

The static ^{13}C NMR spectrum of a typical organic solid is simply a broad featureless hump. The challenge is to design experiments that combine high resolution, i.e. a recovery of the chemical-shift resolution, with the preservation of the valuable information inherent to the anisotropic interactions, i.e., for ^{13}C NMR, the structural and dynamic information inherent to the dipolar coupling.

On account of its angular dependence, molecular motion leads to an averaging of the dipolar coupling; determining the reduction in the dipolar coupling allows the identification of particular dynamic processes. The extreme case is found in solution, where fast isotropic tumbling of the molecules leads to the averaging to zero of the line broadening due to the dipolar couplings as well as the other anisotropic interactions. To achieve high resolution, one must find a method by which to mimic this averaging process. First, we note that anisotropic interactions such as the dipolar coupling of a pair of nuclei, the CSA, and the first-order quadrupolar interaction all have an orientation dependence that can be represented by a second-rank tensor. For such interactions, rather than requiring an isotropic motion, a physical rotation of the sample around an axis inclined at an angle of $\arctan 54.7^\circ$, the so-called magic angle, to the external magnetic field suffices. That this is so can be understood by considering that rotation of a sample around a single axis leads to the components perpendicular to the axis of rotation being zero on average, and only the component parallel to the axis of rotation remains nonzero on average. Thus, in a powdered sample, for any orientation of, e.g., the internuclear vector for a pair of dipole-coupled spins, rotation around an axis yields an “average orientation” parallel to the axis of rotation. Under magic-angle spinning (MAS), this parallel component has an anisotropic frequency equal to zero for all cases, and the anisotropic broadening is averaged to zero for all orientations of the crystallite. A familiar example of the application of MAS is ^{13}C NMR, in which the combination of ^1H – ^{13}C cross-polarization (CP) with MAS, CP MAS NMR, is routinely used to investigate a wide range of systems. Under the application of high-power proton decoupling, the dominant anisotropic broadening is the CSA; the static line shape breaks up into a center-band and spinning sidebands, whose line widths are narrow and independent of ω_{R} .

6.5.7 Heteronuclear dipole coupling

Direct spin–spin coupling is noticeable with solid samples. It is called dipole coupling, because it results from modification of the local field surrounding the i th nucleus by the dipole moments of its neighbors. It is a vector interaction, so the relative orientations of the bonds are important. In solids at room temperature and below, the relative positions of neighboring nuclei do not move very much, so the effect of dipole coupling is clearly defined. It therefore produces lines similar to those created by the chemical shift, but the splitting is independent of the magnetic-field strength. It depends on the neighbor's dipole moment, the distance away of the neighbour, and the bond orientation.

The dipolar coupling constant, D , defining the dipolar coupling between two nuclei is given by

$$D = \left(\frac{\mu_0}{4\pi} \gamma_I \gamma_S \right) r^{-3}$$

where r denotes the internuclear separation. The dependence of D on the product of the magnetogyric ratios of the two nuclei means that the dipolar-coupling constant for two ^1H nuclei is a factor of approximately 16 times larger than that for a pair of ^{13}C nuclei at the same separation. As an example, the ^1H – ^1H D in a CH_2 group (assuming that $r = 0.18\text{ nm}$) is 20 kHz, which is about twice the typically encountered chemical-shift range (15 ppm) and is much larger than the through-bond J couplings which characterize solution-state spectra.

A major difference between the *through-space* dipolar and *through-bond* J couplings is that the former is an *anisotropic* rather than an *isotropic* interaction. This means that the dipolar coupling between a pair of nuclei depends on the orientation of the internuclear vector with respect to the direction of the static magnetic field, B_0 . Specifically, the dipolar coupling is proportional to $3 \cos \theta - 1$, where θ is the angle between the internuclear vector and the direction of B_0 . For a powdered sample, there is a uniform distribution of orientations, and thus the NMR spectrum consists of a superposition of many lines, corresponding to the different dipolar couplings. Such a powder spectrum is referred to as being anisotropically broadened.

The analysis of the solid-state ^{13}C NMR spectra of polymers begins with an examination of the heteronuclear dipolar coupling. The heteronuclear dipolar coupling arises from an interaction between the nuclear magnetic moments of two different nuclear spins. (By convention, nuclear spins are labeled as I for abundant spins, for example, that of the proton, and S for rare spins such as that of ^{13}C or ^{15}N nuclei.) In an external magnetic field, the Zeeman interaction describes the energy of the spin I based on its orientation, either parallel (spin up, $\uparrow$) or antiparallel (spin

down, $\downarrow$), with respect to the external field,

$$E_{\text{Zeeman}} = -h\gamma B_0 m_I$$

where γ is the gyromagnetic ratio, B_0 is the external magnetic field, and m_I is the nuclear-spin quantum number (which is either $+\frac{1}{2}$ or $-\frac{1}{2}$ for a spin $-\frac{1}{2}$ nucleus).

Similarly, spin S will align itself either parallel or antiparallel to B_0 . Since each spin represents a nuclear magnetic moment that produces a small magnetic field, the S spin will feel the magnetic field produced by the I spin and vice versa when the two spins are within reasonable proximity of each other (~ 10 Å). This magnetic field produced by the I spin will either add to or subtract from the external field felt by the S spin, depending on the orientation of the I spin, thereby increasing or decreasing the effective local magnetic field at the site of spin S and thus changing its resonance frequency. The degree to which spin I affects the magnetic field felt by spin S is characterized by the strength of the heteronuclear dipolar coupling, which is represented by the Hamiltonian in the following equation:

$$H_{\text{IS}} = -d(3 \cos^2 \theta - 1)I_z S_z$$

The parameter d is the dipolar-coupling constant. The angle θ describes the orientation of the internuclear vector with respect to the orientation of the external magnetic field. Because the magnitude of the coupling between two nuclear spins depends on the internuclear distance, the dipolar coupling is a through-space interaction. In contrast, J coupling requires the presence of chemical bonds. It is transferred through the electrons engaged in these bonds and thus is confined to nuclei within a molecule. Through-space dipolar coupling, however, also occurs between nuclei in different molecules. The two coupling mechanisms are therefore complementary in information content.

Three properties of the heteronuclear dipolar coupling Hamiltonian stand out.

- (1) The magnitude of the coupling is proportional to the product of the gyromagnetic ratios. This appears intuitively reasonable because the magnetic moment of a nucleus is proportional to γ , and nuclei with greater magnetic moments produce stronger magnetic fields, which in turn increases the magnitude of the dipolar-coupling interaction.
- (2) The dipolar coupling is inversely proportional to the cube of the internuclear distance, so the interaction falls off rapidly as the nuclei are moved farther apart.
- (3) The dipolar coupling is dependent on the orientation, which is evident from the $3 \cos^2 \theta - 1$ term in the dipolar Hamiltonian. This means that, for two nuclei of spins I and S which are separated by a fixed distance, the magnitude of the dipolar interaction will be greater for certain orientations of the I–S internuclear vector than for others.

It is the orientational dependence of the dipolar coupling that limits its role in liquid-state NMR spectroscopy. The reorientation time of a molecule in solution is

much faster than the time the dipolar coupling would need to evolve, thus causing the $3 \cos^2 \theta - 1$ term of the heteronuclear dipolar-coupling Hamiltonian to average to zero. In a static solid sample comprised of randomly oriented crystallites, however, the internuclear vector remains invariant over time, and the resonance frequency produced by each crystallite depends on its orientation with respect to the external field. In a polycrystalline powder sample in which the crystallites are oriented in all possible directions, the presence of a heteronuclear dipolar coupling produces a broad spectrum. The intensity of the pattern at a particular frequency reflects the abundance of the crystallites that resonate at that frequency. Notably, there is also an orientation of the I-S vector relative to B_0 at which the resonance frequency of the crystallites is not altered by the heteronuclear dipolar coupling. This is the case at the magic angle of 54.74° ($3 \cos^2 \theta - 1 = 0$).

The heteronuclear coupling that is responsible for much of the broadening in the solid-state spectrum involves the coupling of ^1H nuclear spins to the detected ^{13}C nuclear spins, since the ^1H - ^{13}C dipolar coupling is typically the dominant interaction experienced by the ^{13}C spin. A typical coupling constant for a bonded ^1H - ^{13}C pair (at a distance of about $1\text{\AA}$) is approximately 30 kHz. However, there are two possible means of eliminating the interaction in order to give narrower lines. One approach is to take advantage of the fact that the dipolar coupling is zero when the internuclear vector is oriented at the magic angle with respect to the magnetic field. This approach is implemented in a technique known as MAS. The second method that can be used to eliminate the effect of the ^1H nuclei on the ^{13}C spectrum is to manipulate the proton spins in such a way that their effect on the ^{13}C nucleus, when it is averaged over time, is equal to zero. This is the solid-state dipolar version of spin decoupling, which is used in solution NMR spectroscopy. In liquid-state NMR spectroscopy, continuous-wave decoupling is used much less often because it has been superseded by a number of multiple-pulse techniques. These techniques are usually not as effective in solid-state NMR spectroscopy.

6.5.8 Chemical-shift anisotropy

The origin of the chemical shift can be understood by examining the effect of B_0 on the electrons around a nucleus. When an external magnetic field is applied to an atom, not only are the nuclear spins perturbed, but also the surrounding electrons are affected since they, too, have magnetic moments. The external field induces circulating currents of electrons that in turn produce small magnetic fields (typically $\sim 10^6$ times smaller than B_0), which either add to or subtract from the external field felt by the nucleus. Therefore, the effective magnetic field experienced by the nucleus is altered, as is its resonance frequency.

The orientation dependence or anisotropy of the chemical shift can be quite dramatic. For a non-sp³-hybridized ¹³C atom, the CSA can be as large as 120–140 ppm. The CSA results from the fact that the atoms in molecules rarely possess spherically symmetric electron distributions; instead, the electron density can be thought of as an ellipsoid, typically elongated along bonds or nonbonding p orbitals. The degree to which the electron density affects the resonance frequency of a nucleus depends on the orientation of the electron cloud (and hence the orientation of the molecule) with respect to B_0 . For example, the resonance frequency of a carbonyl carbon atom can differ by more than 120 ppm, depending on the orientation of the C=O moiety with respect to the external field. The largest chemical shift (i.e. deshielding effect) in the resonance frequency of the ¹³C nucleus occurs when the narrowest part of the electron cloud is oriented along the B_0 axis, whereas the smallest shift occurs when the widest part of the electron cloud is oriented along B_0 . These two chemical shifts, referred to as σ^{11} and σ^{33} , respectively, are two of the three principal values of the CSA. The third value, σ^{22} , is the shift produced by the molecular orientation perpendicular to the axes of σ^{11} and σ^{33} . These three principal values and the information on the orientation of the ellipsoid (usually specified by the three Euler angles) provide all the information necessary to describe the CSA of a nuclear spin.

For powder samples, in which the vast number of randomly oriented crystallites ensures that all of the possible molecular orientations are sampled, a powder pattern emerges. The left and right edges of the C=O signal correspond to the chemical shifts σ^{11} and σ^{33} , respectively, and the position of the maximum intensity of the pattern corresponds to σ^{22} (for the common convention of $\sigma^{11} > \sigma^{22} > \sigma^{33}$). The broad CSA signal is the result of an interaction between the detected spins and the external field, and so there is no simple way to remove this interaction by use of radio-frequency pulses (as we did with the heteronuclear dipolar coupling) without affecting the free precession of the spins required for detection of a signal.

However, liquid-state NMR spectroscopy provides a clue telling us how the effects of the CSA can be eliminated. In liquids, molecules randomly and rapidly sample the full range of orientations, so that even a strongly asymmetric electron distribution will appear spherical when it is viewed on the NMR timescale. One can divide the chemical-shift Hamiltonian H_{cs} into an isotropic term and an anisotropic term.

With a rapidly tumbling molecule, all possible orientations of the ellipsoid are sampled, causing the orientation-dependent term to average to zero and leaving only the isotropic component of the chemical shift, $\sigma_{iso} \gamma B_0 I_z$, which is observed in liquid-state NMR spectra. Imposing a random, liquid-like motion on a solid-state sample is, however, mechanically impractical since it would require motion around

multiple axes at speeds that are currently unattainable. By spinning the sample around a unique well-chosen axis, one can also eliminate the anisotropic term of the chemical-shift Hamiltonian.

6.5.9 Magnetic-resonance imaging

NMR spectroscopy measures the difference in resonance frequency of magnetic nuclei in different molecular environments under the influence of a homogeneous external magnetic field. The method relies on the homogeneity of this magnetic field, such that different frequencies can be attributed to the difference in molecular environment of a specific nucleus. In 1973, two papers [24, 25] independently described how NMR could be used to obtain information on the spatial distributions of specific nuclei in a sample by varying their resonance frequencies. Applying one or more magnetic-field gradients so that the strength of the external magnetic field is varied along certain axes in a controlled way generates these variations. The amplitudes of the different resonance signals yield the local densities of the nuclei in the sample. This method is called magnetic-resonance imaging (MRI). One-dimensional imaging generates a profile of the density of a certain nucleus, usually a proton, along the axis of the gradient in the magnetic field [26].

One way of achieving this gradient that is appropriate to materials research is to make use of the very strong fringe – or stray – field gradient of a large superconducting magnet. This field gradient is strong enough to spread the resonance frequencies in solid systems, in which the resonance lines are broad with high spatial resolution. This MRI technique is known as stray-field imaging (STRAFI) [27]. The rate of relaxation after excitation of the nuclei depends to a large extent on molecular mobility. In water, the protons are very mobile and dissipation of energy through interaction with their surroundings is not very effective. Hence, the relaxation times are long, which leads to narrow NMR line widths. When the proton mobility is low, as for protons contained in polymers or other high-relative-molecular-mass solids, the relaxation is more effective and the signals become broader. One spin-relaxation mechanism, transverse relaxation, or spin–spin relaxation, characterized by a time constant T_2 , is particularly sensitive to the mobility of the nuclei. Measuring their spin–spin relaxation time is thus a good way of assessing the mobility of nuclei. By applying a multiple spin-echo pulse sequence, the T_2 of protons in different parts of the profile can be measured. As the T_2 decreases with decreasing proton mobility, the signals gradually become smaller. Thus, spin-echo pulse sequences can be used to monitor the gradual decrease in proton mobility during, for example, a cross-linking reaction. Using MRI, a profile of the T_2 values for protons can be obtained and attributed to the spatial variations in the extent of cross-linking.

MRI provides quantitative measurements of concentration and molecular mobility as functions of time and, more importantly, as functions of position (i.e. depth) in the coating. A pixel resolution of about 9 μm can be obtained. MRI, with its capability of determining molecular mobility and concentration as functions of depth in a coating, clearly has enormous potential in the field of coatings research.

6.5.10 Polymer blends

Polymer blends are of great industrial interest. Thermodynamically, the miscibility of polymer blends is mainly dependent on the mixing because the contribution of the combinatorial entropy to the free energy of mixing is negligibly small, and thus the miscibility of most pairs of polymers arises from specific intermolecular interactions. Numerous techniques are employed to investigate the miscibility and phase behavior of polymer blends: thermal and mechanical analyses, microscopy, and light-scattering and spectroscopic techniques. FTIR and solid-state NMR have been proven to be powerful for investigating the intermolecular specific interactions in blends. Solid-state NMR can provide insight into the homogeneity of polymer blends at the segmental scale. The ^{13}C chemical shifts and/or line shapes of the carbon resonance in the CP MAS spectra identify the chemical environments of carbon nuclei in the blends and thus changes in them usually reflect the intermolecular interactions between the components of a blend. In the FTIR approach, the information on the intermolecular interactions is obtained through the relative variation of the interacting spectroscopic vibrations.

6.6 Mass spectroscopy

Using mass spectrometers, one can measure m/z (where m is the mass and z is the charge), which is inherently quantized because the charge, z , occurs only in integer multiples of the elementary charge (e.g. that of the electron), and mass, m , is quantized according to its distribution in molecules, functional groups, elements, isotopes, and elemental compositions. An ionized atom or molecule may be characterized by its m/z . At unit-mass resolution, it is possible to discriminate 18 (out of 20) commonly occurring amino acids in terms of their residue masses. Leucine and isoleucine have identical elemental compositions and thus are virtually identical in terms of mass.

The full power of mass analysis emerges from higher resolution (millidalton level) because each nuclide has a different mass defect (i.e. difference between the exact mass and the nominal mass): ^{12}C is of mass 12.000 00 Da, ^1H is of mass 1.007 25 Da, ^{16}O is of mass 15.9949 Da, etc. Thus every different elemental composition, $\text{C}_c\text{H}_h\text{O}_o\text{N}_n\text{S}_s \dots$, has a different mass, so that the chemical formula of a

molecule can be determined uniquely from a sufficiently accurate measurement of its mass. The upper mass limit for the unique determination of elemental composition from mass alone (at an accuracy of ~ 1 ppm) is ~ 300 Da.

Because of its high sensitivity, broad dynamic range, specificity, and selectivity, mass spectrometry (MS) has become an indispensable tool for determination of the structures of organic and inorganic polymeric materials. Over the past decade, matrix-assisted laser desorption/ionization (MALDI) and electrospray ionization (ESI) coupled with MS have been developed and refined into highly versatile experimental tools for polymer characterization. The inherent flexibility of MS techniques is continuously being enhanced by augmentation of mass-detection configurations, experimental functionality (e.g. scanning techniques and data-dependent experiments), and powerful data-interpretation and software applications (e.g. automated data analysis and database searching).

6.6.1 Structural mass spectroscopy

Routine structural approaches with MS include the identification of polymers, which is typically achieved by confirmation of the primary structure via measurement of the molecular mass.

MS in conjunction with database searching has become a powerful tool for analyzing complex mixtures of polymers. One measure of the chemical complexity of a mixture is the number of species with different elemental compositions ($C_cH_hO_oN_nS_s \dots$). Only different elemental compositions are considered and MS does not distinguish among isomers, i.e. molecules of the same elemental composition but different bond arrangements. If the dynamic range (the ratio of highest- to lowest-abundance species) in the mixture is $< 10\,000$ or so, then components present in the most complex systems can be distinguished. MALDI MS and ESI MS are well suited for resolution and identification of complex mixtures of components below ~ 1000 Da in mass, because the number of mass-spectral peaks does not greatly exceed the number of components to be distinguished.

The successful resolution of more than 11 000 singly charged ions, corresponding to ~ 8000 different elemental compositions (the remaining 3000 constitute the same molecules but with one ^{13}C or ^{34}S instead of a ^{12}C or ^{32}S) from a single one-dimensional positive-ion ESI FT-ion-cyclotron-resonance mass spectrum with no prior chromatographic separation has been achieved [28]. That result established a new record for the most complex chemical mixture ever analyzed in a single step and also established a standard for analysis of similarly complex mixtures (biological, environmental, etc.).

MS can be combined with traditional multidimensional separation techniques that significantly improve the selectivity and specificity of the experimental approach for use in increasingly complex polymer applications.

6.6.2 MALDI techniques

The structural and compositional analysis of synthetic polymers by MALDI MS has developed rapidly. The MALDI technique involves embedding the analyte in a matrix that absorbs at the wavelength of the laser. The energy is then transferred from the matrix to the analyte, which is desorbed and subsequently ionized in the gas phase. The ions produced can be analyzed in a time-of-flight (TOF) mass analyzer, a natural choice for pulsed-ionization techniques.

MALDI–TOF MS can be used to detect synthetic polymer molecules with relative molecular masses in excess of 10^6 Da. With state-of-the-art MALDI MS instruments equipped with time-lag focusing and operations in the reflector mode, qualitative determination of chemical composition, including end-group identification, can be performed for relative molecular masses up to 36 kDa. The strength of MALDI MS lies in the simplicity of the mass spectra, which arise mainly from singly charged quasimolecular ions, and the relatively high tolerance of contamination of the sample.

TOF MS techniques have two major advantages. First, the mass range is limited only by the detector, ion transmission, and ionization processes; secondly, in contrast to quadrupole analyzers, because all the ions are registered simultaneously, without scanning, TOF analyzers can address the scan-speed/elution-time problem; this makes them applicable to separations combined with MS. During the last decade improvement of MALDI–TOF MS instrumentation, chiefly arising from the use of reflectron technology, time-lag focusing, and Fourier-transform technology, has dramatically increased mass resolution, sensitivity, and accuracy of measurement of mass.

6.6.3 Electrospray-ionization mass spectroscopy

The term ESI is used to denote the overall process by which an intense electric field disperses a liquid sample into a bath gas as a fine spray of highly charged droplets. Evaporation of these charged droplets produces gas-phase ions by mechanisms that remain the subject of much argument and debate. Since the first quadrupole ESI MS experiments the technique has become one of the most widely used in analysis. Advances in ESI MS instrumentation have also involved the TOF mass analyzer. The difficulty in coupling a continuous ESI source to a TOF instrument was circumvented by use of orthogonal injection, which transforms a continuous ion beam into a pulsed mode. Employment of TOF analyzers has allowed more efficient coupling of ESI MS to liquid chromatographs, primarily because of the rapid acquisition of data and improvement in dynamic range.

ESI is a method that can successfully ionize polymers with little or no fragmentation. A drawback of ESI is the requirement that the polymer being analyzed be soluble in a solvent that can be electrosprayed. Another reason why ESI is less

used for polymer characterization than is MALDI is its strong tendency to form multiply charged ions that especially complicate the analysis of polymers having relative molecular masses above a few kilodaltons. The multiply charged ions also complicate quantization by ESI. One distinct advantage of ESI is the ease with which it can be interfaced to methods for separation of liquids.

The unique ability of ESI to produce multiply charged ions extends this extremely soft technique to a higher mass range, even for an analyzer with a limited mass range. Unfortunately, as a result of multiple charging, even polymers with narrow dispersity and high mass give very complex mass spectra.

6.6.4 Separation techniques

To determine the molecular heterogeneity of a real polymer system, combination of separation techniques with spectroscopic techniques is required. The polymer chains are usually first fractionated by means of a separation technique such as liquid chromatography, supercritical-fluid chromatography, or temperature-rising elution fractionation. The characterization step can be performed by using a molecular spectral technique, either off-line or as a detector for the separation technique.

The value of coupling MS with separation techniques has already been recognized. Such methods have proved to be among the most powerful for molecular characterization of complex polymer systems [29].

References

- [1] G. Socrates, *Infrared Characteristic Group Frequencies* (John Wiley & Sons, Chichester, 1994).
- [2] M. C. Etter, *Acc. Chem. Res.*, **23** (1990), 120.
- [3] A. J. Berger, T-W. Koo, I. Itzkan, and M. S. Feld, *Anal. Chem.*, **70** (1998), 623.
- [4] B. Jasse and J. L. Koenig, *J. Macromol. Sci. Rev. Macromol. Chem.*, **C17** (1997), 135.
- [5] D. Lefebvre, B. Jasse, and L. Monnerie, *Polymer*, **22** (1981), 1616.
- [6] R. G. Messerschmidt and M. A. Harthcock, *Infrared Microscopy: Theory and Applications* (Marcel Dekker, New York, 1998).
- [7] E. N. Lewis, P. J. Treado, R. C. Reeder, G. M. Story, A. E. Dowrey, C. Marcott, and I. W. Levin, *Anal. Chem.*, **67** (1995), 3377.
- [8] P. Colarusso, L. H. Kidder, I. W. Levin, J. C. Fraser, J. F. Arens, and E. N. Lewis, *Appl. Spectrosc.*, **52** (1998), 106A.
- [9] B. Foster, *Am. Laboratory*, February (1997), 21.
- [10] E. N. Lewis, L. H. Kidder, J. F. Arens, M. C. Peck, and I. W. Levin, *Appl. Spectrosc.*, **51** (1997), 563.
- [11] A. S. Haka, I. W. Levin, and E. N. Lewis, *Appl. Spectrosc.*, **54** (2000), 753.
- [12] L. H. Kidder, I. W. Levin, E. N. Lewis, V. D. Kleiman, and E. J. Heilweil, *Opt. Lett.*, **22** (1997), 742.
- [13] C. M. Snively and J. L. Koenig, *Appl. Spectrosc.*, **53** (1999), 170.

- [14] C. A. Michaels, L. J. Richter, R. R. Cavanagh, and S. J. Stranick, *Proc. SPIE*, **4098** (2000), 102.
- [15] C. A. Michaels, *et al.*, *J. Appl. Phys.*, **88** (2000), 4832.
- [16] S. J. Stranick, D. B. Chase, and C. A. Michaels, *Polym. Mater. Sci. Eng.*, **87** (2002), 172.
- [17] B. Knoll and F. Keilmann, *Nature*, **399** (1999), 134.
- [18] B. Schrader, *Raman/Infrared Atlas of Organic Compounds* (VCH Publishers, New York, 1989).
- [19] F. A. Bovey, *Chain Structure and Conformation of Macromolecules* (Academic Press, New York, 1982).
- [20] Mehring, M., *High Resolution NMR Spectroscopy in Solids* (Springer-Verlag, New York, 1983).
- [21] C. A. Fyfe, *Solid State NMR for Chemists* (CFC Press, Guelph, 1984).
- [22] H. W. Spiess, *Ann. Rev. Mater. Sci.*, **21** (1991), 131.
- [23] SpecInfo data base, Chemical Concepts, STN, Karlsruhe, see W. Robien, CSEARCH, http://felix.orc.univie.ac/~wt/csearch_server_info.html; S. V. Trepalin, A. V. Yarkov, I. M. Doimatova, N. S. Zefirov, and S. A. E. Finch, *J. Chem. Inf. Comput. Sci.*, **35** (1995), 405; CNMR data base, Advanced Chemistry Development, Inc., 133 Richmond Street West, Suite 605 Toronto, Ontario, Canada M5H 2L5.
- [24] P. Mansfield and P. K. Granel, *J. Phys. C*, **6** (1973), L422.
- [25] P. C. Lauterbur, *Nature*, **242** (1973), 190.
- [26] P. T. Callaghan, *Principles of Nuclear Magnetic Resonance Microscopy* (Clarendon Press, Oxford, 1991).
- [27] P. J. McDonald and B. Newling, *Rep. Prog. Phys.*, **61** (1998), 1441.
- [28] C. A. Hughey, R. P. Rodgers, and A. G. Marshall, *Anal. Chem.*, **74** (2002), 4145.
- [29] R. Murgasova and D. M. Hercules, *Anal. Bioanal. Chem.*, **373** (2002), 481.

Small-angle-neutron-scattering characterization of polymers

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7.1 Introduction

7.1.1 Background

Neutron scattering had its origin in 1932, the year that marked the discovery of the neutron by Chadwick, and the first nuclear reactors were successfully operated in Chicago and Oak Ridge in the early 1940s. It is there that the technique of neutron scattering can be said to have begun and, during its initial stages, it was used mainly for the study of “hard” crystalline materials. For example, the pioneering research of C. G. Shull, E. O. Wollan, and B. N. Brockhouse, which led to the 1997 Nobel Prize for Physics, began with studies of materials such as iron, chromium, cobalt, and iridium, and was followed by the development of polarization analysis [1] to determine the structure of magnetic materials. Such studies continue to give important structural information [2], though, during the last two decades, the technique has been used increasingly by scientists from other disciplines (polymer science, chemistry, biology). Thus, many of these more recent applications have involved “soft” matter such as polymers [3] and colloids [4], which have become some of the most practical and widely used materials today. This development may be seen as part of an even broader trend within the sciences, as noted by P. G. de Gennes [5]:

Our species initially learned to work hard objects, like flint, bronze, stone, brick or even wood. But soon, it found itself in need of more nuances, of more pliant materials; leathers, natural fibers, waxes, starches . . . Likewise, twentieth century physics first devoted itself to hard materials, such as metals, semiconductors (which opened the way to modern forms of communication), and later, ceramics. But the recent trend has been in the direction of soft materials, of which polymers, detergents and liquid crystals are the most common forms around us.

Most polymeric and colloidal systems contain copious amounts of hydrogen, either in their molecular constitution or when materials to be studied are suspended in aqueous or ^1H -containing solvents so that they are particularly suitable for applying deuterium-labeling¹ techniques (see below).

Scattering techniques have been employed since the beginnings of polymer science to provide information on the spatial arrangements of macromolecules and C. W. Bunn used X-rays to determine the crystal structure of polyethylene [6] via Bragg's law

$$\lambda = 2D \sin \theta \quad (7.1)$$

where D is the distance between crystallographic planes, λ is the wavelength and 2θ is the angle of scatter. For elastic scattering, in which the energies of the incident and scattered radiation (neutrons, X-rays etc.) are the same, the intensity, $I(Q)$, is measured as a function of the momentum transfer, Q :

$$Q = 4\pi\lambda^{-1} \sin \theta \quad (7.2)$$

Combining equations (7.1) and (7.2) gives

$$D \simeq 2\pi/Q \quad (7.3)$$

Although Bragg's law (Eq. (7.1)) does not apply to amorphous materials, the Fourier or inverse relationship between the structure in real space (r) and the scattering in Q -space means that Eq. (7.3) may be applied to first order for all types of scattering. Thus, data at lower Q -values probe longer length-scales in the system, and, in order to use neutrons to study the length-scales (~ 10 – 1000 Å) that are important for polymers (e.g. the size of the polymer “coil”), we need to work at low Q -values (10^{-3} – 10^{-1} Å $^{-1}$) and collect data at small angles ($\theta < 15^\circ$) using long-wavelength (5 Å $< \lambda < 20$ Å) or “cold” neutrons.² These measurements are conventionally referred to as small-angle scattering, though it is the Q -range which determines the size of objects studied and radiations with other wavelengths (e.g. light, X-rays) can obviously provide similar information in different angular ranges (see Section 7.1.4). Before proceeding to a detailed description of neutron-scattering theory, it may be of interest to give illustrative examples of the power of the small-angle neutron-scattering (SANS) technique, as an introduction to the unique information that it can provide.

¹ The symbol ^2H is normally used in Cambridge University Press publications to denote the deuterium isotope, though the symbol ^2D is more often used in the SANS literature. It has also been used in publications by the author, including the previous edition of this chapter, and is therefore preferred in this review for consistency.

² The ångström unit (1 Å = 10^{-8} cm) has been used widely in the SANS literature over the past three decades and is retained in this chapter in place of the SI unit (1 nm = 10 Å), as in previous publications by the author.

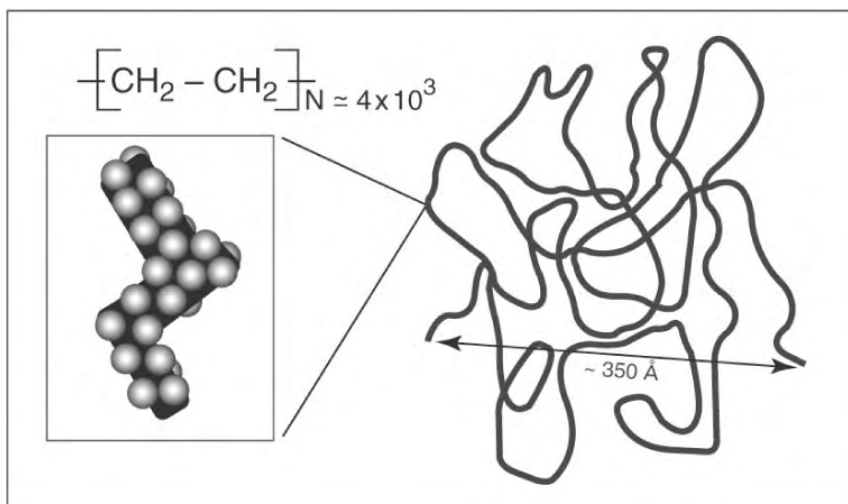


Fig. 7.1. A schematic diagram of the configuration of the polyethylene molecule in the amorphous (melt) state, showing how individual chains share the same space with hundreds of other molecules and are thus profusely intertwined or entangled. For $M \sim 10^5$, the average end-to-end distance is $\sim 350 \text{ \AA}$ and the molecule pervades a volume of $\sim 10^8 \text{ \AA}^3$, whereas the volume it occupies is $\sim 2 \times 10^5 \text{ \AA}^3$. Thus ~ 500 other molecules interpenetrate the same volume.

7.1.2 Illustrative example using SANS to study global and local conformations of polymers

SANS has proven to be one of the most important tools for the evaluation of polymer-chain conformation. This is because neutrons are scattered differently by hydrogen (^1H) and deuterium (^2D) and the scattering from an object depends on the *difference* in scattering power between the particle and its environment. Thus, one way to create such a difference (contrast) is to deuterate (or “color” or “stain” isotopically) individual chains [7, 8] or parts of molecular aggregates, to make them “visible” in the condensed state. Thus, the combination of SANS and ^2D -labeling techniques has been able to answer many long-standing questions concerning the way in which polymer molecules pack together and to measure their dimensions.

Figure 7.1 shows a typical chain of polyethylene, the most widely used commercial polymer. Assuming that there are ~ 4000 ethylene (C_2H_4) units (segments) covalently bonded together to give an overall molecular weight of $M \sim 10^5$, the average “size” of the chain, or the “end-to-end distance,” is $\sim 350 \text{ \AA}$ [9, 10]. Thus, the chain pervades a volume of $\sim (4\pi/3)350^3 \sim 10^8 \text{ \AA}^3$, whereas the molecule itself occupies a volume of only $\sim 2 \times 10^5 \text{ \AA}^3$. It follows that the space penetrated by the molecule is shared with ~ 500 other chains, all of which are copiously entangled and intertwined together. Thus, a typical segment can in principle interact

with each of 4000 segments on the same chain and also with 500 other chains, each of which contains another 4000 segments!

This illustrates the difficulty of calculating the chain trajectory, which is truly a many-body problem that would be hard to address, even with the massive computing power which is available today. In the 1940s, when industrial chemists started synthesizing such macromolecules, the problem was even more intractable. However, it was known that the segments on the same chain would interact with each other and that no two units could occupy the same space. This phenomenon, called *excluded volume*, works to expand the chain dimensions in dilute solutions by forcing the segments on the (same) chain to avoid each other. It was also known from studies of polymers in organic solvents (e.g. polystyrene in cyclohexane) that the dimensions depend on the sign and magnitude of the interactions between the chain segments and the molecules of surrounding liquid. In “good” solvents, the *intra*-chain repulsion or excluded volume between the segments works to expand the polymer dimensions, as does the solvent–solute interaction. In less-favorable solvents, however, the solvent–solute and solute–solute interactions have opposite signs, and, when they are balanced, the chain dimensions are independent both of segment–segment and of solvent–solute interactions. This phenomenon occurs at the “theta temperature” (T_Θ), at which the size of the chain corresponds to the dimension of a non-interacting polymer coil, unperturbed by excluded-volume effects.

Over 50 years ago, Flory [11] pointed out that, because a typical polymer chain interacts with so many other chains in the solid state, it could not experience the expansion due to excluded-volume effects, because it has no way of knowing whether the segment–segment interactions arise from the same chain or from a different one. Hence, it was predicted, on intuitive grounds, that excluded-volume effects should be annulled, thus allowing polymer chains to adopt random-walk configurations. The parameter used to describe the overall size of a polymer chain is the radius of gyration (R_g), or the root-mean-square distance of all scattering elements from the center of gravity:

$$R_g^2 = \frac{\sum_k f_k r_k^2}{\sum_k f_k} \quad (7.4)$$

The summation runs over all scattering elements (k), which are nuclei for SANS, and is weighted by the scattering length of each atom (see Section 7.2.2). For random (Gaussian) configurations, unperturbed by long-range excluded-volume effects, R_g is proportional to the square root of the number of steps (segments) or molecular weight ($R_g \sim M^{0.5}$), and the overall dimensions are the same as in an ideal (theta) solvent. Only indirect evidence was available to support this

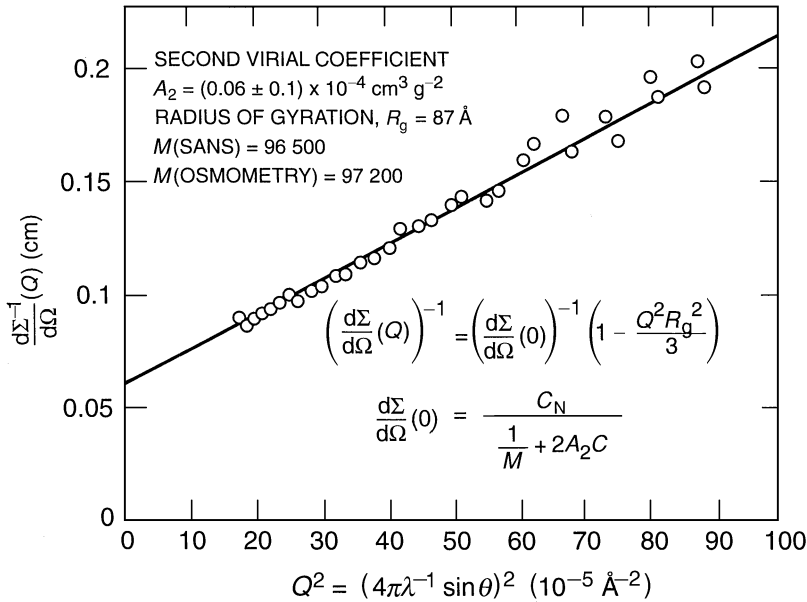


Fig. 7.2. $[d\Sigma/d\Omega(Q)]^{-1}$ versus Q^2 for a sample containing 5 wt% deuterium-labeled PSD molecules in normal (^1H -labeled) polystyrene. (Reproduced with permission from [69]. Copyright 1996 Springer-Verlag.)

assertion, until the development and application of SANS techniques in the 1970s. Figure 7.2 shows data from one of the first SANS experiments [12] performed in the condensed (amorphous) state on a sample of 5 wt.% ^2D -labeled polystyrene (PSD) dispersed in a matrix of normal (^1H -labeled or protonated) polymer. The data are shown in the form of a Zimm [13] plot

$$\frac{d\Sigma^{-1}}{d\Omega}(Q) = \frac{d\Sigma^{-1}}{d\Omega}(0) \left(1 + \frac{Q^2 R_g^2}{3} + \dots \right) \quad (7.5)$$

where $d\Sigma/d\Omega(Q)$ is the differential scattering cross section per unit sample volume, per unit solid angle (Ω) and is equivalent to the intensity $I(Q)$ apart from a multiplicative calibration constant (see Section 7.5.1). $d\Sigma/d\Omega(0)$ is the value of the cross section at $Q = 0$ and the (z -averaged) R_g and (weight-averaged) molecular weight may be determined from the slope and intercept, respectively. The extrapolated cross section ($d\Sigma/d\Omega(0) = 17.4 \pm 0.5 \text{ cm}^{-1}$) leads to a polymerization index of the labeled chains of $N_D = 928 \pm 30$ or a molecular weight of $(96.5 \pm 3) \times 10^3$, in reasonable agreement with independent determinations via osmometry [12]. The radius of gyration is close to that measured in ideal Θ -solvents [3, 12, 14] and the results from this and other SANS measurements [9, 10, 15] demonstrate that

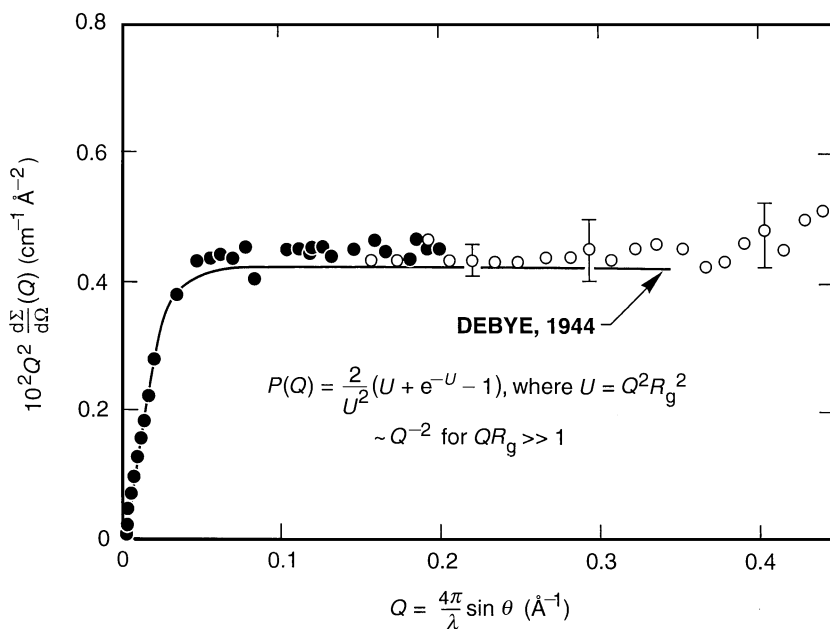


Fig. 7.3. Kratky plot for atactic polystyrene. (Reproduced with permission from [66]. Copyright 1993 American Chemical Society.)

$R_g \sim M^{0.5}$, with a constant of proportionality given by the Flory hypothesis within the typical errors ($\pm 4\%$) of the measurements.

While such results support this model, they are not in themselves conclusive, since the radius of gyration is an average over the whole configuration and, hence, quite different molecular trajectories can have the same R_g . Thus, in order to probe the local chain conformation, as opposed to the overall R_g , measurements have been extended to higher values of Q . As described above, SANS data at higher Q -values are sensitive to shorter length-scales in the system ($D \sim 2\pi/Q$), and thus, as Q increases, the scattering is increasingly determined by the local molecular conformation. Measurements in the intermediate-angle neutron-scattering (IANS) Q -range ($\sim 0.1 \text{ \AA}^{-1} < Q < 0.6 \text{ \AA}^{-1}$) are therefore sensitive to the local conformation of the chain over distances of $\sim 10\text{--}50 \text{ \AA}$, and Fig. 7.3 shows IANS data for atactic (glassy) polystyrene [12] compared with the Debye model of the form factor³ of a single chain with a Gaussian distribution of chain elements [16]:

$$P(Q) = 2[R_g^2 Q^2 + \exp(-R_g^2 Q^2) - 1]/(R_g^4 Q^4) \quad (7.6)$$

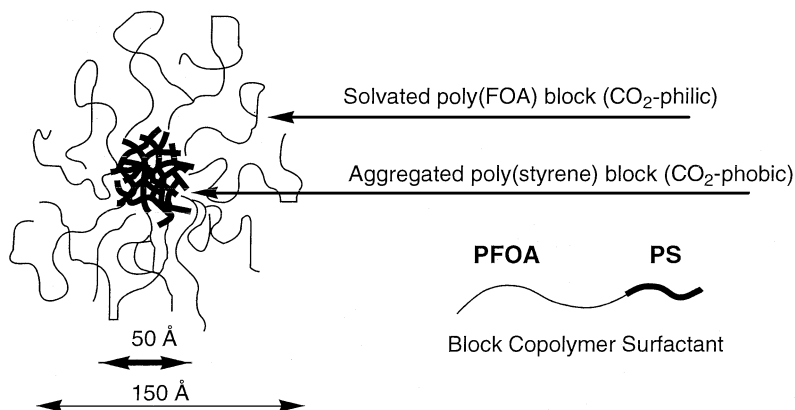
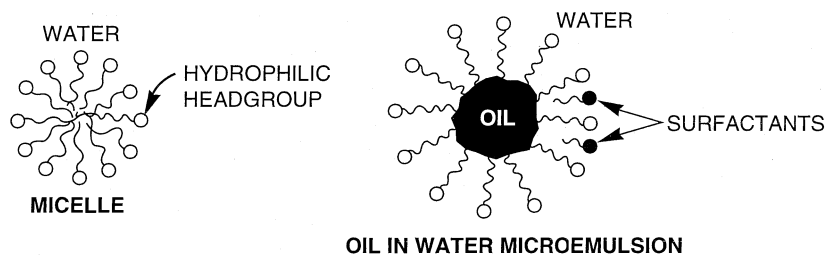
³ Here $P(Q)$ is used to describe the scattering of a single entity, which is a Gaussian single chain in Eq. (7.6). However, the *same* nomenclature is used for a non-Gaussian chain (Eq. (7.24)), a solid sphere (Eq. (7.35)), and a hollow sphere (Eq. (7.36)), all with $P(0) = 1$.

The data are plotted as $Q^2 d\Sigma(Q)/d\Omega$ versus Q (conventionally referred to as a Kratky plot), since this representation enhances the scattering at higher Q and facilitates comparison with models. It may be seen from Fig. 7.3 that $d\Sigma(Q)/d\Omega$ varies as Q^{-2} in this region, leading to a plateau in the Kratky plot, which is closely fitted by the Gaussian coil function (Eq. (7.6)). Surprisingly, the Debye model [16], which is based on general assumptions that are independent of the local chain structure, provides a better fit to the data than that obtained from calculations employing the rotational isomeric state (RIS) model by Yoon and Flory [17], which reflect the local architecture (covalent-bond lengths/angles etc.) of the chain and predict a *positive* slope for the plateau region of the Kratky plot. The data shown in Fig. 7.3 are for fully labeled (D8) PSD molecules, though subsequent measurements [18] on polystyrene labeled only in the chain backbone (D3) indicate that the Kratky plot does exhibit a positive slope as predicted by the RIS model. Thus the agreement with the Debye model is probably fortuitous, resulting from the cancellation of this (positive) slope and the (negative) trend due to the finite lateral dimensions ($\sim 4 \text{ \AA}$) of a fully labeled chain. IANS data from polymethylmethacrylate (PMMA) indicate that the scattering in the intermediate Q -range depends on the tacticity of the chain, and comparisons with theory [15, 19] indicate that the shapes of the curves for atactic, isotactic, and syndiotactic material are accounted for by the RIS model [20]. Similar comparisons have also been made with polycarbonate [21], amorphous polyethylene [22], and polyisobutylene [23] and in each case reasonable agreement with the RIS theory was achieved.

7.1.3 Illustrative example using SANS to study colloidal aggregates (micelles) formed from copolymer surfactants

Above its critical point, carbon dioxide forms a supercritical fluid (SCF), which is widely used in the food industry because of its nontoxic nature, for example in “ultra-clean” processes employed to decaffeinate coffee and to extract cholesterol and triglycerides from eggs. Similarly, SCFs promise to be an environmentally responsible replacement for the organic solvents currently used in polymerizations and many other industrial applications. SANS has been used [24] to elucidate the thermodynamics of CO_2 -soluble polymers (e.g. fluoropolymers and siloxanes) and the technique is particularly suited to studying the structure of matter under pressure, due to the well-known high neutron transmission of many of the materials used in the construction of pressure vessels.

However, many industrially important polymers such as polystyrene (PS) do not dissolve in supercritical CO_2 at readily accessible temperatures ($< 100^\circ\text{C}$) and pressures ($< 500 \text{ bar}$), though DeSimone and co-workers have shown that they may



MODEL OF POLY(FOA-b-STYRENE) MICELLE IN SUPERCRITICAL CO₂

Fig. 7.4. A schematic representation of colloidal aggregates in water and supercritical carbon dioxide.

be “solubilized” by means of emulsifying agents [25]. Such surfactants are generally amphiphilic (i.e. the various components of the molecule have different solubilities) and diblock copolymers, consisting of “CO₂-phobic” and “CO₂-philic” blocks, have been developed that function as surfactants, in much the same way that oil may be solubilized in water by means of detergents (soaps), which surround the oil with a hydrophilic (water-soluble) shell (Fig. 7.4).

SANS has been used widely to study the way in which these molecules self-assemble into aggregates (micelles, microemulsions etc.) in aqueous media [4, 26, 27]. The possibility of forming analogous micelles in SCFs has been debated for a decade [28, 29] and has subsequently been demonstrated via SANS [30, 31], SAXS [32], and other techniques [33]. These micelles consist of a CO₂-phobic core surrounded by a CO₂-philic (fluoropolymer) shell and Fig. 7.4 shows a schematic representation of such micellar aggregates both in aqueous and in CO₂-based systems. SANS has illustrated the way in which polystyrene may be solubilized by means of polystyrene-poly(fluorooctyl acrylate) (PS-PFOA) stabilizers, which form

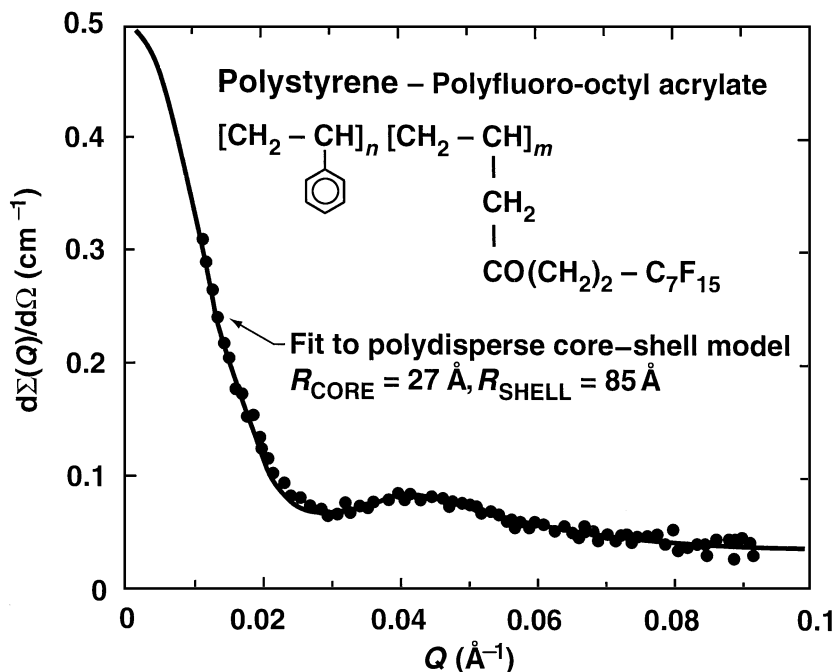


Fig. 7.5. SANS characterization of a block-copolymer micelle in supercritical CO_2 . (Reproduced with permission from [31]. Copyright 1999 International Union of Crystallography.)

micelles within which the CO_2 -insoluble material is solubilized in the core. Thus, styrene may be polymerized in CO_2 using PS-*b*-PFOA surfactants, with yields $>90\%$.

Figure 7.5 illustrates the phenomenon of micelle formation for a PS-*b*-PFOA copolymer with (number-averaged) block molecular weights (M_n) of 3700 and 16 600, respectively, at a temperature of 65°C and a pressure of 343 bar. The cross section is much higher than that for single molecules ($d\Sigma/d\Omega(0) \sim 0.5 \text{ cm}^{-1}$), indicating that the particle has a larger molecular weight than that of an isolated single chain (unimer). The subsidiary maximum at $Q \sim 0.04 \text{ \AA}^{-1}$ is related to the spherical shape and the core-shell morphology of the particle.

The SANS data were modeled [34, 35] as a system of particles with an inner core radius (R_{core}) and outer shell radius (R_{shell}), assuming that there are no orientational correlations, using the same methodology [26, 27, 34] as that developed for aqueous aggregates. For dilute solutions, interparticle interactions may be neglected [4] and several particle shapes were used. The best fits were given by a spherical core-shell model with a Schultz distribution [35] of particle sizes, with a breadth (polydispersity) parameter (Z) and an aggregation number (i.e. the number of molecules per micelle) N_{agg} . A comparison of independently calibrated

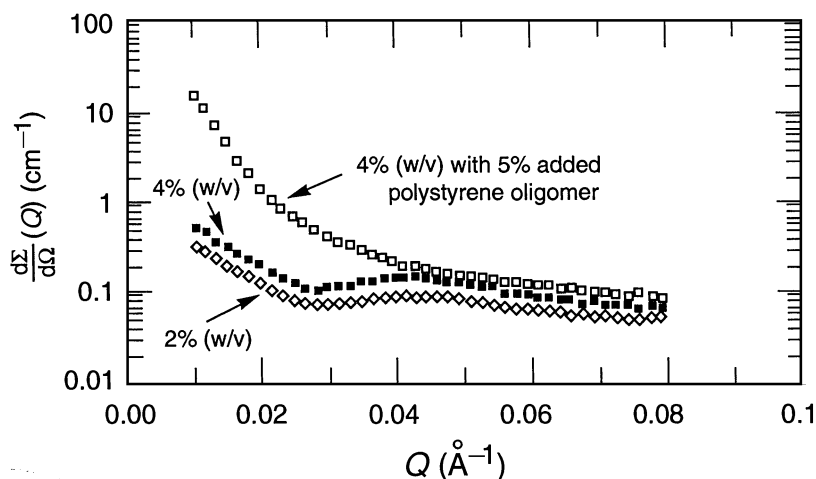


Fig. 7.6. $d\Sigma/d\Omega(Q)$ versus Q for a 3700–16 600 polystyrene–polyFOA block copolymer in supercritical CO_2 as a function of concentration and added polystyrene oligomer. (Reproduced with permission from [24]. Copyright 1999 Institute of Physics (UK).)

SANS and small-angle-X-ray-scattering (SAXS) data obtained under the same experimental conditions gave virtually the same values of the core radii (R_{core}) and aggregation numbers (N_{agg}) and formed a useful cross check on the methodology, since the contrast factors (see below) for SANS and SAXS are quite different [31].

Figure 7.6 shows how the SANS intensity or cross section $d\Sigma/d\Omega(Q)$ (see Section 7.3.1) grows by well over an order of magnitude, along with increases in particle size and aggregation number, when polystyrene is added to the block-copolymer solutions and solubilized within the micelle core. Londono *et al.* [31] have also observed that an increase in density of the solvent has the effect of breaking apart a collection of aggregates and this suggests the existence of a critical micellar density (CMD), which corresponds to the density of the solvent at which the micellar aggregates disappear [30]. Experiments on poly(vinyl acetate)-b-PFOA diblock copolymers have confirmed this phenomenon [35], which is illustrated in Fig. 7.7. Thus, as the pressure is raised from 165 bar to 344 bar, the shapes and absolute magnitudes of the scattering change dramatically from curves characteristic of unimers ($d\Sigma/d\Omega(0) \sim 0.5 \text{ cm}^{-1}$; $R_g \sim 50 \text{ \AA}$), to those reflecting the presence of micellar aggregates ($d\Sigma/d\Omega(0) \sim 14 \text{ cm}^{-1}$; $R_g \sim 150 \text{ \AA}$). The transition from random coils to aggregates is reasonably sharp, falling between 210 and 241 bar. The effect is analogous to that caused by changing the concentration of surfactants in aqueous media, in which a micelle–unimer transition [27, 34] occurs at the familiar critical micelle concentration. Such transitions are also observed in SCF media

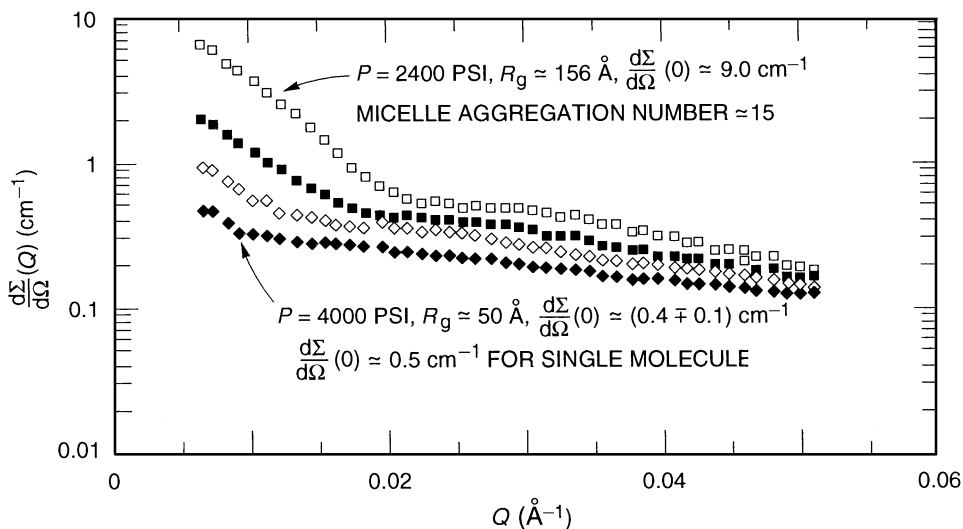


Fig. 7.7. $d\Sigma/d\Omega(Q)$ for 6% (wt/vol) poly(vinyl acetate)-b-polyFOA block copolymers in CO_2 . At high pressures, the scattering arises from single molecules; as the pressure is lowered, micelles form below a critical CO_2 density. (Reproduced with permission from [24]. Copyright 1999 Institute of Physics (UK).)

[31], which also display quite new and unique attributes. Thus, the strength of the solvent is a strong function of the CO_2 -density and the system may be driven from an aggregated to a dispersed state simply by changing the pressure (Fig. 7.7) or temperature [35]. The ability to create and disperse micelles, within which CO_2 -phobic materials can be solubilized, is a property that may be of technological importance.

7.1.4 Why neutron scattering is appropriate and comparison with other low- Q scattering techniques

As described in Section 7.1.1, data at low Q -values probe long length-scales ($D \sim 2\pi/Q$), and X-ray methods have been used widely to determine chain dimensions in dilute solution, lamellar spacings in crystalline polymers, etc. [36]. As mentioned above, such measurements are referred to as small-angle scattering, though it is the Q -range (typically $10^{-3} \text{ \AA}^{-1} < Q < 10^{-1} \text{ \AA}^{-1}$) which determines the size of objects studied and radiation with other wavelengths (e.g. light, neutrons) can provide similar information in different angular ranges. For example, light scattering (LS), with wavelengths in the range 2000–6000 $\text{\AA}$, probes a much smaller Q -range ($\sim 2 \times 10^{-6} \text{ \AA}^{-1} < Q < 2 \times 10^{-3} \text{ \AA}^{-1}$) than does SAXS, even though the angular range can be quite large (up to $2\theta \sim 160^\circ$). Hence, LS measurements probe distance scales, via Eq. (7.3), up to $\sim 10 \mu\text{m}$ and the technique has

been used extensively since the 1940s to determine the molecular weights and global dimensions of polymer molecules, for example in dilute solution [36].

Similarly, SAXS can provide such information, though neither SAXS nor LS could be applied to the condensed state or to concentrated solutions, due to the difficulties of separating the *inter*- and *intra*-chain contributions to the structure, which could be done only in the limit of zero concentration. However, SANS has removed this limitation and, due to a fortuitous combination of several factors (high bulk penetrating power, the ability to manipulate local scattering amplitudes through isotopic labeling (deuteration) or an appropriate choice of solvent (contrast variation), minimal radiation damage and small absorption for most elements), the technique has developed into a powerful tool for the study of polymers. By ^2D -labeling a fraction of the polymer, it is possible to measure the single-chain structure factor and thus the R_g of the polymer chains in the condensed state [3, 9, 10, 13–15, 19, 22, 23, 37] and also in concentrated solutions [38–40]. High-concentration labeling methods have been developed in order to maximize the signal-to-noise ratio of such experiments [41] and SANS has also been applied widely to study the self-assembly of colloidal aggregates of amphiphiles in aqueous [34, 42, 43] and supercritical media [24, 30, 31, 35].

In principle, SANS measurements in dilute solution offer the same information as LS or SAXS, which permits the elucidation of chain dimensions via the electron-density contrast between a macromolecule and solvent. However, even in this limit, SANS has distinct advantages, insofar as greater signal-to-noise ratios may be obtained with the neutron technique since it is less sensitive to dust particles. Contrast for LS depends on the difference in refractive index, whereas that for X-ray techniques depends on the difference in electron density. These differences between polymers and their contaminants are not great, so in general the signal-to-noise ratio is less than that for neutron scattering, for which strong contrast may be achieved by means of deuterium labeling [44].

For LS, the scattering patterns are very dependent on the directions of polarization, though, because of the much higher energies of X-rays, chemical bonding has little effect on SAXS and there is negligible influence of the differences between the directions of polarization of the radiation and molecular orientation [45]. Hence polarization effects, which are important for LS, can be neglected in SAXS and also for SANS experiments on polymers.⁴

Neutrons demonstrate convincingly the wave–particle duality of matter and scattering experiments exploit both aspects of their behavior. A typical “cold” neutron with incident particle velocity $v_0 \simeq 750 \text{ m s}^{-1}$ has a wavelength of $5.3 \text{ \AA}$ (via the de

⁴ Except in the hypothetical case of a material containing elements with unpaired spins (e.g. Fe, Mn, rare earths etc.), in which polarization effects can theoretically occur, due to the interaction with the neutron spin. In practice, polymers do not contain such elements, so polarization effects can also be neglected in SANS experiments.

Broglie relation, $\lambda = h/(mv_0)$, where h is Planck's constant and m is the mass of the neutron), which is of the same order as the nearest-neighbor spacing between polymer molecules. The lifetime of the neutron is 885.7 ± 0.8 s [46], and, since the maximum length of neutron-scattering instruments is $<10^2$ m for SANS (and even less for other instruments), the time of flight during an experiment is typically $\ll 1$ s, so the probability of neutron decay occurring during a measurement is negligible.

The kinetic energy, E_0 , is given by $E_0 = mv_0^2/2 = 0.003$ eV or 4.7×10^{-15} ergs [37], which is much lower than the energy of X-ray photons (~ 10 keV). If no change in energy takes place during the process of scattering, the energies of the incident and scattered beams are equal and the scattering is termed elastic. If energy is transferred, there is a finite difference ($\Delta E \neq 0$) between the energies of the incident (E_0) and scattered (E) beams, which may be regarded as a Doppler shift in the scattered wavelength due to thermal motion of the nucleus, and the process is termed inelastic. If ΔE is small relative to the incident energy ($\Delta E \ll E_0$), the scattering is termed quasi-elastic.

Exchanges of energy between the incident particle and the molecule reflect the dynamics of the system studied [3]. While the angular dependence of the scattering is easily measured both for X-rays and for neutrons, the vibrational and diffusional energies of molecular systems (~ 1 meV) are much lower than the energies of incident X-ray photons and thus energy transfers are difficult to detect for X-ray scattering. In contrast, the energy transfers resulting from neutron scattering are easily resolved and permit the elucidation of dynamic processes. Neutrons are thus a unique probe for studying the condensed state in that they simultaneously have the appropriate wavelength and energy to investigate the structure and dynamics of materials such as polymers [3, 37].

Most neutron-scattering measurements on polymers have involved scattering at small values of the momentum transfer ($Q \rightarrow 0$) and, as mentioned above, this type of measurement is conventionally referred to as *small-angle* (rather than *small- Q*) neutron scattering, though the terms are equivalent for the long-wavelength or "cold" neutrons ($\lambda > 5$ Å). It can be shown [47] that, for such long wavelengths, $Q \rightarrow 0$ implies $E \rightarrow E_0$ and the scattering is predominantly elastic, since any neutron scattered with a large energy transfer ΔE could not satisfy conservation both of energy and of momentum at small Q .

Experiments in the range $\sim 0.6 \text{ Å}^{-1} < Q < 15 \text{ Å}^{-1}$ are conventionally referred to as wide-angle neutron scattering (WANS) or wide-angle X-ray scattering (WAXS), which probe ($D \sim 2\pi/Q$) a distance scale $\sim 0.4 \text{ Å} < D < 10 \text{ Å}$, and contain most of the information relevant for the determination of unit-cell dimensions. WAXS, with a wavelength ~ 1 Å, has been the principal technique for the determination of crystal structures of polymers [6, 48]. Unit-cell dimensions [49], together with details of the

WAXS technique, are given in standard reference works [48–50] and, subsequently, WANS, with wavelengths in the range $1 \text{ \AA} < \lambda < 3 \text{ \AA}$ has supplemented these measurements of crystal structures [51, 52].

In the amorphous state, the intermolecular correlations are more diffuse, and the information available from wide-angle scattering is less precise. A Fourier transform of the data gives a radial distribution function (RDF), which is a weighted sum of interatomic pair-correlation functions $g_{ij}(r)$, which express the probability of finding atomic species i and j separated by a distance r . In the crystalline regions of polymers the $g_{ij}(r)$ reduce to a series of delta-functions defining the interatomic distances in the unit cell. For amorphous materials, the RDFs are generally featureless for $r > 10 \text{ \AA}$, indicating the absence of long-range order between neighboring chains [53].

For most applications in polymer science, neutron and X-ray scattering are examples of predominantly elastic scattering, in which the incident radiation and scattered radiation have the same energy or wavelength. Such experiments give information on the time-averaged structures and conformations of polymer molecules and form the bulk of the work undertaken on polymers. There has been less work involving inelastic processes, in which there is a change of energy on scattering and the incident radiation and scattered radiation have different wavelengths. This technique gives valuable information on polymer dynamics [3, 37, 54–57], though this methodology is beyond the scope of this chapter. Similarly, the reader is referred to existing reviews of structural studies of polymers involving X-rays [36, 58–60] and LS techniques [61]. Over the past two decades, SANS has provided a great deal of new information on polymeric and colloidal structures, as illustrated in Sections 7.1.2 and 7.1.3. This chapter will seek to illustrate how it has complemented and expanded the information from other scattering techniques, while emphasizing the analogies and differences between neutron and photon scattering. The aim of this chapter is to aid potential users who have a general scientific background, but no specialist knowledge of scattering, to apply the technique to provide new information in areas of their own particular interests. This chapter will therefore attempt to explain the physics of scattering with the minimum of unnecessary detail and mathematical rigor.

7.2 Elements of neutron-scattering theory

7.2.1 Transfer of energy and momentum

Scattering in the context of this chapter means the deflection of a beam of radiation (neutrons, X-rays, etc.) from its original direction by interaction with the nuclei or electrons of polymer or solvent molecules in a sample. In an experiment, a

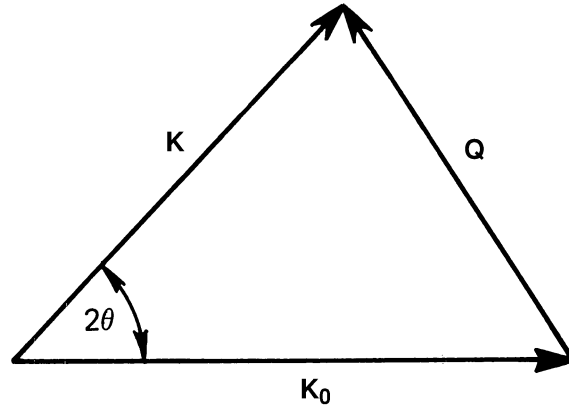


Fig. 7.8. The relationship between the momentum transfer, Q , the scattered wave vector $\mathbf{k}$ and the incident wave vector $\mathbf{k}_0$ in a neutron-scattering event.

proportion of the incident neutrons is scattered and the remaining fraction is transmitted through the sample. The intensity of the scattered neutrons is measured as a function of the scattering angle and/or energy. Figure 7.8 shows the vector diagram for an incident neutron of wavelength λ_0 and velocity v_0 , which is scattered through an angle 2θ , resulting in a final wavelength of λ and velocity v , and the energy gained by the sample (and lost by the neutron) is given by

$$\Delta E = \frac{m}{2}(v^2 - v_0^2) = \frac{\hbar}{2m}(k^2 - k_0^2) = \hbar\omega \quad (7.7)$$

where $\mathbf{k}_0$ and $\mathbf{k}$ are the initial and final wave vectors ($k = 2\pi/\lambda$; $\hbar = h/(2\pi)$). The momentum transfer is

$$\hbar\mathbf{Q} = \hbar(\mathbf{k} - \mathbf{k}_0) \quad (7.8)$$

$$\hbar|\mathbf{Q}| = \hbar[k^2 - k_0^2 - 2kk_0\cos(2\theta)]^{1/2} \quad (7.9)$$

As mentioned above, if $\Delta E \neq 0$, the process is termed inelastic, whereas if $\Delta E = \hbar\omega = 0$ and $\lambda = \lambda_0$, the scattering is termed elastic and $|\mathbf{Q}| = 4\pi\lambda^{-1}\sin\theta$, as in Eq. (7.2).

7.2.2 The scattering length and cross section

SANS, SAXS, and LS all involve interference phenomena of the wavelets scattered by different elements in the system. When a plane wave, described by a wavefunction of unit density [37] interacts with a single nucleus (Fig. 7.9), the scattered wave

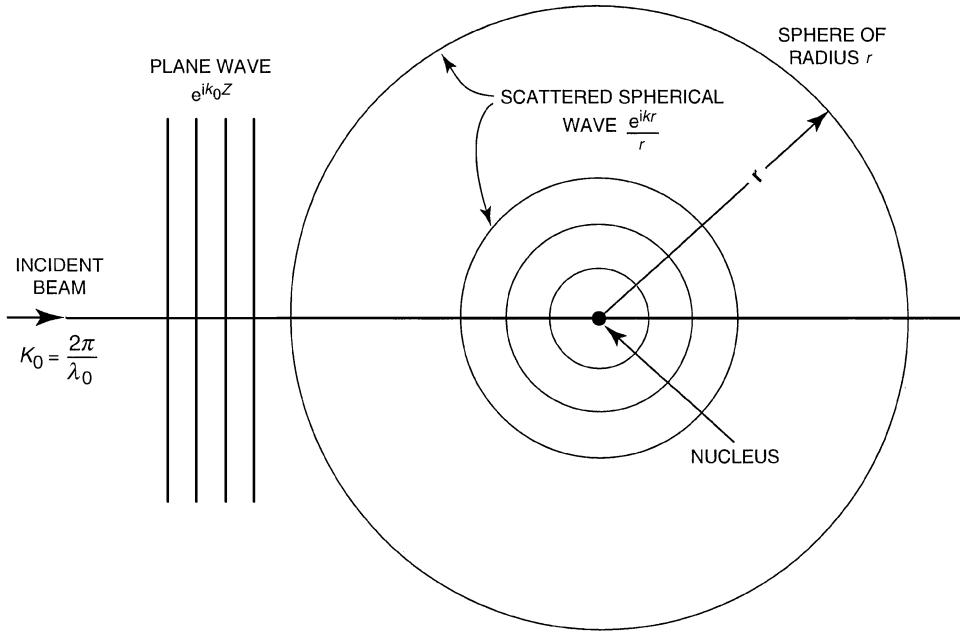


Fig. 7.9. The incident plane wave and scattered spherical wave.

is given by

$$\psi_1 = -\frac{b}{r} \exp(ikr) \quad (7.10)$$

The quantity b has the dimensions of length and is called the scattering length, which may be regarded as a real (known) constant for a given nucleus (isotope). The scattered single-atom cross section is given [62, 63] by

$$\sigma = 4\pi b^2 \quad (7.11)$$

It can be seen from Eq. (7.11) that σ has the dimensions of area. The magnitude of b is typically of the order of 10^{-12} cm, and this gives rise to the usual unit for a cross section which is called a barn⁵ (10^{-24} cm² = 10^{-28} m²). To a first approximation the cross section may be regarded as the effective area which the target nucleus presents to the incident beam of neutrons for the process of elastic scattering. The above cross section (Eq. (7.11)) is usually called the bound-atom cross section because the nucleus was considered fixed at the origin. Where the atom is free to recoil, however (e.g. in the gaseous state), the cross section applicable to this condition is called the free-atom cross section [3,37]. The bound-atom cross section

⁵ The origin of the barn unit is thought to lie in the colloquialism “as big as a barn,” and was recommended in 1950 by the Joint Commission on Standards, Units and Constants of Radioactivity, because of its common usage in the USA (see page 9, *The Atomic Nucleus*, R. D. Evans, McGraw-Hill, New York, 1955).

is generally relevant to polymer studies, which are virtually always conducted on samples of macroscopic dimensions in the solid or liquid state.

Neutrons are scattered isotropically from individual nuclei, whereas, for LS and SAXS, the scattering originates in the electron cloud, so the atomic form factors are in principle Q -dependent. However, the variation is small in practice ($<1\%$ for $Q < 0.1 \text{ \AA}^{-1}$) and is usually neglected for SAXS and LS [36]. The Thompson-scattering amplitude of a classical electron is $r_T = 0.282 \times 10^{-12} \text{ cm}$ [65], so the X-ray scattering length of an atom, f , is proportional to the atomic number ($f = r_T Z$) and increases with the number of electrons per atom. For neutrons, values of b vary from isotope to isotope (see below). If the nucleus has nonzero spin, it can interact with the neutron spin, and the total cross section (σ_{tot}) splits into coherent and incoherent components as explained below.

7.2.3 Coherent and incoherent cross sections

Unlike the X-ray scattering factor, f , which increases with the atomic number (Z) of the atom, there is no general trend throughout the periodic table in the values of b , which vary from isotope to isotope and from nucleus to nucleus of the *same* isotope *if it has nonzero spin*. Because the neutron has spin $\frac{1}{2}$, it can interact with a nucleus of spin I , to form one of two compound nuclei with spins $I \pm \frac{1}{2}$, which have different scattering lengths b^+ and b^- associated with the spin-up and spin-down states, respectively. For a given spin state, J , the number of orientations is $2J + 1$ and thus the number of possible orientations for the compound-spin states of $I + \frac{1}{2}$ and $I - \frac{1}{2}$ are $2(I + 1)$ and $2I$, respectively. The total number of spin states is $2(2I + 1)$ and, because the probabilities of each of these states are equal, the statistical weights are $(I + 1)/(2I + 1)$ and $I/(2I + 1)$, so the average (coherent) scattering length is

$$\langle b \rangle = \frac{I + 1}{2I + 1} b^+ + \frac{I}{2I + 1} b^- \quad (7.12)$$

where the angle brackets represent a thermal average over the spin-state population. We may define a coherent cross section for each isotope by

$$\sigma_{\text{coh}} = 4\pi \langle b \rangle^2 \quad (7.13)$$

whereas the total scattering cross section is given by

$$\sigma_{\text{tot}} = 4\pi \langle b^2 \rangle \quad (7.14)$$

The difference between the two is the incoherent cross section, σ_{inc} , which is given by

$$\sigma_{\text{inc}} = \sigma_{\text{tot}} - \sigma_{\text{coh}} = 4\pi(\langle b^2 \rangle - \langle b \rangle^2) \quad (7.15)$$

If the isotope has no spin (e.g. ^{12}C), then $\langle b^2 \rangle = \langle b \rangle^2$ since $\langle b \rangle = b$ and there is no incoherent scattering. Only the coherent-scattering cross section contains information on interference effects arising from spatial correlations of the nuclei in the system, i.e. the structure of the sample. The incoherent cross section contains no information on interference effects and forms an isotropic (flat) background that must be subtracted in SANS structural investigations (see Section 7.5.4). The incoherent component of the scattering does, however, contain information on the motion of single atoms (particularly hydrogen), which may be investigated via energy analysis of the scattered beam [3, 37, 56].

While most of the atoms encountered in neutron scattering from polymers are mainly coherent scatterers (eg. carbon, oxygen), there is one important exception. In the case of hydrogen (^1H), the spin-up and spin-down scattering lengths have opposite signs ($b^+ = 1.080 \times 10^{-12} \text{ cm}$; $b^- = -4.737 \times 10^{-12} \text{ cm}$), and, since $I = \frac{1}{2}$, we have

$$\sigma_{\text{coh}} = 1.76 \times 10^{-24} \text{ cm}^2 \quad (7.16)$$

$$\sigma_{\text{tot}} = 81.5 \times 10^{-24} \text{ cm}^2 \quad (7.17)$$

$$\sigma_{\text{inc}} = 79.7 \times 10^{-24} \text{ cm}^2 \quad (7.18)$$

For photons, there is no strict analog of incoherent scattering of neutrons due to nonzero spin in the scattering nucleus. Compton scattering, which occurs for X-rays, is similar in that it contains no information on interference effects, i.e. the structure of the sample, and forms a background to the coherent signal. However, to a good approximation this background goes to zero in the limit $Q \rightarrow 0$ and is usually neglected in SAXS studies. Table 7.1 gives the cross sections and scattering lengths for atoms commonly encountered in synthetic polymers, natural polymers, and biopolymers.

These cross sections refer to bound protons and neglect inelastic effects arising from interchange of energy with the neutron. For coherent scattering, which is a collective effect arising from the interference of scattered waves over a large correlation volume, this approximation is reasonable, especially at low Q , for which recoil effects are small. However, for incoherent scattering, which depends on the uncorrelated motion of individual atoms, inelastic effects become increasingly important for long-wavelength neutrons, with the result that the ^1H incoherent cross section, and hence the transmission through the sample, is a function both of the

Table 7.1. *Bound-atom scattering lengths and cross sections for typical elements in synthetic polymers, natural polymers, and biopolymers*

Atom	Nucleus	b_{coh} (10^{-12} cm)	$\sigma_{\text{coh}} = 4\pi b_{\text{coh}}^2$ (10^{-24} cm ²)	σ_{inc} (10^{-24} cm ²)	σ_{abs} (10^{-24} cm ²)	$f_{\text{X-ray}}$ (10^{-12} cm)
Hydrogen	¹ H	−0.374	1.76	79.7	0.33 ^b	0.28
Deuterium	² D (2H)	0.667	5.59	2.01	0	0.28
Carbon	¹² C	0.665	5.56	0	0	1.69
Nitrogen	¹⁴ N	0.930	11.1	0	1.88 ^b	1.97
Oxygen	¹⁶ O	0.580	4.23	0	0	2.25
Fluorine	¹⁹ F	0.556	4.03	0	0	2.53
Silicon	²⁸ Si	0.415	2.16	0	0.17 ^b	3.94
Chlorine	Cl ^a	0.958	11.53	5.9	33.6 ^b	4.74

^aValues are for the naturally occurring element and are an average over the mixture of isotopes; $f_{\text{X-ray}}$ is given for $\theta = 0$, though the angular dependence is small ($<1\%$ for $Q < 0.1 \text{ \AA}^{-1}$).

^bValues of the absorption cross section (σ_{abs}) are a function of wavelength (λ) and are given at $\lambda = 1.8 \text{ \AA}$. As $\sigma_{\text{abs}} \sim \lambda$, values at other wavelengths may be estimated by scaling via the ratio $\lambda/1.8$.

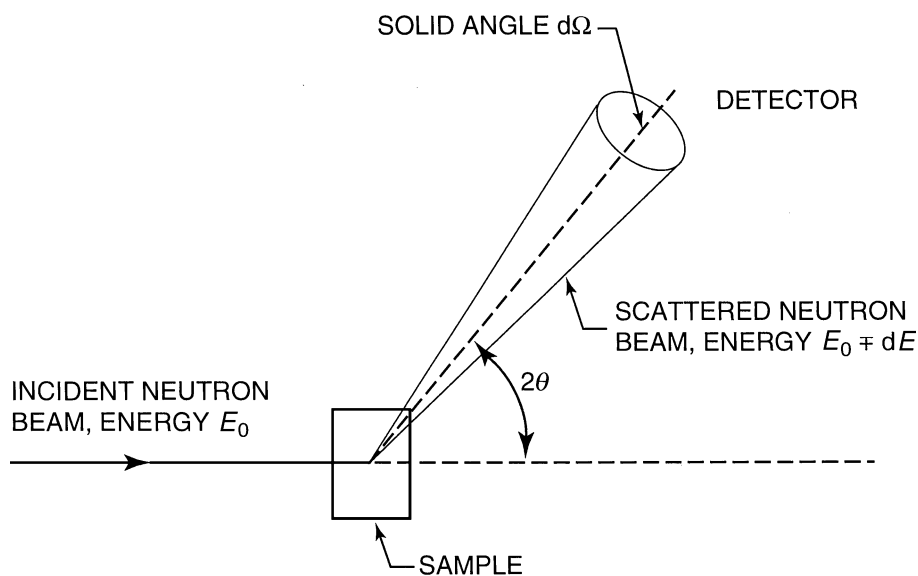
energy of the incident neutron and of the temperature of the sample [66]. Thus, the ¹H incoherent cross section ($\sigma_{\text{inc}} = 79.7 \times 10^{-24} \text{ cm}^2$), although it is widely quoted in the literature, almost never applies to real polymer systems. For example, the effective incoherent cross section σ_{inc} changes by $\sim 30\%$ for polymethyl methacrylate as λ changes from 4.7 to 10 $\text{\AA}$ [67].

Also, because of inelastic effects due to torsion, rotation, and vibration, the effective ¹H incoherent cross section is a function of the particular chemical group (methyl, hydroxyl, etc.) in which the proton is situated [68]. This is illustrated in Table 7.2, which shows the total ¹H-atom cross section in various liquids and polymers, which is dominated by the incoherent component (σ_{inc}), and hence is a strong function of λ and only approaches ~ 80 barns at $\lambda \sim 4.5 \text{ \AA}$ [66, 67]. Note that *none* of these values corresponds to σ_{tot} from Table 7.2.

It can be seen from Table 7.1 that there is a large difference between the coherent scattering lengths for deuterium (²D) and hydrogen (¹H) and that the latter value is actually negative. This arises from a change of phase of the scattered wave and results in a marked difference in scattering power (contrast) between polymer molecules synthesized with deuterium and those with hydrogen atoms along the chain. The basic experiment [37, 66] involves an incident neutron beam (wavelength λ), which is scattered by an assembly of nuclei through an angle 2θ into a solid angle $d\Omega$ (Fig. 7.10), and, as described previously both for SANS and for SAXS, it is conventionally assumed that any change in energy on scattering (ΔE) is small

Table 7.2. *Experimental (total) hydrogen-atom cross sections (σ_{tot}) in various liquids and polymers at room temperature*

Compound	Formula	Cross section per ^1H atom, σ_{tot} (10^{-24} cm ^{2})	
		$\lambda = 9.0 \text{ \AA}$ [68]	$\lambda = 4.75 \text{ \AA}$ [69]
Methanol	CH_3OH	137	
Ethanol	$\text{CH}_3\text{CH}_2\text{OH}$	124	
Isopropanol	$\text{CH}_3\text{CHOHCH}_3$	123	
n-Butanol	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	117	
n-Propanol	$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	113	
Ethenediol	$\text{HOCH}_2\text{CH}_2\text{OH}$	108	
Propanetriol	$\text{HOCH}_2\text{CHOHCH}_2\text{OH}$	100	
Poly(vinyl alcohol)	$-(\text{CH}_2\text{CHOH})_n-$	97	
Polymethylmethacrylate	$-(\text{C}_5\text{O}_2\text{H}_8)_n-$	115	92
Polyethylene	$-(\text{CH}_2\text{CH}_2)_n-$	113	89
Water ($T = 23^\circ\text{C}$)	H_2O	114	89

**Fig. 7.10.** The basic scattering experiment.

relative to the incident energy, E_0 . The coherent component of the scattering contains information on the correlations between *different* nuclei [37, 66] and hence reflects the relative spatial arrangement of atoms in the system (i.e. the structure). Thus, the angular or Q dependence of the scattering is related inversely, via a Fourier transform, to the spatial variation of the structure (Eq. (7.3)).

In principle, the incoherent cross section contains information on the correlations for the *same* nucleus and hence gives information on the time dependence of the position of an individual atom (e.g. vibration, diffusion, etc.). However, extracting such information would require an energy analysis of the scattered beam, which has not hitherto been performed for the vast majority of SANS experiments. These are conventionally undertaken by integrating the scattered neutrons over all energies, so information on the time dependence of the structure is not normally obtained in practice, and the incoherent component of the cross section forms an isotropic (flat) background that must be subtracted in SANS structural investigations. This signal arises from nuclei with nonzero spin (e.g. hydrogen, see Section 7.2.3). Owing to multiple-scattering effects, this background is a function of the sample dimensions, transmission etc. and thus cannot be expressed as a true cross section (see Section 7.5.2). However, it is usually smaller than the coherent signal and can be subtracted to good accuracy by empirical methods [70].

Most of neutron-scattering experiments undertaken on polymers fall into the category of SANS from a fraction of deuterated chains in a matrix of normal (i.e. ^1H -labeled or protonated) polymer and such experiments are examples of predominantly coherent elastic scattering, peaked at $Q = 0$, which gives information on the time-averaged structure (e.g. the chain configuration in the condensed state, polymer compatibility, segregation, etc.). Similarly, for X-ray scattering, the changes in energy are much less than the incident energy, so SAXS and WAXS are effectively elastic processes, which give complementary information on lamellar spacings, the chain configuration in dilute solution, crystal structures, etc. [36, 48, 53].

7.3 Contrast and deuterium labeling

7.3.1 High-concentration labeling

As has already been mentioned, it is well known that LS is particularly sensitive to contaminants (dirt, dust, etc.), and that samples must be carefully filtered [44]. This is one factor that has largely restricted LS methods to dilute solutions and, similarly, neither SAXS nor LS could be applied to the condensed state or to concentrated solutions, due to the difficulties of separating the *inter*- and *intra*-chain contributions to the structure. Accordingly, SANS has been the preferred technique for investigating concentrated solutions [38–41] and polymers in the condensed state [3, 9, 10, 13–15, 19, 22–23, 37]. For such experiments, we may define the coherent-scattering length of a protonated repeat monomer unit (segment) by

$$a_{\text{H}} = \sum_k b_k \quad (7.19)$$

where the summation runs over all the atoms in the ^1H -labeled monomer unit and a similar equation may be written for the coherent-scattering length of a ^2D -labeled monomer unit, a_{D} . If the two polymers, each with polymerization index N and segment (monomer) volume V are blended together so that the volume fractions of ^1H - and ^2D -labeled components are φ_{H} and φ_{D} , respectively, the coherent cross section is given [37, 66] by

$$\frac{d\Sigma}{d\Omega}(Q) = V^{-1}N\varphi_{\text{H}}\varphi_{\text{D}}(a_{\text{H}} - a_{\text{D}})^2 P(Q) \quad (7.20)$$

after subtracting the coherent background due to voids, catalyst residues, or density fluctuations (e.g. crystal–amorphous boundaries, thermal vibrations), and also the incoherent signal (mainly due to ^1H atoms). According to Eq. (7.20), the coherent scattering is governed by the single-chain form factor, $P(Q)$, originating from pairs of monomers belonging to the same chain ($P(0) = 1$) for all values of φ_{H} and φ_{D} . This equation was derived on the assumption that the molecular configurations and interactions are independent of deuteration, which in general is a reasonable approximation. The circumstances under which isotope effects become measurable and perturb SANS experiments are discussed in Section 7.5.1.

Nuclear cross sections have the dimensions of area, and, because sample cross sections are normalized to unit volume, $d\Sigma(Q)/d\Omega$ has the dimensions of inverse length and is typically given in units of cm^{-1} . It is directly analogous to the Rayleigh ratio used in LS [15] and contains information on the single-chain (intramolecular) configuration. The coherent scattering is governed by $P(Q)$, and the mole fraction of each component modulates the scattered intensity with the maximum coherent scattering of the blend occurring for a 50–50 mixture of the two components. Thus $P(Q)$ may be obtained from the measured coherent intensity at labeling levels up to 50%. Although Eq. (7.25) is essentially the same formula as that given in 1918 by Von Laue [71] for random binary alloys, the result was not appreciated in the earliest SANS studies of bulk polymers and concentrated solutions. These investigations relied on analogies with scattering of light and X-rays, in which the limit of zero concentration was required in order to eliminate interchain interference. It can easily be seen that, for $\varphi_{\text{D}} \ll 1$, $\varphi_{\text{H}} \sim 1$ and the cross section is proportional to the mole fraction or concentration, as assumed in the Guinier [57] and Zimm [13] approximations.

7.3.2 Contrast

The quantity $(a_{\text{D}} - a_{\text{H}})^2$ is related to the difference in scattering power between labeled and unlabeled chains and is called the contrast factor. In general, radiation

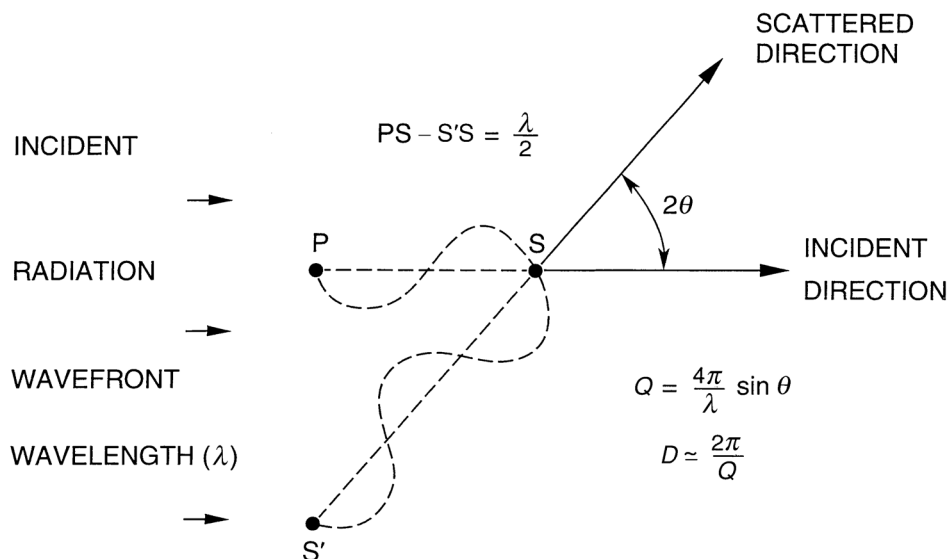


Fig. 7.11. For every point S that scatters radiation through an angle $2\theta > 0$, there is another point S', which scatters radiation exactly 180° out of phase. Therefore, all scattering cancels out unless the scattering power at S is different from that at S', i.e. the scattering power fluctuates from point to point in the sample.

incident on a medium whose scattering power is independent of position is scattered only into the forward direction ($\theta = 0$). For every volume element (S) that scatters through an angle $\theta > 0$, there is another volume element (S') that scatters exactly (180°) out of phase (see Fig. 7.11, in which $PS - S'S = \lambda/2$). Therefore, all scattering cancels out unless the scattering power at S is different from that at S', i.e. fluctuates from point to point in the sample. X-rays and photons of light interact with electrons in the sample and hence are scattered by fluctuations in electron density. Neutrons do not interact with electrons (apart from unpaired spins, for which the interaction arises from the magnetic moment of such elements as rare earths, transition metals, etc.). In general, organic polymers and colloids do not contain such elements, so the only interaction is via nuclear scattering, which arises from differences in the neutron refractive index or scattering-length density (SLD). Because each nucleus has a different scattering amplitude (Table 7.1), the SLD is defined as the sum of coherent-scattering lengths over all atoms lying in a given volume ΔV , divided by ΔV [37, 72]. For example, the SLD of a particular polymer is given by the coherent (neutron)-scattering length (Eq. (7.19)) divided by the monomer volume (V), and Table 7.3 gives typical values of the SLDs of common polymers and solvents. For X-rays or light, the (photon) scattering-length density is the electron density multiplied by the (Thompson) scattering factor of one electron, $r_T = 0.282 \times 10^{-12}$ cm, as explained in Sections 7.2.2, 7.3.3, and 7.6.2.3.

Table 7.3. Neutron SLDs of various polymers and solvents

Polymer or solvent	Density ^a , ρ (g cm ⁻³) (at $T \simeq 23^\circ\text{C}$)	Neutron-scattering-length density, ρ_n (10 ¹⁰ cm ⁻²)
Carbon disulfide	1.63	1.24
Water	1.0	-0.56
D ₂ O		6.4
Xylene	0.880	0.79
Xylene-d ₁₀		6.04
Toluene	0.867	0.94
Toluene-d ₈		5.66
Benzene	0.876	1.18
Benzene-d ₆		5.4
Polybutadiene	0.89	0.41
Polyethylene	0.95	-0.34
Polyethylene-d ₄	1.08	8.13
Polymethylmethacrylate	1.2	1.06
PMMA-d ₈		7.09
Polystyrene	1.05	1.41
Polystyrene-d ₈		6.47

^a The values of SLD are calculated at the indicated densities (ρ), which vary slightly with temperature, tacticity (e.g. for PMMA), degree of crystallinity (e.g. for polyethylene), etc. For different densities, the SLD is proportional to ρ and may be scaled from the values shown. For deuterated materials, it is assumed that the number of monomers per unit volume is independent of deuteration to a good approximation.

The coherent cross section of a system of uniform scattering-length density is zero, though fluctuations may be introduced by means of isotopic substitution, thus giving rise to a finite cross section, which is proportional to $(a_H - a_D)^2$. In order to produce observable SAXS contrast, which can be used to give direct information on $P(Q)$, it is necessary to change the electron density of the chain. Such experiments have been performed by Hayashi and co-workers [73], who labeled polystyrene chains statistically with iodine atoms, and by this means concentrated solutions and bulk polymers were investigated by X-ray scattering. The method seems to give reasonable results after extrapolation to infinite dilution of the iodine-labeled molecules, but this type of labeling relies on changing the chain chemistry and in general it produces a greater perturbation of the configuration than does deuterium labeling. Thus, deuterium labeling in conjunction with SANS has been used in the vast majority of studies of polymer configurations in the condensed state.

The contrast-variation methods which have found wide application in structural biology can sometimes be used to remove a component of the scattering by matching its scattering power with that of the medium in which it is dispersed, and thus

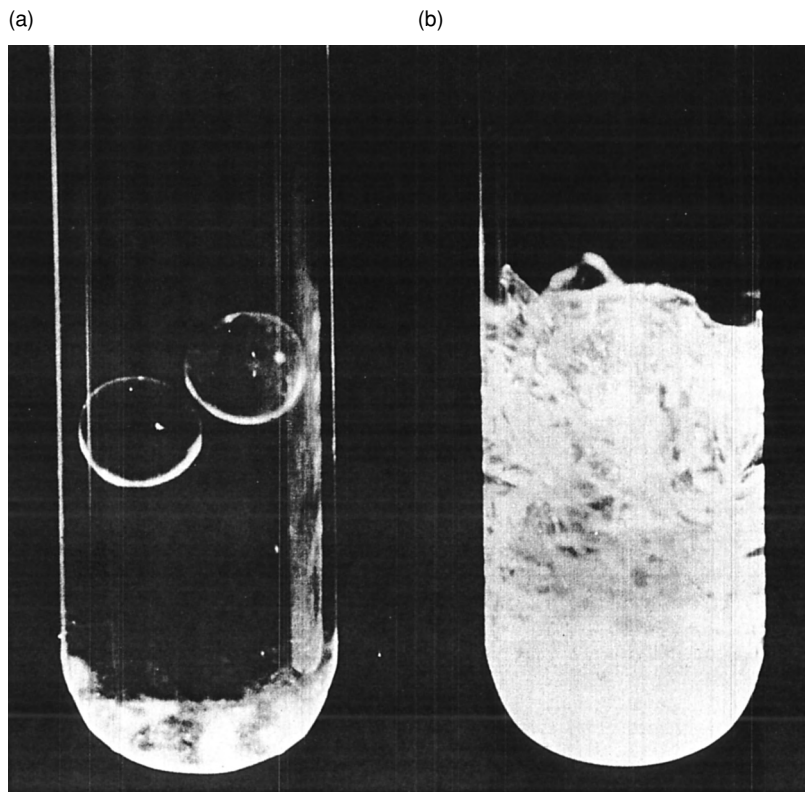


Fig. 7.12. Two tubes containing Pyrex beads in glass wool and solvent: (a) the refractive index of solvent matches that of glass wool; and (b) the refractive index of solvent is different from that of glass wool or pyrex beads and scattering from the glass wool dominates. (Reproduced with permission of D. M. Engelman.)

removing the fluctuation giving rise to the scattering. This principle is illustrated in Fig. 7.12, which was made by Professor D. M. Engelman (Yale University). Both tubes contain two Pyrex beads embedded in (borosilicate) glass wool, which has a different refractive index from that of the beads. When light shines on the tube on the right, both the beads and the glass wool scatter light, but only the glass wool can be seen because it dominates the scattering. In order to observe the beads, the tube on the left has been filled with a solvent that has the same refractive index as the glass wool. Thus, the electron density and hence the scattering power of the glass wool have been matched with those of the solvent, thus eliminating this component of the scattering and making the wool transparent to light. This principle can be applied in SANS experiments by using isotopic solvent mixtures (e.g. $\text{H}_2\text{O}/\text{D}_2\text{O}$) to adjust the scattering power (SLD) of the medium, as for example in studies of core-shell polymer latexes [74–76], as described in Section 7.6.5.

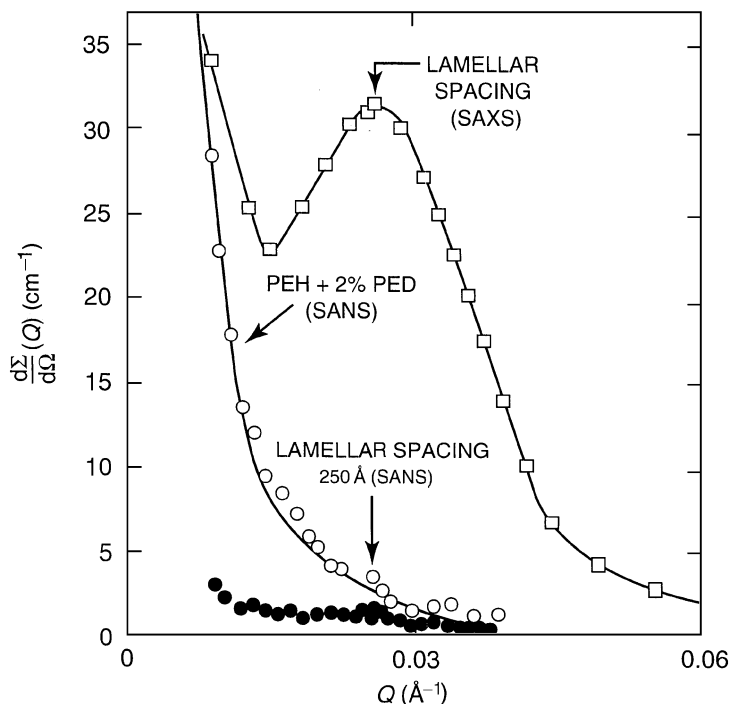


Fig. 7.13. $d\Sigma/d\Omega(Q)$ versus Q for SAXS and SANS data from melt-crystallized polyethylenes.

7.3.3 Examples of SANS and SAXS contrast factors for crystalline polymers

Figure 7.13 shows the SAXS differential scattering cross section of normal (protonated or ^1H -labeled) polyethylene (PEH) after quenching from the melt [22]. The background due to Compton scattering is virtually zero in this Q -range [50] and the SAXS signal arises from fluctuations in density [66, 69]. The interlamellar peak at $Q \sim 0.025 \text{ \AA}^{-1}$ is proportional to the square of the difference in electron density between the amorphous and crystalline regions (lamellae). The up-turn as $Q \rightarrow 0$ probably arises from voids and other large-scale structures, such as spherulites. Figure 7.13 also shows the SANS data for PEH (solid circles), for which a small coherent signal is superposed on a flat (incoherent) background of $\sim 1 \text{ cm}^{-1}$. The open circles show the extra (coherent) cross section produced by adding 2%-deuterated molecules (PED), which is proportional to the difference in contrast $(a_{\text{H}} - a_{\text{D}})^2$ between deuterated and protonated segments. The scattering lengths of PEH (C_2H_4) and PED (C_2D_4) are $-0.166 \times 10^{-12} \text{ cm}^{-1}$ and $4.00 \times 10^{-12} \text{ cm}$, respectively (via Eq. (7.19) and Table 7.1), and, with an average density of $\rho \simeq 0.94 \text{ g cm}^{-3}$, the segment volume is $49.5 \times 10^{-24} \text{ cm}^3$. Because PED and PEH have the same electron density, there is no SAXS contrast between the

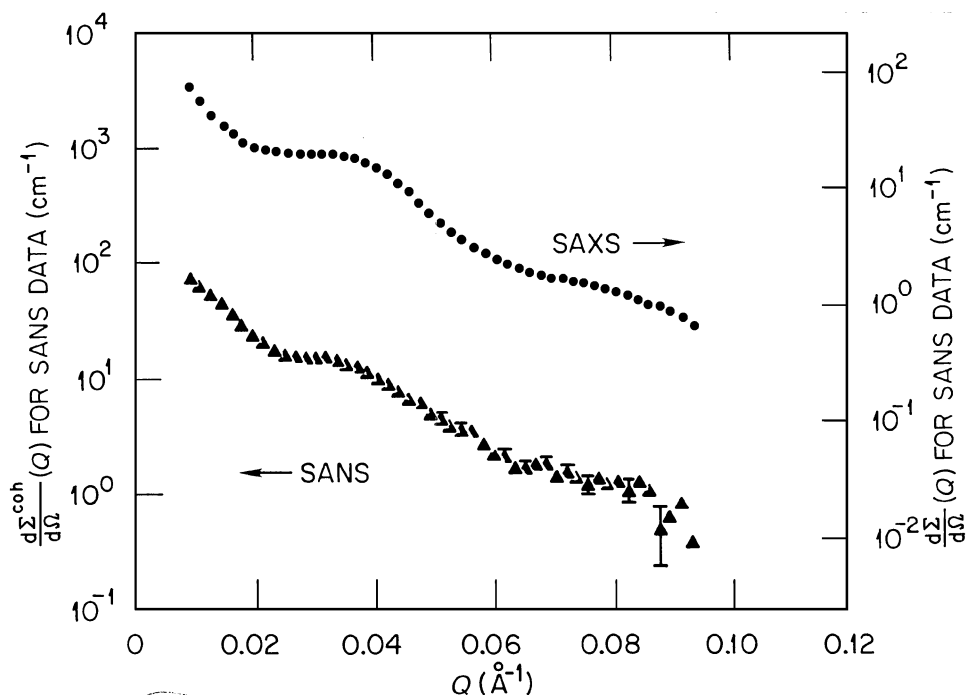


Fig. 7.14. $d\Sigma/d\Omega(Q)$ versus Q for a deuterated polyethylene sample after subtraction of incoherent background. (Reproduced with permission from [77]. Copyright 1988 International Union of Crystallography.)

different isotopes and PEH, PED, and partially labeled samples all have the same SAXS profile.

Departures from the flat incoherent background of the PEH sample (solid circles) are caused by fluctuations in density in the sample and it is just possible to see the peak ($Q \sim 0.025 \text{ \AA}^{-1}$) due to the alternating crystalline and amorphous regions within the lamellae. The coherent signal from SANS is very weak in PEH, however, due to the mutual cancellation between the scattering lengths of carbon and hydrogen (Table 7.1), which makes the SLD for PEH very small ($a_H/\Delta V = (-0.166 \times 10^{-12})/(49.5 \times 10^{-24}) = -0.34 \times 10^{10} \text{ cm}^{-2}$). For PED, there is no cancellation between the coherent-scattering lengths of ^{12}C and ^2D (Table 7.1), and the incoherent background is very much smaller than that for PEH (Table 7.1). Thus, PED should have virtually identical SAXS and SANS coherent cross sections, apart from a scale factor proportional to the square of the ratio of SANS and SAXS SLDs. Since the number of segments per unit volume is the same for SAXS and SANS, this term cancels out and the ratio (R) of the X-ray and neutron cross sections is $R = [16r_T/(4.00 \times 10^{-12})]^2 = 1.27$, where $r_T = 0.282 \times 10^{-12} \text{ cm}$ is the Thompson scattering factor of one electron (see Sections 7.2.2 and 7.3.2), and $4.00 \times 10^{-12} \text{ cm}$

is the neutron-scattering length of a C_2D_4 monomer, which contains 16 electrons. Thus the calculated (1.27) and measured (1.31 ± 0.1) ratios are in reasonable agreement for PED (Fig. 7.14) and for other two-phase materials [77].

7.4 SANS instrumentation

7.4.1 Reactor-based facilities

The first instrument [78, 79] suitable for the study of polymers was built in the early 1970s at the FRJ2 reactor at the Forschungszentrum (formerly Kernforschungsanlage), Jülich, Germany, and pioneered the use of long-wavelength neutrons and a large overall length of the instrument (>20 m). This was a direct consequence of the low brilliance of neutron sources, orders of magnitude below the brilliance of X-ray sources [78]. In order to compensate for this difference, it is necessary to use large sample areas ($1\text{--}20\text{ cm}^2$), which means that the overall size of the instrument must also be large (>10 m) in order to maintain resolution in the range $5\text{--}2000\text{ \AA}$. The FRJ2 SANS facility was also the first to boost the flux of the long-wavelength ($\lambda > 5\text{ \AA}$) or “cold-neutron” component of the Maxwellian spectrum by moderating the neutrons to a lower temperature by means of a cold source containing a small volume of liquid hydrogen at $T \sim 20\text{ K}$. This gives flux gains of over an order of magnitude at $\lambda \sim 10\text{ \AA}$, and it was on this instrument that the initial SANS experiments on polymers were performed. The D11 facility, built during the early 1970s on the High Flux Reactor (HFR) at the Institut Laue–Langevin (ILL), Grenoble, France, incorporated many of the features of the FRJ2 instrument, including a cold source and long (~ 80 m) dimensions [80]. The FRJ2 and HFR facilities have both been upgraded [81, 82] and expanded to be among the most productive SANS facilities worldwide.

At the time of writing, over 30 SANS instruments are now in operation or under construction worldwide, most of which are reactor-based. This number is due in large part to the successful application of SANS to study polymeric and colloidal structures, and the unique information that this technique can provide (see Sections 7.1.2 and 7.1.3). This section will give a brief outline of the operation of a typical SANS instrument, though, in practice, details of instrumental design, operation, calibration, etc. are the responsibility of instrument scientists, and knowledge of all these areas is not needed in order to be able to use the technique. Thus, the use of SANS has spread far beyond recognized experts in the field, and much of the work described in this chapter has been undertaken by nonspecialists, who have applied the technique in areas of their own particular interests. This has been made possible by the development of national and international facilities that routinely provide technical assistance and access to scattering facilities to a wide spectrum of outside users.

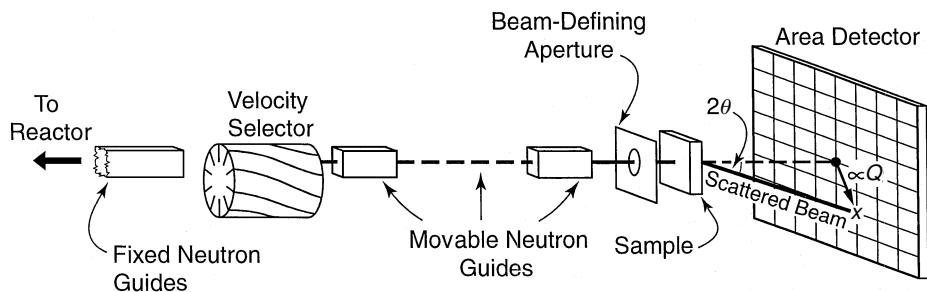


Fig. 7.15. A schematic diagram of a reactor-based SANS facility. Typical ranges are $10^{-3} \text{ \AA}^{-1} < Q < 1 \text{ \AA}^{-1}$ and $0.1^\circ < 2\theta < 15^\circ$.

A schematic diagram of a reactor-based facility is shown in Fig. 7.15, together with typical ranges of Q and 2θ scanned. Fission neutrons are produced in the core, which is surrounded by a moderator (e.g. D_2O , H_2O) and reflector (e.g. Be, graphite), which reduce the energy of the neutrons. A typical moderator/reflector temperature is 310 K, which produces a Maxwellian spectrum of wavelengths, which is peaked at $\lambda \sim 1 \text{ \AA}$ (thermal neutrons). Because of the factor λ^{-4} which enters into the calculation [79] of the scattering power for a given resolution ($\Delta Q/Q$), it is highly advantageous to use long wavelengths and to increase the flux in this region. This may be accomplished by further moderating the neutrons to a lower temperature by means of a cold source containing a small volume of liquid or superfluid hydrogen, placed near the end of the beam tube. Alternative refrigerants include liquid deuterium, and the SANS cameras on the FRJ-2 [78, 79] and ILL [80, 81] reactors were the first to use the combination of a cold source and neutron-guide tubes, as proposed by Maier-Leibnitz and Springer [83]. These are often coated with natural Ni or isotopic ^{58}Ni , and operate by total internal reflection to transport the neutron beam from the cold source to the sample, in a manner analogous to the way in which light may be transported by fiber optics. The guide system (Fig. 7.15) provides a gap for the insertion of a velocity selector to define the wavelength ($5 \text{ \AA} < \lambda < 30 \text{ \AA}$) and bandwidth ($\Delta\lambda/\lambda \sim 5\%–35\%$) of the neutron beam. In addition to fixed neutron guides, most instruments have translatable guide sections and apertures that may be moved in and out of the neutron beam to define the collimation of the incident beam. This is followed by an accessible section (1–2 m) at the sample position to accommodate sample changers, cryostats, furnaces, etc. Thus, when all the movable guides are removed from the beam, the source slit is typically $\sim 10\text{--}20$ m from the sample, and this distance is reduced to 1–2 m when all the guides are translated into the beam to increase the flux through the sample. An area detector (typically a $64 \text{ cm} \times 64 \text{ cm}$ or $100 \text{ cm} \times 100 \text{ cm}$ proportional counter) is often positioned via a motor-driven carrier mounted on rails [84] in the post-sample flight-tube, which is $\sim 1\text{--}20$ m long. Like the incident-neutron

guides, this is normally evacuated to reduce scattering by air, which would otherwise be strong, given overall instrument lengths of $\sim 20\text{--}40$ m.

Most area detectors are multiwire proportional counters [80, 86], with active areas of up to 1 m^2 , and an element (cell) size of $\sim 0.5\text{--}1\text{ cm}^2$, which is chosen to be of the same order as the sample size in order to equalize the various contributions to the instrumental resolution [79]. In general, the detector-response function, $R(Q)$, is Gaussian with a full width at half maximum (FWHM) of $\sim 0.5\text{--}1\text{ cm}$ and the spatial variation of the detector efficiency (ε) is usually measured via an incoherent scatterer (light water, vanadium), which has an angle-independent intensity in the Q -range measured. Thus, to a first approximation, any variation in the measured signal can be attributed to the detector efficiency, and used in the data-analysis software to correct for this effect together with the instrumental background. Second-order corrections representing departures from truly isotropic scattering and unequal path lengths through different regions of the active gas (e.g. ^3He) are usually wavelength- and instrument-dependent [87].

Reactor sources also produce appreciable background (e.g. fast neutrons, γ -rays), which can also be recorded by area detectors. By introducing some curvature into the guides, it is possible to separate out this component, which is not reflected as efficiently as are cold ($\lambda \sim 5\text{--}30\text{ \AA}$) neutrons. Alternatively, the beam may be deflected by supermirrors, which operate on the basis of the discrete thin-film multilayer equations of Hayter and Mook [85], and such mirrors may be designed to reflect up to three or four times the critical angle for internal reflection that can be achieved by natural Ni guide coatings ($\theta_c \simeq 0.1\lambda\text{ (\AA)}$).

The size of the beam at the sample is usually defined by slits (irises) made of neutron-absorbing materials (e.g. ^6Li , cadmium, boron), for which the ratio of scattering to absorption is virtually zero. This has the result that neutron beams can be very well collimated [47, 78] and the ratio of parasitic scattering to the main beam intensity is very small (typically $\leq 10^{-5}$ within $\sim 1\text{ mm}$ of the beam stop). For SAXS, on the other hand, materials which have high absorption (to define a SAXS beam) also have high scattering power, since both parameters are strong functions of the atomic number, and parasitic scattering is usually higher for SAXS.

7.4.2 Ultra-high resolution SANS

The maximum spatial resolution of the “pinhole” SANS instruments described above (Fig. 7.15) is determined by the minimum Q -value ($Q_{\min}$), which has typically been $\sim 10^{-3}\text{ \AA}^{-1}$. Thus, the maximum spatial dimension that can be studied is $\sim 10^3\text{ \AA}$, though recent developments [88] have shown promise for lifting this limit to study the microstructural organization on distance scales $10^3 \leq D \leq 10^5\text{ \AA}$ and overlap with LS techniques. This implies a resolution limit that corresponds to very

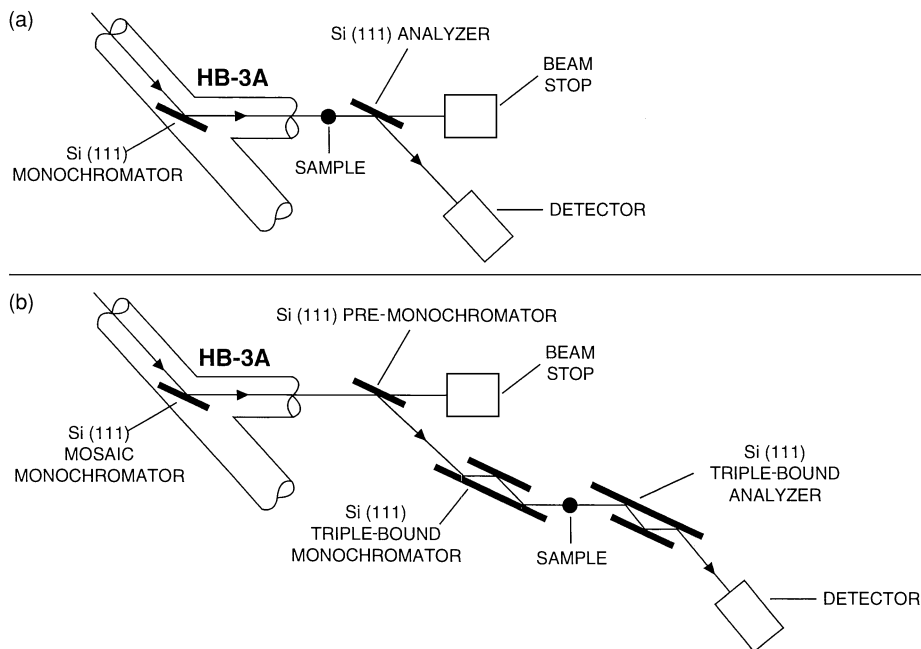


Fig. 7.16. The ORNL double-crystal (Bonse-Hart) USANS facility. (a) $4 \times 10^{-4} \text{ \AA}^{-1} \leq Q \leq 3.5 \times 10^{-3} \text{ \AA}^{-1}$. (b) $3.5 \times 10^{-5} \text{ \AA}^{-1} \leq Q \leq 3.5 \times 10^{-3} \text{ \AA}^{-1}$.

low Q -values (i.e. $Q_{\min} \sim 10^{-5} \text{ \AA}^{-1}$) or scattering angles ($2\theta \sim 1$ arcsec). Such techniques are conventionally referred to as ultra-small-angle neutron scattering (USANS), and the associated instrumentation is quite different from the pinhole SANS analogs. USANS cameras are based on extremely highly collimated neutron beams, which are Bragg-reflected and are also known as double-crystal diffractometers (DCDs), because the main elements are monochromator and analyzer crystals (Fig. 7.16). Thus, an initial monochromator crystal reflects a neutron beam and, when the second (analyzer) crystal is rotated to obtain a “rocking curve,” the beam is reflected into the detector only at the same Bragg angle. When a sample is placed in between the two crystals, it “spreads” the highly collimated beam, thus broadening the rocking curve and making it possible to measure the scattering from the sample, which is exhibited in the difference between the two rocking curves obtained with and without a sample. This signal may be measured down to ultra-small angles, limited only by the inherent width of the Bragg reflection and thus the width of the rocking curve in the absence of a sample characterizes the ultimate resolution, and is the crucial parameter of the DCD. A range of DCD instruments is currently available [88–97], as a result of the growing worldwide interest in this field of structural analysis.

At the time when USANS techniques were first initiated, ultra-small-angle X-ray scattering (USAXS) instruments had already reached a high degree of maturity, on the basis of principles developed by Bonse and Hart [98]. The basic elements of the Bonse–Hart DCD are two channel-cut single crystals wherein X-rays undergo multiple Bragg reflections, which suppress the wings of the rocking curve by orders of magnitude, dramatically improving the sensitivity of the DCD without significant loss of the peak intensity. Thus, USAXS Bonse–Hart DCDs (e.g. with two five-bounce channel-cut crystals [99]) are used in many synchrotron laboratories throughout the world. The rocking curve of a typical USAXS instrument has a FWHM of several arcseconds and the width can be characterized in terms of the intensity of the wings (relatively to the peak intensity) at a given angle (e.g. $2\theta = 10$ arcsec). USAXS cameras typically achieve wing-suppression factors of $I(2\theta = 10)/I(0) \sim 10^{-5}$, and, in principle, this technique should be equally effective in the case of USANS, leading to a similar resolution. However, in practice, experimentally measured rocking curves of neutron DCDs with multi-bounce crystals have not lived up to this expectation, and the wing-suppression factor at $2\theta = 10$ arcsec has been about two orders of magnitude higher than that for X-rays [90, 92, 99].

Figure 7.16(a) shows the original USANS facility [100] installed on the horizontal beam line (HB-3A) at the Oak Ridge National Laboratory High Flux Isotope Reactor (HFIR), with two single-bounce crystals, which was subsequently upgraded [95] with two triple-bounce crystals as monochromator and analyzer (Fig. 7.16(b)). The beam is reflected from a Si(111) mosaic crystal with an average wavelength $\langle\lambda\rangle = 2.59$ Å and angular divergence in the horizontal plane of ± 11 arcmin, which is reduced to ± 2 arcsec by a Si(111) pre-monochromator. The beam then enters the Bonse–Hart (multiple-bounce) DCD and a comparison (Fig. 7.17) of rocking curves shows that the triple/triple combination suppresses the wings by an order of magnitude at $2\theta = 10$ arcsec compared with the original single/single layout (Fig. 7.16(a)). However, the wing-suppression factor, $I(2\theta = 10)/I(0) \sim 10^{-3}$, is about two orders of magnitude higher than that for an optimized Bonse–Hart USAXS instrument [98, 99].

It was subsequently shown [95] that the wings of the rocking curve were contaminated by neutrons propagating inside the walls of the channel-cut crystal and undergoing Bragg reflections from the back surfaces of the walls. This propagation is vanishingly small in the case of X-rays, due to a strong natural absorption in Si, which exceeds that for neutrons by about four orders of magnitude, thus explaining why the wings of USAXS curves are not broadened by this effect. As a result of these findings, the channel-cut crystals [95] were modified with an additional groove in the long wall for a Cd absorber, to prevent the propagation of neutrons through the transparent Si crystal. The rocking curve (Fig. 7.17) of the modified

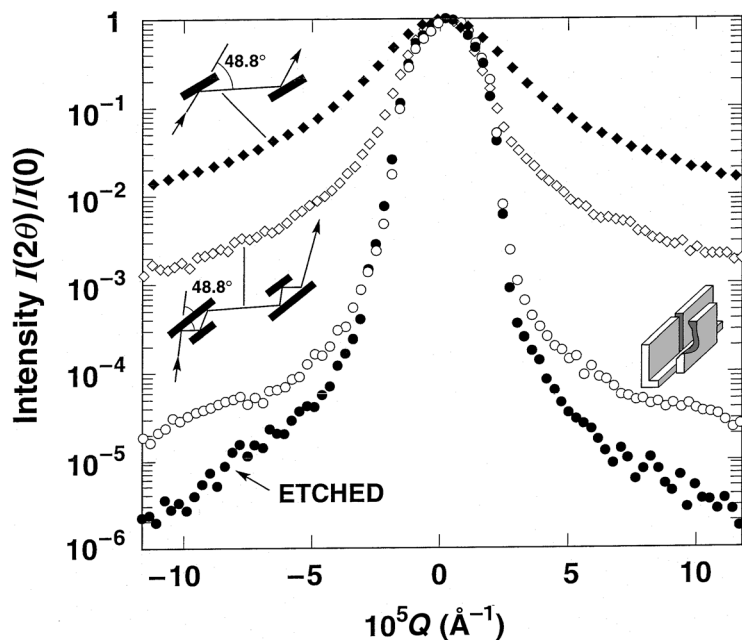


Fig. 7.17. Rocking curves for single- and triple-bounce crystals. A Cd absorber prevents neutron propagation inside the Si walls and improves the USANS sensitivity. Etching removes the surface imperfections and further enhances the signal-to-noise ratio. (Reproduced with permission from [95]. Copyright 1997 International Union of Crystallography.)

triple-/triple-bounce collimation shows that a significant additional reduction of the wings by two orders of magnitude has been achieved and the suppression factor, $I(2\theta = 10)/I(0) = 2 \times 10^{-5}$ is consistent with the performance of USAXS instruments. Etching removes surface imperfections and further enhances the sensitivity by another order of magnitude (Fig. 7.17). These improvements in the signal-to-noise ratio allow the study of particles with dimensions up to $10\ \mu\text{m}$, thus overlapping with LS techniques, and Fig. 7.18 shows combined USANS and pinhole-SANS data [95] for a heterogeneous linear low-density (branched) polyethylene blended with 20%-deuterated (linear) material to provide contrast (see Section 7.6.2.1). The lowest- Q data correspond to polymer domains with dimensions in the range $2\text{--}7\ \mu\text{m}$ arising from liquid–liquid phase separation [96]. Other examples of how USANS complements and extends the information from pinhole SANS are given in [88].

However, Bonse–Hart instruments do not measure a two-dimensional pattern and the data are slit-smeared [95, 96] (see Section 7.5.3). Alefeld *et al.* [101, 102] have proposed an alternative design using focusing toroidal mirrors (FTMs), which

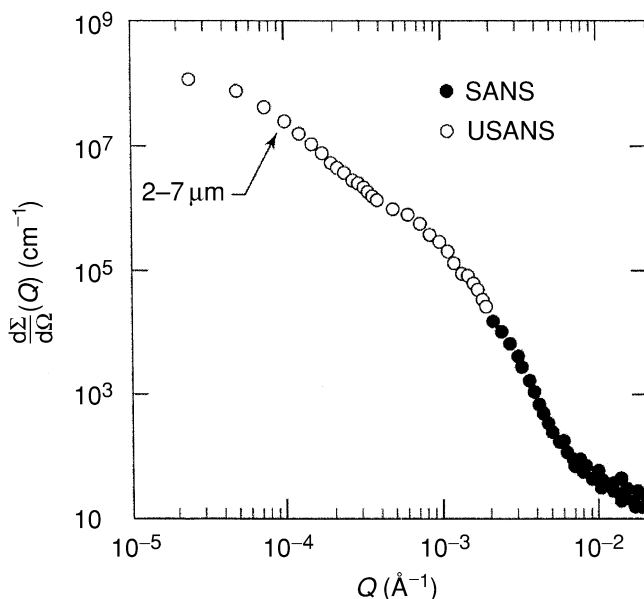


Fig. 7.18. Overlap of SANS and USANS data from heterogeneous linear low-density polyethylene. (Reproduced with permission from [95]. Copyright 1997 International Union of Crystallography.)

have the advantage that the FTM-SANS instrument is quite compact and the count rates remain high. Furthermore, it measures a two-dimensional scattering pattern. Provided that the technological problems of mirror fabrication and the need for a high-count-rate detector with millimeter resolution can be overcome, this type of instrument would facilitate a new range of structural investigations near the borderline where neutron scattering and LS overlap at Q -values $< 10^{-3} \text{ \AA}^{-1}$.

7.5 Practical considerations

7.5.1 Isotope effects

As pointed out in Section 7.3.1, SANS studies of deuterium-labeled polymers were initially based on the assumption [8] that the molecular configurations and interactions are independent of deuteration, or alternatively that the Flory–Huggins interaction parameter for labeled and unlabeled segments of the same species, χ_{HD} , is zero. However, it was subsequently discovered that isotopic substitution *can* influence polymer thermodynamics, in that deuterated and protonated polyethylenes exhibit melting temperatures differing by $\sim 6^\circ\text{C}$, so their mixtures can segregate in the solid state (see Section 7.5.2), due to differential-crystallization effects [103]. Also, the

theta temperature (T_Θ) of solutions of polystyrene (PS) was shown to depend on the isotopic constitutions of the polymer and solvent [104] and the critical temperature of PS–polyvinylmethylether blends depends on the PS isotope employed [105]. Thus, isotopic labeling may influence phase transitions and Buckingham and Hentschel [106] suggested that this might arise from a finite interaction parameter for the segments of the ^1H - and ^2D -labeled species ($\chi_{\text{HD}} \sim 10^{-4} - 10^{-3}$). Subsequently, SANS was used to measure χ_{HD} for a range of isotopic mixtures [107–114]. For a blend of two isotopic polymer species (A and B), one of which is labeled with deuterium, the coherent cross section (after subtracting the coherent and incoherent backgrounds) is given [37, 66] by

$$\frac{d\Sigma}{d\Omega}(Q) = V^{-1}(a_{\text{H}} - a_{\text{D}})^2 S(Q) \quad (7.21)$$

where the segment volume (V) is assumed to be the same for each isomer. $S(Q)$ is the structure factor, which contains information regarding both molecular architecture and thermodynamic interactions. In the mean-field random-phase approximation (RPA), $S(Q)$ is given [115] by

$$S^{-1}(Q) = [\varphi_{\text{A}} N_{\text{A}} P_{\text{A}}(Q, R_{\text{gA}})]^{-1} + [(1 - \varphi_{\text{A}}) N_{\text{B}} P_{\text{B}}(Q, R_{\text{gB}})]^{-1} - 2\chi_{\text{HD}} \quad (7.22)$$

where φ_{A} is the volume fraction of species A ($\varphi_{\text{B}} = 1 - \varphi_{\text{A}}$), R_{gA} , R_{gB} , N_{A} , N_{B} , $P_{\text{A}}(Q)$, and $P_{\text{B}}(Q)$ are the radii of gyration, polymerization indices, and single-chain form factors of the two species. The intra-chain functions, $P_{\text{A}}(Q)$ and $P_{\text{B}}(Q)$, are represented by Debye functions (Eq. (7.6)), based on the assumption of a Gaussian distribution of chain elements. For $\chi_{\text{HD}} = 0$, Eqs. (7.21) and (7.22) reduce to Eq. (7.20).

Equations (7.21) and (7.22) may be generalized to the case in which the species are chemically different (with unequal segment volumes, V_{A} and V_{B}) and applied to polymer blends (see Section 7.6.2.1). However, when this approach is applied to isotopic mixtures, the ^1H - and ^2D -labeled molecules may be regarded as different “species” with the same segment volume (V) and volume fractions, $\varphi_{\text{A}} = \varphi_{\text{H}}$ and $\varphi_{\text{B}} = \varphi_{\text{D}}$. The RPA (Eq. (7.22)) may then be fitted to the data with χ_{HD} as the only adjustable parameter [107–109, 112–114]. Measurements on polybutadiene [107, 109], polystyrene [110], polybutene [109], polyethylene [114], and polydimethylsiloxane [111] confirm the existence of a universal isotope effect arising from small differences in volume and polarizability between $\text{C}-^1\text{H}$ and $\text{C}-^2\text{D}$ bonds [107, 112]. Table 7.4 lists typical values of the isotopic interaction parameter in the range $0.2 < \varphi_{\text{D}} < 0.8$, where χ_{HD} has been shown to be relatively independent of concentration [114].

Table 7.4. *Typical isotopic interaction parameters for various polymers*

Polymer	T (°C)	$10^4 \chi_{\text{HD}}$	Reference
Polystyrene	160	1.8	[108]
		2.3	[110]
1,4-Polybutadiene	50	7.2	[107]
1,2-Polybutadiene (polyvinylethylene)	47	6.8	[109]
1,2-Polybutene (polyethylethylene)	47	8.8	[109]
Polydimethylsiloxane	~296	17	[111]
Polyethylene	160	4.0	[114]

The above results raise the important question of how SANS studies are influenced by isotope effects. As explained earlier, initial SANS experiments on polymers relied on analogies with LS, whereby the limit of zero concentration was required in order to eliminate inter-chain scattering. Under such conditions, the isotope effect contributes almost insignificantly to the intensity, and this may be illustrated by calculating $d\Sigma/d\Omega(0)$ via Eqs. (7.21) and (7.22) for the sample of 5.0 wt% PSD in PSH discussed in Section 7.1.2. The inclusion of an isotopic interaction parameter $\chi_{\text{HD}} \simeq 1.8 \times 10^{-4}$ changes $d\Sigma/d\Omega(0)$ to 17.5 cm^{-1} , compared with 17.4 cm^{-1} , calculated from Eq. (7.5) in the absence of isotope effects. Upon recognizing that information on chain dimensions could also be obtained from concentrated isotopic mixtures, many experiments were conducted under such conditions in order to enhance the intensity and it is under these conditions that isotope-induced segregation effects are manifested. In the condensed state many of the systems studied are solids at room temperature and have been exposed for only a limited time in the liquid state, for example during melt pressing. For polybutadiene, with a glass-transition temperature below -90°C , isotopic blends are liquid at room temperature, and this facilitates the attainment of equilibrium. Hence, isotope effects can be particularly dramatic in this system and Fig. 7.19 shows the scattering cross sections of mixtures of deuterated ($N_{\text{D}} = 4600$) and protonated ($N_{\text{H}} = 960$) polybutadienes as functions of temperature [107]. It can be seen that the extrapolated zero- Q cross section exceeds by large factors the value it would have ($\sim 100 \text{ cm}^{-1}$) if the ^1H - ^2D interactions were negligible. For sufficiently high molecular weight, this system will even undergo phase separation [113], as will other isotopic mixtures (e.g. polyethylene [114]). Thus, it is prudent to evaluate future experiments on the basis of measured values of χ_{HD} (Table 7.4), and to check for excess scattering. This is best accomplished by calibrating data on an absolute scale (see Section 7.5.2) and comparing the measured and theoretical intensities. Some examples of how to make such comparisons are given in [69].

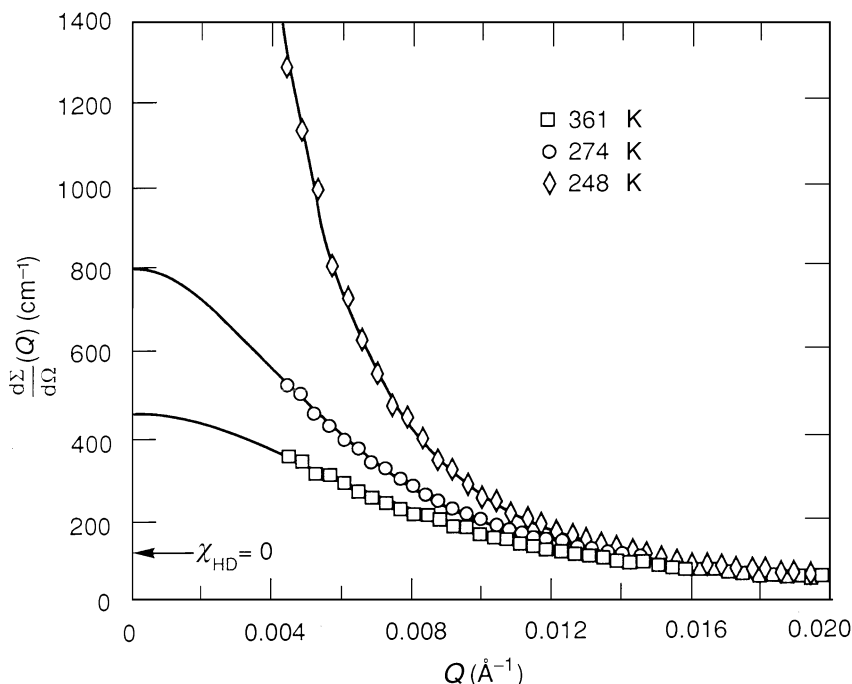


Fig. 7.19. $d\Sigma/d\Omega(Q)$ versus Q for a blend of 69 vol% protonated and 31% deuterated 1,4-polybutadiene at the critical composition. The curves were obtained from the homogeneous-mixture (RPA) scattering function by adjusting λ_{HD} . (Reproduced with permission from [66]. Copyright 1993 American Chemical Society.)

7.5.2 The importance of absolute calibration

The following examples will emphasize the importance of placing intensity data on an absolute scale, typically in the form of a differential scattering cross section $d\Sigma/d\Omega(Q)$, in units of cm^{-1} . As explained in Section 7.3.1, the equivalent quantity for LS is the Rayleigh ratio [15, 66, 69], and, while the use of absolute units is not essential for the measurement of the spatial dimensions (e.g. determining the R_g of a polymer coil), it forms a valuable diagnostic tool for the detection of artifacts, to which scattering techniques are sometimes vulnerable.

Because the cross section varies as the sixth power of the dimensions [57], it is a very sensitive indicator of whether an appropriate structural model has been chosen. For example, scattering results of colloidal micellar solutions may be modeled in terms of core-shell spherical micelles as functions of a set of parameters describing the particle structure (see Section 7.1.3) and interactions [4]. On an arbitrary intensity scale, Hayter has pointed out that it is possible to produce excellent fits of the particle *shape*, which may be in error by as much as *three or four orders of magnitude* in intensity [4]. Thus, absolute calibration allows such artifacts to be

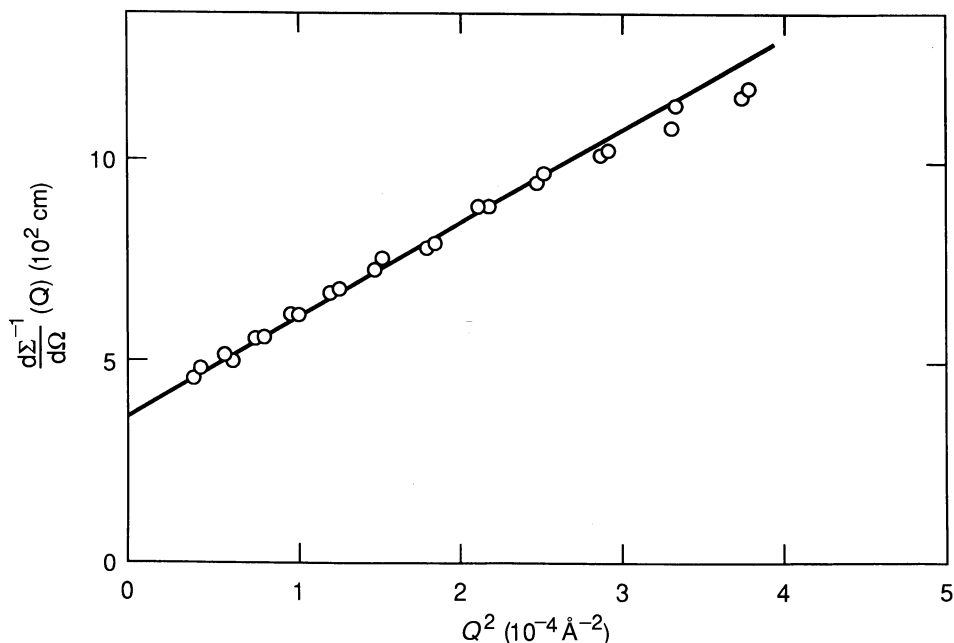


Fig. 7.20. A typical Zimm plot for 6 wt% of PED molecules in a PEH matrix quenched from the melt. $M = 4.5 \times 10^4$ (SANS). $M = 6.0 \times 10^4$ (GPC). $R_g = 132 \text{ \AA}$. (Reproduced with permission from [69]. Copyright 1996 Springer-Verlag.)

recognized, and the model parameters may be restricted to those which reproduce the observed cross section.

Similarly, absolute SANS measurements of melt-crystallized blends of ^1H - and ^2D -labeled polyethylenes (PEH and PED) showed that the scattering could also exceed the expected intensity for randomly mixed molecules by orders of magnitude. This indicated that some kind of aggregation phenomenon was taking place [66, 103]. Figure 7.20 shows a plot of the SANS differential scattering cross section for 6.0 wt% ($\varphi_D = 0.053$) of PED in a matrix of PEH after quenching from the melt. As explained in Section 7.3.3, the coherent-scattering lengths of PEH (C_2H_4) and PED (C_2D_4) are $a_H = -0.166 \times 10^{-12} \text{ cm}$ and $a_D = 4.00 \times 10^{-12} \text{ cm}$, respectively, and the segment volume is $49.5 \times 10^{-24} \text{ cm}^3$. Thus the extrapolated cross section ($d\Sigma/d\Omega(0) = 28.0 \pm 2 \text{ cm}^{-1}$) leads (via Eq. (7.20) with $P(0) = 1$) to a polymerization index (N) of 1600, which is of the same order as the value from gel-permeation chromatography [103]. However, when the same sample is slowly cooled from the melt (Fig. 7.21), the extrapolated cross section increases by over an order of magnitude, together with the “apparent” molecular weight. It is clear that these data do not originate from the scattering from single molecules, and it has been shown that the excess intensity is caused by aggregation or clustering of the labeled

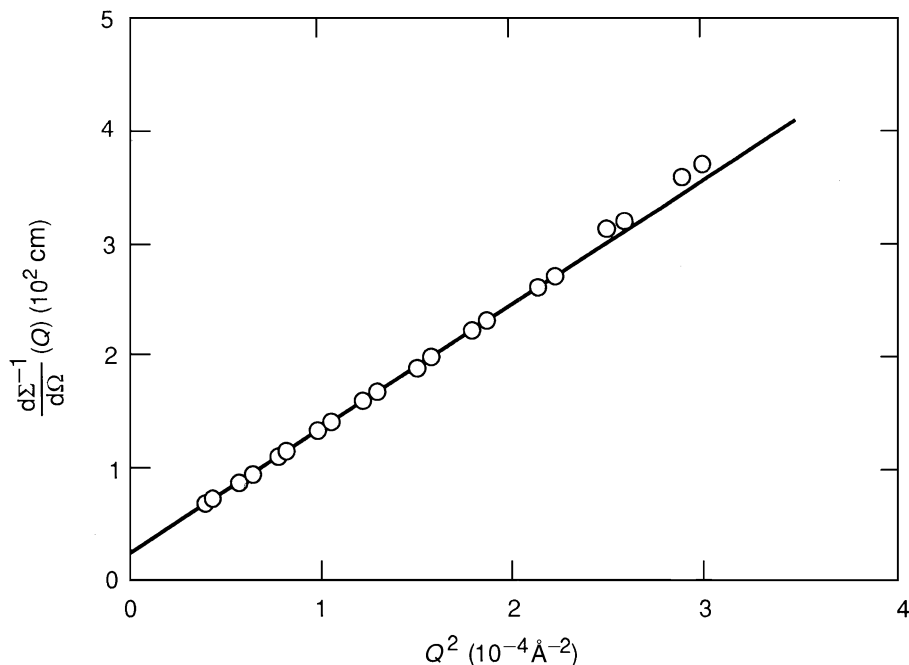


Fig. 7.21. A typical Zimm plot for 6 wt% of PED molecules in a PEH matrix slowly cooled (at 1°C min^{-1}) from the melt. $M = 6.93 \times 10^5$ (SANS). $M = 6.0 \times 10^4$ (GPC). $R_g = 368 \text{ \AA}$. (Reproduced with permission from [69]. Copyright 1996 Springer-Verlag.)

molecules [66, 103], though this would not be clear if the data were in arbitrary units. This behavior illustrates the point referred to above, namely that the intensity is extremely sensitive to the particle or molecular dimensions and even an approximate ($\pm 25\%$) absolute calibration is sufficient to reveal the presence of such artifacts.

In view of the maturity of the SANS technique it is surprising that data are still published in arbitrary units that are functions of the timescale of the experiment and/or the sample dimensions (e.g. thickness). Conversion to an absolute scale may be accomplished by multiplying by a calibration constant and, as explained in Section 7.1.2, the absolute cross section $d\Sigma/d\Omega(Q)$ is defined [116] as the ratio of the number of neutrons scattered per second into unit solid angle divided by the incident neutron flux (neutrons $\text{cm}^{-2} \text{ s}^{-1}$) and thus has the dimensions of area (cm^2). On normalizing with respect to unit sample volume, $d\Sigma/d\Omega(Q)$ has units of cm^{-1} . From the above definition, the relationship between the cross section and the measured count rate $I(Q)$ (counts s^{-1}) in a detector element with area Δa and counting efficiency ε , situated normal to the scattered beam at a distance r from the sample, is given by

$$\frac{d\Sigma}{d\Omega}(Q) = \frac{I(Q)r^2}{\varepsilon I_0 \Delta a A t T} \quad (7.23)$$

where I_0 is the intensity (counts $\text{s}^{-1} \text{cm}^{-2}$) for a sample of area A , thickness t , and irradiated volume At . The measured transmission T is given by $T = \exp(-\mu t)$, where μ is the linear-attenuation coefficient and accounts for the attenuation of the beam on passing through the sample. For SANS it is assumed that the attenuation factor is the same for all scattered neutrons and this approximation is reasonable for $2\theta < 10^\circ$. Similarly, Eq. (7.23) assumes that the solid angle subtended by a detector element is independent of 2θ and this approximation again holds for small angles, for which $\cos(2\theta)$ is close to unity. Since the time dimension cancels out both in the numerator and in the denominator of Eq. (7.23), absolute calibration reduces to measuring the constant $K_N = \varepsilon I_0 \Delta a$, which may be determined by comparison with a standard of known cross section, run in the same scattering geometry for the same time. If an incident-beam-intensity monitor is employed, as is normally the case, comparisons are made for the same number of monitor counts, i.e. the same number of incident neutrons. Various calibration measurements have been used to measure the calibration constant [117], including direct measurement of the beam flux, and calibration via measurements on a predominantly incoherently scattering material (e.g. vanadium or water), monodisperse blends of ^1H - and ^2D -labeled homopolymers (as in Section 7.1.2), and various other standards.

Specific factors that must be considered with each of these methods have been discussed [117] and, in particular, multiple scattering and sample preparation are important when one is using vanadium, which has virtually no coherent cross section because of the fortuitous combination of scattering lengths for parallel and antiparallel scattering with respect to the spin of the nucleus [118]. One disadvantage of this standard is that the cross section is low and also isotropic (see below), so the run times for calibration are relatively long. Owing to limitations on beam-time allocations, arising from the high demand for SANS facilities, users are naturally reluctant to devote a significant fraction of their instrument time to calibration runs. For this reason, it has been a matter of policy at many SANS facilities to provide strongly scattering precalibrated samples in order to allow users to perform absolute scaling with brief calibration runs, which do not detract significantly from the available beam time.

To the author's knowledge, the use of such precalibrated samples was pioneered by Schelten [119] at the FRJ-2 SANS facility (see Section 7.4.1), where an isotropically scattering polyethylene (LupolenTM) standard was calibrated against vanadium. Figure 7.22 compares the angle-independent, predominantly incoherent, cross sections of thin (~ 1 mm) samples of vanadium with normal (^1H -labeled) polystyrene and polyethylene, both of which have signals an order of magnitude higher, thus shortening the time required for calibration runs. However, even with the higher cross section of protonated polymers, such isotropic scatterers cannot be used at low Q -values (long sample–detector distances, r) as the intensity falls as $1/r^2$, and standardization involves a measurement at a low sample–detector

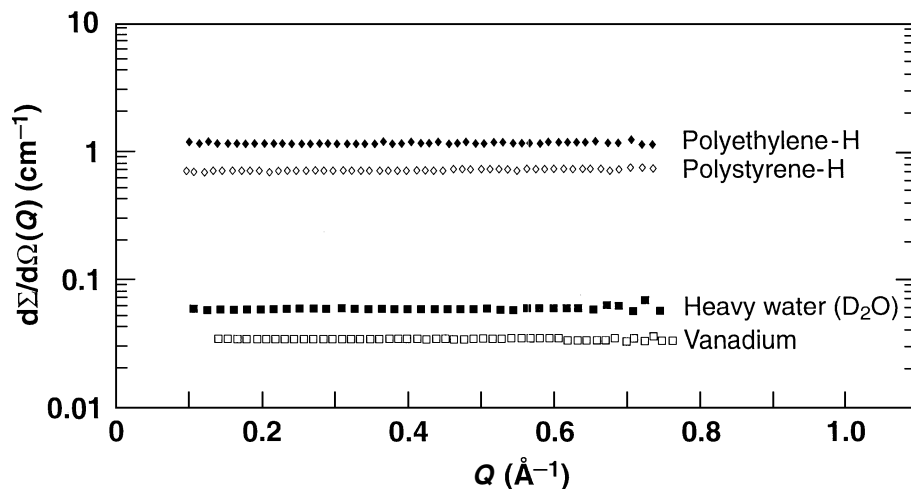


Fig. 7.22. Angle-independent cross sections of predominantly incoherent scattering from vanadium, heavy water (D_2O), polystyrene, and polyethylene.

distance, followed by scaling to the r -value of the measurement via the inverse-square law [119].

The scattering from light water (H_2O) is predominantly incoherent and, because the absorption cross section is small (see Table 7.1), this system has the advantage of providing a much higher intrinsic scattering for calibration purposes [120], and hence has a lower sensitivity to statistical errors and artifacts than does use of vanadium. One disadvantage is that, for samples 1–2 mm thick, the multiple scattering is much higher ($>30\%$) than for vanadium ($\sim 10\%$) and cannot be calculated to the same degree of accuracy [117], because an appreciable fraction of the incident neutrons is scattered inelastically. Such effects are very difficult to model [121, 122] and, moreover, the detector efficiency is a function of the wavelength and this introduces sample- and instrument-dependent factors, depending on how a given detector responds to the inelastically scattered neutrons [123]. The use of Eq. (7.23) would lead to apparent cross sections that are functions of wavelength and are also detector-dependent [123]. Also, because of the strong multiple scattering, the intensity for water or protonated-polymer samples is not proportional to the product tT , Eq. (7.23), and hence it is not possible to define a true cross section that is a material (intensive) property independent of the sample dimensions. The scattering is a nonlinear function of the sample thickness and this is illustrated dramatically in Fig. 7.23, which shows the “cross section” produced by applying Eq. (7.23) to water samples. For a sample thickness of ~ 1 mm, the cross section is ~ 1 cm^{-1} for H_2O (compared with ~ 0.06 cm^{-1} for D_2O as shown in Fig. 7.22). However, due to strong multiple scattering, the “apparent” cross section varies by $>1000\%$ as the H_2O thickness increases from 1 to 10 mm! In spite of this, such samples may still be

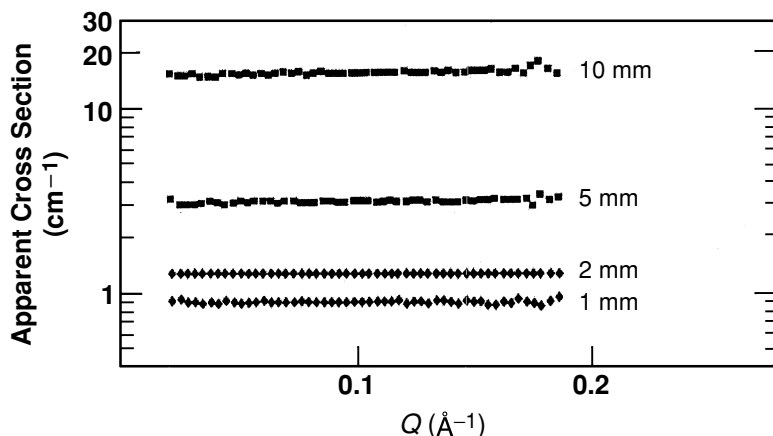


Fig. 7.23. Apparent cross sections from 1-, 2-, 5- and 10-mm-thick samples of light water (H_2O).

used for calibration, provided that the thickness is minimized (~ 1 mm) and they are calibrated against primary standards for a given instrument to take advantage of the intrinsically high signal-to-noise ratio for light-water samples [87, 117, 120–123].

As mentioned in Section 7.4.1, the spatial variation of the detector efficiency (ε) is usually measured via an incoherent scatterer such as light water or a protonated polymer, and Figs. 7.22 and 7.23 show that, despite the fact that multiple scattering in such materials is not fully understood, the data, measured on the ORNL 30-m SANS instrument [84] for predominantly protonated materials (H_2O , polymethyl methacrylate, polystyrene, etc.) are independent of angle. Thus, to a good approximation, the variation in the measured signal is proportional to the detector efficiency, and may be used in the data-analysis software to correct for this effect on a cell-by-cell basis. Second order corrections representing departures from truly isotropic scattering and unequal path lengths through different regions of the active gas (e.g. ^3He) are usually wavelength-, instrument-, and even detector-dependent, and Lindner and co-workers have discussed how such adjustments may be customized for a particular facility [87].

7.5.3 Instrumental-resolution (smearing) effects

Experimentally measured scattering data differ from the actual (theoretical) cross sections because of departures from point geometry in a real instrument. In general, instrumental-resolution effects are smaller for SANS than they are for SAXS. This is because most SANS experiments are performed in point geometry whereas long-slit sources (e.g. Kratky cameras), for which smearing effects are larger, particularly at small angles [124–131], have been used in a significant proportion of X-ray

experiments. Similarly, long-slit sources are used routinely for USANS experiments in order to increase the intensity and most data from such instruments must be corrected for smearing effects [95, 96]. The main contribution to this smearing arises from the large angular divergence of the incident and scattered beams for the long-slit geometry and hence desmearing corrections are often applied to the measured curve in SAXS [129] and USANS [95, 96] experiments. Less attention has been paid to resolution effects in SANS experiments, largely because the corrections are in general smaller for point geometry. However, the corrections are not always negligible, particularly for sharply varying scattering patterns and large scattering dimensions.

In a pinhole SANS instrument (Fig. 7.15), there are essentially three contributions to the smearing of an ideal curve: (a) the finite angular divergence of the beam, $\Delta\theta/\theta$, (b) the finite resolution of the detector, $R(Q)$, and (c) the polychromatic nature of the beam, $\Delta\lambda/\lambda$. For many systems the scattering is azimuthally symmetric about the incident beam, i.e. $d\Sigma/d\Omega(Q)$ is a function only of the magnitude of the scattering vector $|\mathbf{Q}| = 4\pi\lambda^{-1} \sin \theta$. In this case, once instrumental parameters have been characterized, it is possible by numerical techniques not only to smear a given ideal scattering curve, but also to desmear an observed pattern by means of an indirect Fourier transform (IFT) to obtain the actual Q -dependence [123–128]. Where the assumption of azimuthal symmetry cannot be made, the above smearing and desmearing procedures are not applicable, and alternative procedures based on Monte Carlo (MC) techniques have been developed in order to simulate the experimental smearing of a given theoretical scattering pattern that can be expressed analytically or numerically [124]. This procedure permits the estimation of resolution effects even in anisotropic systems, but cannot facilitate the desmearing of the observed pattern. Taken together, MC and IFT methods permit a realistic evaluation of the circumstances under which resolution effects warrant correction. Both procedures have been illustrated via a range of results of experiments that have been performed in a typical pinhole SANS facility [124], where it was shown that smearing effects are small ($<5\%$) for experiments with scattering dimensions $<200 \text{ \AA}$ and that dimensions up to $\sim 1000 \text{ \AA}$ may be accurately resolved after proper evaluation of resolution effects (see Section 7.6.5). Smearing effects may be reduced by decreasing the wavelength range ($\Delta\lambda/\lambda$) or the angular spread ($\Delta\theta/\theta$), though the measured intensity is a strong function of the resolution and Schelten has pointed out that a reduction of $\Delta Q/Q$ by a factor of two will reduce the scattered intensity by over three orders of magnitude [79].

7.5.4 Other experimental considerations and potential artifacts

For sample containment, there are several materials (e.g. quartz, single-crystal Si), that give very little absorption or scattering of neutrons. For SAXS on the

other hand, materials which have high absorption (to define a SAXS beam) also have high scattering power, because both parameters are strong functions of the atomic number, and parasitic scattering is usually higher for SAXS. Similarly, it is much harder to contain samples in a SAXS camera because most materials have substantial absorption, which attenuates the beam. Thus, the high penetrating power of neutrons makes it relatively easy to contain samples in furnaces, cryostats, etc. with a minimum of instrumental backgrounds.

For singly scattered neutrons, the intensity $I(Q)$ is proportional to the sample thickness (t) and transmission ($T = e^{-\mu t}$) and is maximized for $\mu t = 1$, where μ is the linear-attenuation coefficient. Thus, the optimum sample thickness is ~ 1 – 2 mm for H_2O and protonated polymers (H-blanks) and ~ 1 cm for D_2O and D-blanks. Measurements in the IANS range ($\sim 0.1 \text{ \AA}^{-1} < Q < 0.6 \text{ \AA}^{-1}$) are particularly sensitive to the incoherent background, which can be of the same order of magnitude as the coherent signal. This is because the coherent scattering falls rapidly with angle (e.g. as Q^{-2} for polymer coils as in Eq. (7.6), or as Q^{-4} in the Porod regime (see Section 7.6.2.2)). The coherent intensity of singly scattered neutrons, $I(Q)$, is proportional (Eq. 7.23) to the sample thickness (t), transmission (T), and sample area (A). Thus, measurements on samples with different dimensions (t , A) and transmissions (T) may be normalized with respect to the same volume in order to give a (coherent) cross section that is an intensive (material) property independent of the sample dimensions. This is based on the assumption that neutrons are scattered only once before being detected and this has been shown to be a reasonable approximation for coherent SANS from polymers [132] and other materials [133], with cross sections $d\Sigma/d\Omega(0)$ typically $< 10^3 \text{ cm}^{-1}$. For samples with higher cross sections that exhibit substantial coherent-coherent multiple scattering, a common way to recognize and minimize this artifact is to measure the cross section as a function of the sample thickness and to extrapolate to $t = 0$.

For incoherent scattering, samples 1–2 mm thick containing hydrogen (H_2O , protonated polymers, etc.) give rise to appreciable multiple scattering, as explained in Section 7.5.2. The difficulties in estimating an incoherent background to subtract from a given “sample” and thus isolate the residual coherent cross section are illustrated in [19], where the apparent cross section produced by three protonated PMMA-H blanks, after normalizing via Eq. (7.23), was shown to vary by $> 50\%$ over a typical range (~ 0.2 – 1.2 mm) of sample thicknesses. An even more dramatic variation of the apparent cross section occurs for predominantly incoherent scattering samples (e.g. water), as is shown in Fig. 7.23. Thus, both for PMMA and for water, the data contain appreciable multiple scattering (which is not proportional to the thickness or transmission), and cannot be normalized to a true cross section that is independent of the sample dimensions. Moreover, as explained in Section 7.2.3, the bound-atom cross section (Table 7.1) cannot be used to calculate the background, because the incoherent cross section for hydrogen

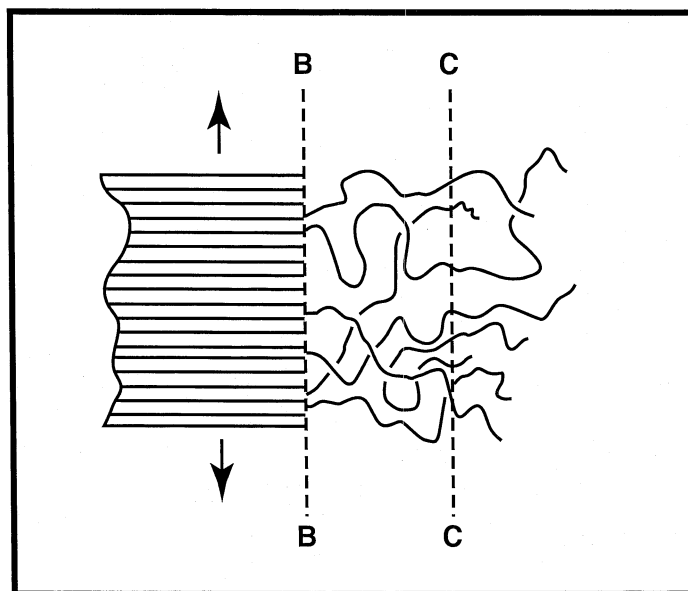


Fig. 7.24. A schematic representation of the interfacial zone transverse to the chain axis.

($\sigma_{\text{inc}} = 79.7 \times 10^{-24} \text{ cm}^2$), although it is quoted widely in the literature, almost never applies to real polymer systems. However, the incoherent scattering is independent of Q to a good approximation (see Figs. 7.22 and 7.23), and empirical methods for subtracting this background have been developed [70, 73].

7.6 Some applications of scattering techniques to polymers

7.6.1 Semicrystalline polymers and chain folding

7.6.1.1 Melt-crystallized polymers

As early as the 1950s, it was known that polymer crystals precipitated from solution had the form of thin platelets or lamellae with lateral dimensions orders of magnitude larger than the crystal thickness ($\sim 10^2 \text{ \AA}$). Moreover, the chain axis was known to be perpendicular to the lateral (wide) face and thus, for high molecular weight chains, its length was much larger than the crystal thickness. Crystals with similar dimensions were also discovered in melt-crystallized polymers, and the chain orientation was shown to be the same as that in those grown from solution. It therefore follows that the molecule must traverse the crystal many times and fold back at the surface of the lamellae for both types of material. A complementary line of reasoning supporting the concept of chain folding in lamellar crystals is illustrated in Fig. 7.24, where the plane B–B is located at the surface of the crystal and C–C is located in the isotropic amorphous region. The flux of chains (i.e. the

number per unit area) emanating from the crystal is given by $N_c = 1/A_c$, where A_c is the cross-sectional area in the crystalline state. The flux of chains (N_a) intersecting the plane C–C was estimated by Flory [134] as $N_a = 1/(2A_a)$, where A_a is the cross-sectional area of a chain in the amorphous state. For flexible polymers, $A_a/A_c \sim 1$, so it follows that $N_a/N_c \sim \frac{1}{2}$ and approximately half the flux of neutrons emanating from the crystal must be dissipated before entering the amorphous region. This implies that there must be an interfacial region on the surface of the crystal over which the dissipation takes place and one way for this to occur is for a significant number of the chains to “fold back” and re-enter the crystallite of origin.

Thus, it is generally agreed that lamella-like crystals are the main component of the morphology both of melt- and of solution-grown semicrystalline polymers, with amorphous material between the lamellae. The chains are at an angle (0 – 45°) to the lamellar normals and have lengths much greater than the lamellar thickness, so a considerable fraction of chains must return to the same crystal. However, the arrangement of the molecular chains within the lamellae has been debated extensively, and various models concerning the ways that molecules fold at the surface of the lamellae have been proposed. These range from tight, “hairpin,” connections (with the chain exiting and re-entering the crystal in an adjacent crystallographic lattice site) to models postulating long loops or “loose folds” or even a “switch-board” model in which “sharp” folding events are rare. Electron microscopy has widely been used to study lamellae, though this technique cannot provide detailed information concerning the nature of the re-entry. In principle, this information is available from neutron scattering from polymers in which some of the chains are deuterium-labeled to make them “visible” in the condensed state (see Section 7.3.1).

In general, SANS experiments reveal that the overall radius of gyration, R_g , remains largely unchanged upon crystallization from the melt and hence has an $M^{1/2}$ dependence in both the molten state and in the crystalline states [22, 37, 52, 66]. This indicates that the molecules crystallize with a similar distribution of mass elements to that possessed in the melt and hence are distributed over several lamellae in the crystalline state. These measurements were made in the small-angle range at low Q -values (10^{-3} – $10^{-1} \text{ \AA}^{-1}$), and are therefore sensitive to long length-scales ($D \sim 2\pi/Q$). Hence, they contain no information on the mutual arrangement of stems (i.e. the straight sections of a chain traversing a crystalline lamella). This may be obtained from experiments in the intermediate-angle range ($0.1 \text{ \AA}^{-1} < Q < 0.6 \text{ \AA}^{-1}$), which are sensitive to the correlation of stems over distances of ~ 10 – $50 \text{ \AA}$. This type of measurement has been made for several systems [22, 135, 136] and results have been compared with a variety of model calculations that simulate the chain trajectory [22, 137–143]. Figure 7.25 shows

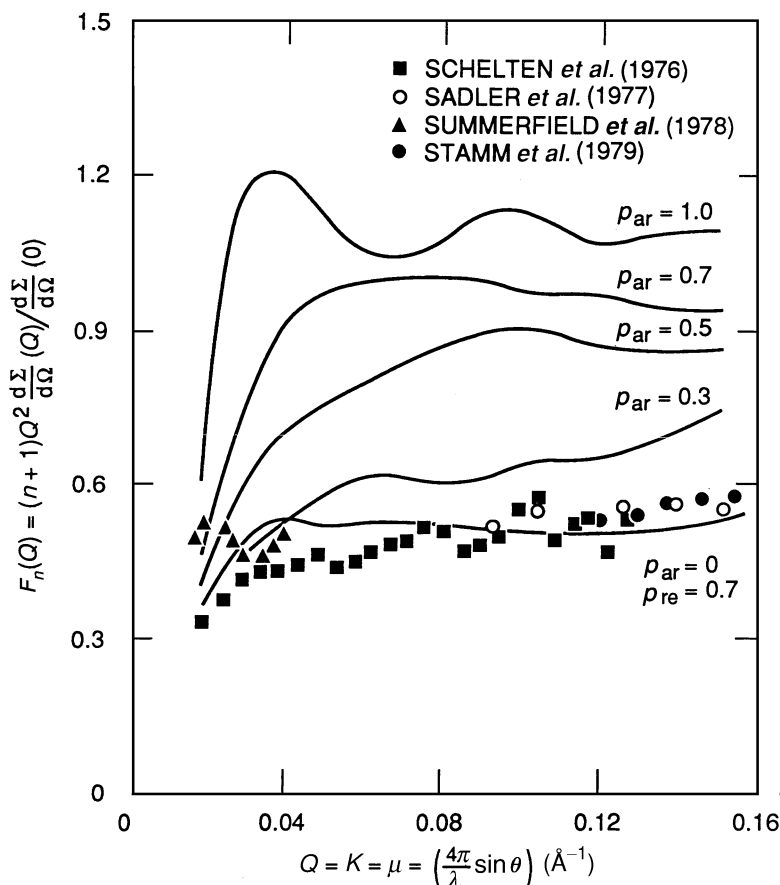


Fig. 7.25. Calculation of $F_n(Q)$ for PE ($n = 2000$) as a function of the probability of regular (adjacent) folding (p_{ar}). (Reproduced with permission from [66]. Copyright 1993 American Chemical Society.)

IANS data for quench-crystallized polyethylene, for which the scattering function $F_n(Q)$ is defined by

$$F_n(Q) = (n+1)Q^2 P(Q) = (n+1)Q^2 \frac{d\Sigma/d\Omega(Q)}{d\Sigma/d\Omega(0)} \quad (7.24)$$

and $P(Q)$ is the form factor of a single chain⁶, which contains n bonds. There is excellent consistency among several independent measurements with samples of different molecular weights and levels of ^2D -labeling, indicating that the data are not perturbed by isotope effects due to the thermodynamic differences between ^1H - and ^2D -labeled segments (see Section 7.5.1).

⁶ The same nomenclature, $P(Q)$, is used for the single-chain form factor both in the amorphous state (Eq. (7.6)) and in the crystalline state (Eq. (7.24)), though the chain is not assumed to be Gaussian in the latter.

Figure 7.25 compares the IANS data with results from model calculations based on Monte Carlo statistics as a function of the probability (p_{ar}) that the stem will fold adjacently along the (110) plane. It may be seen that this leads to an approximate Q^{-2} -dependence for $d\Sigma/d\Omega(Q)$ and hence a plateau in the (Kratky) plot of $Q^2 d\Sigma/d\Omega(Q)$ versus Q . The plateau levels differ by a factor of about two for the extremes of random ($p_{\text{ar}} = 0$) and adjacent ($p_{\text{ar}} = 1$) re-entry and Yoon and Flory [138] concluded that $p_{\text{ar}} < 0.3$, which is inconsistent with regular folding. Alternatively, calculations performed as a function of the number of stems folded adjacently in a central-cluster model [141, 142] were interpreted in terms of higher probabilities ($p_{\text{ar}} \sim 0.7$) of adjacent folding. The latter conclusion involved plotting the experimental data as a function of the molecular weight (M) of the labeled chains, measured both by SANS and by chromatographic techniques. This procedure introduces further uncertainty ($\sim 30\%$, depending on which value of M is used) into the height of the plateau level in $F_n(Q)$ and hence makes the comparison less precise. It may be seen from Eq. (7.24) that, for high molecular weight material ($n > 1000$; $n \simeq (n + 1)$), $F_n(Q)$ is independent of M , since $d\Sigma/d\Omega(0)$ is proportional to n . This parameter may therefore be canceled out, thus making $F(Q)$ independent of M , and this would lead to a lower estimate of p_{ar} .

Sadler has reviewed data both on quenched and on slowly cooled melt-crystallized polymers and estimated that the probability of adjacent re-entry rows is ~ 0.3 – 0.5 . The average number of stems in adjacent sequences is $\sim (1 - p_{\text{ar}})^{-1}$, so probabilities < 0.5 are inconsistent with regular uninterrupted folding of more than two or three stems in one crystallographic plane [143]. Longer sequences of adjacent stems would lead to a modulation of the wide-angle-scattering pattern ($Q \sim 1 \text{ \AA}^{-1}$), and such features are not observed for melt-crystallized polyethylene [144, 145]. However, the fact that nearest-neighbor re-entry is improbable does not mean that re-entry is completely random. Calculations [138, 141, 142] indicate that most folds are relatively close, and that the folds which are not adjacent are “near” and rarely involve stem separations of greater than three nearest neighbors.

Hoffman *et al.* [141, 142] have pointed out that anomalously high densities could arise in the interfacial boundaries between amorphous and crystalline regions, as a result of the space-filling considerations noted by Flory [134]. If the stems are at an angle to the lamella normals, or the transition between crystal and amorphous regions is not abrupt, space-filling anomalies are avoided [146, 147]. Such considerations support the idea that the boundary between the crystalline and amorphous regions is not sharp, and the width of the interfacial region (10 – $30 \text{ \AA}$) represents the distance over which the flux of chains emanating from the crystal is dissipated and accommodated within the isotropic interlamellar regions [134].

7.6.1.2 Solution-crystallized material

As pointed out by Sadler and Keller [148, 149], the radius of gyration of polyethylene chains in solution-crystallized materials is much smaller than that in melt-crystallized samples and is relatively independent of the molecular weight. The IANS data are also qualitatively different from those for melt-crystallized material and exhibit a peak [143, 148–151] at $Q \sim 0.1\text{--}0.2 \text{ \AA}^{-1}$ in the Kratky plot (Fig. 7.26). On the basis of these results, a “superfolding” model in which the folding of a chain is not confined to a single layer and, after executing a number of folds in a given plane, the molecule continues to fold in an adjacent layer was proposed [148–150]. This produces a peak in the Kratky plot [138, 143, 148, 149], though the model overestimates the measured intensity. In order to produce agreement with experiment, the adjacent stem arrangement must be “diluted” by a factor of $\sim 2\text{--}3$. One mode of “dilution” is an array of stems confined to several layers, but not densely packed in any of them, such that the stems are seldom adjacent in a given growth plane [138].

Alternatively, it has been proposed [148, 149, 151] that a molecule may be distributed over several (110) sheets, but $\sim 75\%$ of the folds are connected to adjacent

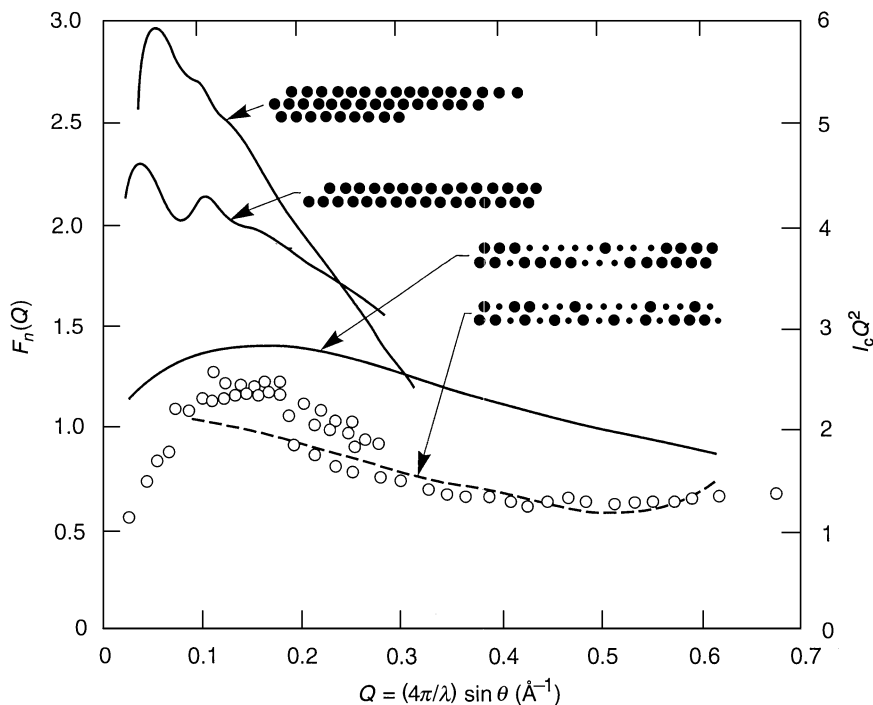


Fig. 7.26. Kratky plots and model calculations for solution-crystallized polyethylene. (Reproduced with permission from [66]. Copyright 1993 American Chemical Society.)

sites. These possibilities are illustrated in Fig. 7.26, where $I_c(Q)$ is an equivalent intensity for infinitely thin stems and $Q^2 I_c(Q)$ is proportional to $F_n(Q)$. The calculations are represented schematically for a polyethylene lattice viewed along the chain direction (c axis). The heavy dots indicate sites occupied by stems of a given molecule folding in the (110) plane. The model with approximately “next-but-one” re-entry fits the data well up to $Q \sim 0.6 \text{ \AA}^{-1}$, though the IANS data are not sufficiently sensitive to serve as a unique fingerprint for a given stem sequence or mode of stem dilution. However, the neutron data rule out the possibility that a typical molecule is regularly folded in one plane over many stems without interruption. This model had gained widespread support over the previous decades both for melt- and for solution-crystallized material. Similarly, the extremes of random configurations have been ruled out, with a large fraction of molecules usually folding in “near” re-entry within a few nearest neighbors and readers are referred to other reviews [37, 134, 143, 150, 152] for more detailed discussions of these issues.

7.6.2 Polymer blends and composite materials

7.6.2.1 One-phase mixtures of polymers

Because of difficulties in commercializing new polymers, industry has turned increasingly to combining (blending) existing polymers in order to optimize their end-use properties. Such materials currently account for a growing fraction of the polymer market, so these materials are the subject of intense scientific and commercial interest. SANS has developed into a powerful method for the study of their structure and interactions and revolutionized the field by providing detailed thermodynamic information at the molecular level. Because these developments have important applications in materials science, SANS has been used extensively by industrial scientists [153, 154] to investigate polymer–polymer thermodynamics.

Prior to this method, polymer–polymer phase behavior could be investigated only in the limit of phase separation by LS (cloud point), or by using various indirect thermal or mechanical spectroscopic methods. These methods could indicate macroscopic segregation, but could not demonstrate fine-grained separation or intermixing at the molecular level. In principle, this information could be obtained from LS or SAXS [66], though there are very few cases in which there is sufficient electron-density contrast between the components to apply these methods. Deuterium-labeling together with SANS has revolutionized this field and the technique was applied to investigate compatibility of polymers as soon as the first instruments became available [155–160]. Since that time, such studies have become so numerous that space considerations preclude a comprehensive description of all aspects of the field. This section will therefore seek to give illustrative examples

of the types of thermodynamic information that the technique can provide for the homogeneously mixed state.

Pairs of chemically dissimilar polymers are incompatible in most cases, though SANS demonstrated that several polymer blends form truly compatible mixtures [155–159] at the molecular level. The initial applications were based on an extension to polymer blends of the Zimm analysis [13, 159], which was originally developed for LS and SAXS to give R_g , M , and the second virial coefficient, A_2 , for polymer solutions. In principle, this formalism is limited to the regime in which one of the species is dilute, though it has been extended to concentrated homogenous mixtures to give the Flory–Huggins interaction parameter (χ), which is related to A_2 for dilute systems [159, 161].

As mentioned above, an important development was the application [115] of the RPA, and, for a blend of two polymer species A and B, with volume fractions φ_A and $\varphi_B = 1 - \varphi_A$, we may generalize Eqs. (7.21) and (7.22) to the case in which the segment volumes (V_A and V_B) are unequal. The coherent cross section is given [159–162] by

$$\frac{d\Sigma}{d\Omega}(Q) = \left(\frac{a_A}{V_A} - \frac{a_B}{V_B} \right)^2 S(Q) \quad (7.25)$$

$$\frac{1}{S(Q)} = \frac{1}{N_A \varphi_A V_A P_A(Q, R_g)} + \frac{1}{N_B (1 - \varphi_B) V_B P_B(Q, R_g)} - \frac{2\chi}{V_0} \quad (7.26)$$

where V_0 is a reference volume (usually $V_0 = (V_A V_B)^{1/2}$), and a_A and a_B are the scattering lengths of monomers of the species A and B, one of which is usually deuterated in order to increase the SANS contrast (e.g. $a_A \rightarrow a_{AD}$). R_g and N are the radius of gyration and degree of polymerization of the two species, and the single-chain form factor $P(Q, R_g)$ is assumed to be of the Debye form (Eq. (7.6)), with a Gaussian distribution of chain elements in the amorphous state. In the dilute ($\varphi \rightarrow 0$) limit, Eqs. (7.25) and (7.26) reduce to the Zimm equation used in early SANS studies of mixtures of polymers [159, 161]. Similarly, for isotopic blends of the same species, one of which is deuterium-labeled ($V_A \cong V_B \cong V$, $a_A \rightarrow a_D$, $a_B \rightarrow a_H$), Eq. (7.25) reduces to Eq. (7.21), which has been used to investigate isotope effects (see Section 7.5.1) and the thermodynamics of mixtures of linear and branched polymers (see below).

RPA theory⁷ has successfully been applied to the evaluation of $\chi(T, \varphi, N)$ for a variety of polymer–polymer mixtures [158–176] and some illustrative examples

⁷ Several different systems of nomenclature have been used in the RPA formalism, for example in [160, 161], where V is defined as the *specific* volume of the polymer segments as opposed to the *actual* segment volume (e.g. $V_{\text{seg}} \sim 164 \times 10^{-24} \text{ cm}^3$ for polystyrene). The specific volume ($N_A V_{\text{seg}}$) is $\sim 100 \text{ cm}^3$ for the same species (where $N_A = 6.018 \times 10^{23}$ is Avogadro's number) but, apart from nomenclature, the equations are essentially the same.

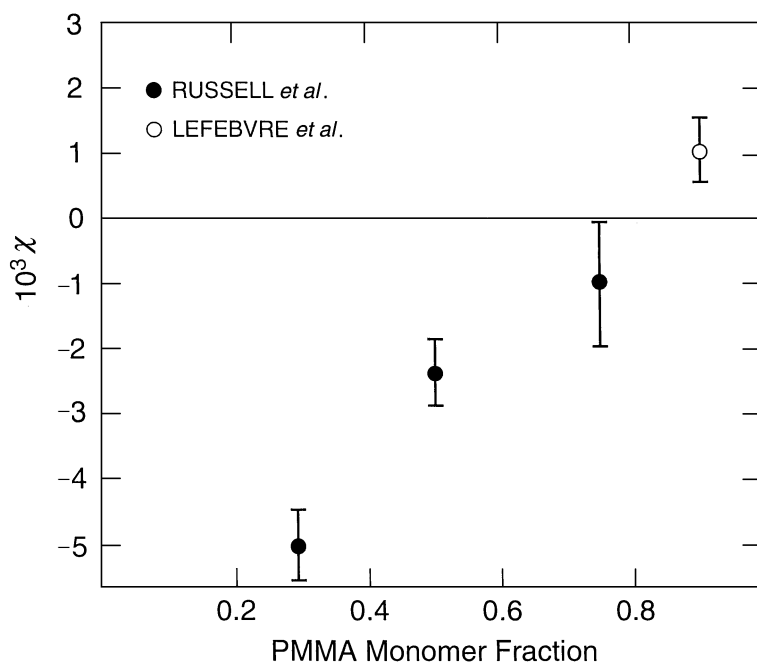


Fig. 7.27. The interaction parameter for interaction between PEO and PMMA as a function of the monomer fraction (H + D) of PMMA. (Reproduced with permission from [66]. Copyright 1993 American Chemical Society.)

are described below. For example, Fig (7.27) depicts the interaction parameter for PMMA–poly(ethylene oxide) (PEO) blends [173, 174]. The values of χ obtained in two independent studies are in good agreement, and confirm that the magnitude is not only small, but also concentration-dependent, like most other experimentally determined interaction parameters. For low concentrations of PMMA, χ changes sign, indicating that the entropic, as opposed to enthalpic, contributions are dominant.

Several studies have been directed at elucidating the limits of applicability of the mean-field approximation for mixtures of polymers. At small scattering wave vectors ($Q \rightarrow 0$) Eqs. (7.25) and (7.26) reduce to the well-known Ornstein–Zernike form [115],

$$\frac{d\Sigma}{d\Omega}(Q) = \frac{d\Sigma}{d\Omega}(0) / (1 + Q^2 \xi^2) \quad (7.27)$$

where the composition-fluctuation correlation length ξ is given by

$$\xi_s \sim [\chi_s - \chi(T)]^{-\nu} \quad (7.28)$$

with $\nu = \frac{1}{2}$ in the mean-field limit and $\nu = 0.63$ near the critical point (Ising regime); χ_s is the magnitude of the segment–segment-interaction parameter at the stability temperature.

Schwahn *et al.* [175] were the first to report a transition from mean-field to non-mean-field behavior in polymer mixtures on the basis of SANS results obtained from a PS–poly(vinyl methyl ether) (PVME) mixture. Subsequently, Bates *et al.* [176] quantitatively verified these conclusions using a model polyisoprene–poly(ethylene–propylene) mixture above the upper critical solution temperature ($T_c = 38^\circ\text{C}$), which revealed a transition from $\gamma = 2\nu = 1$ (mean-field behavior) to $\gamma = 1.26$ (non-mean-field behavior) approximately 30°C above the critical temperature. These SANS crossover studies established the limitations of mean-field theory, which has been used extensively for evaluating polymer–polymer thermodynamics, and similar crossover phenomena have been investigated via SANS for polymers in small-molecule solvents (e.g. polystyrene in cyclohexane) and supercritical media (e.g. polydimethylsiloxane in CO_2), as described in Section 7.6.4

SANS has been used extensively [96, 169, 177–192] to characterize the miscibility of a wide range of mixtures of linear and branched polyolefins, including high-density (HD), low-density (LD) and linear low-density (LLD) polyethylenes (PE). HDPE chains contain very little branching, though LDPE contains both long (~ 0.3 per 100 backbone carbon atoms) and short chain branches (1–3 per 100 backbone carbon atoms). LLDPE is produced by catalytically copolymerizing ethylene with an α -olefin (hexene, octene etc.) and can have a wide range of branch contents, depending on the type of catalyst and concentration of added comonomer, with a homogenous side (short)-branch length. SANS indicates that, for HDPE–LDPE blends with molecular weights $\sim 10^5$, the melt is homogenous for all compositions after proper accounting for $^1\text{H}/^2\text{D}$ isotope effects [182, 184]. Similarly, mixtures of HDPE and LLDPE have been shown to be homogeneous in the melt when the branch content is low (i.e. fewer than three branches per 100 backbone carbons). However, when the branch content is higher (more than seven branches per 100 backbone carbons), the blends undergo phase separation [188]. This is illustrated in Fig. 7.28, which shows Zimm plots of mixtures of model polyethylenes ($M \sim 10^5$), one of which is deuterium-labeled, as a function of the *difference* in branch content between the species [188], where phase separation is manifested via a *negative* intercept in this representation.

In this experiment, the LLDPEs were simulated by hydrogenated (or deuterated) polybutadienes, because they can be prepared as monodisperse molecules (with a ratio of weight- and number-averaged molecular weights, $M_w/M_n < 1.1$) and a homogenous branch distribution within the chains. Such studies are therefore unaffected by polydispersity effects, either in the branch content or molecular

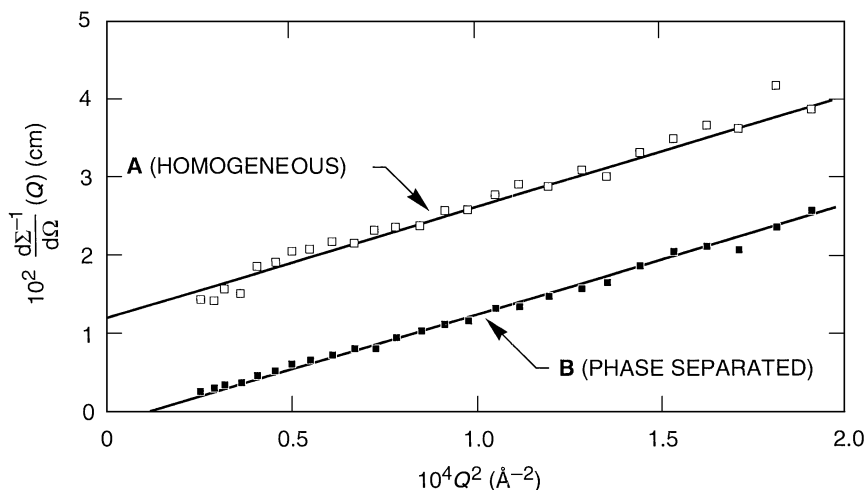


Fig. 7.28. Zimm plots for model polyethylenes at $T = 130^\circ\text{C}$ as a function of the difference in branching of the components. (Reproduced with permission from [188]. Copyright 1997 American Chemical Society.)

weight. However, for LLDPEs prepared with heterogeneous-type Ziegler–Natta catalysts, it is well known that the multisite nature of catalysts typically leads to a wide distribution of chain compositions [193]. The branch content and molecular weight are strongly correlated and the low- M chains exhibit the most branching [194, 195]. Thus, a heterogeneous LLDPE may be thought of as a “blend” of different species and, when the composition distribution is broad enough, the multicomponent system can, in principle, undergo phase separation [177, 195]. Thus, SANS experiments [186] have shown that an ethylene–hexene copolymer, representative of many LLDPEs, contained a dispersed minority phase (volume fraction $\sim 10^{-2}$), which was manifested by departures from a Q^{-2} variation of the neutron-scattering cross section at low Q -values (Fig. 7.29(a)). In contrast, a metallocene-based LLDPE, which has a more homogeneous distribution of branch contents, does not exhibit an upturn in the cross section in the limit of low momentum transfer ($Q < 10^{-2} \text{ \AA}^{-1}$), indicating (Fig. 7.29(b)) that the LLDPE forms only a single phase in the melt [191]. These findings support previous conclusions [186] regarding compositionally polydisperse LLDPEs, whereby the highly branched molecules in the distribution may undergo phase segregation, even if the overall branch content is low. When this component is not present, as in metallocene-based LLDPEs, the system forms a single phase in the melt.

These experiments were conducted using a pinhole SANS spectrometer with an upper resolution limit of $\sim 10^3 \text{ \AA}$, whereas microscopy indicates that the dimensions of the disperse phase extend to the μm range. Complementary

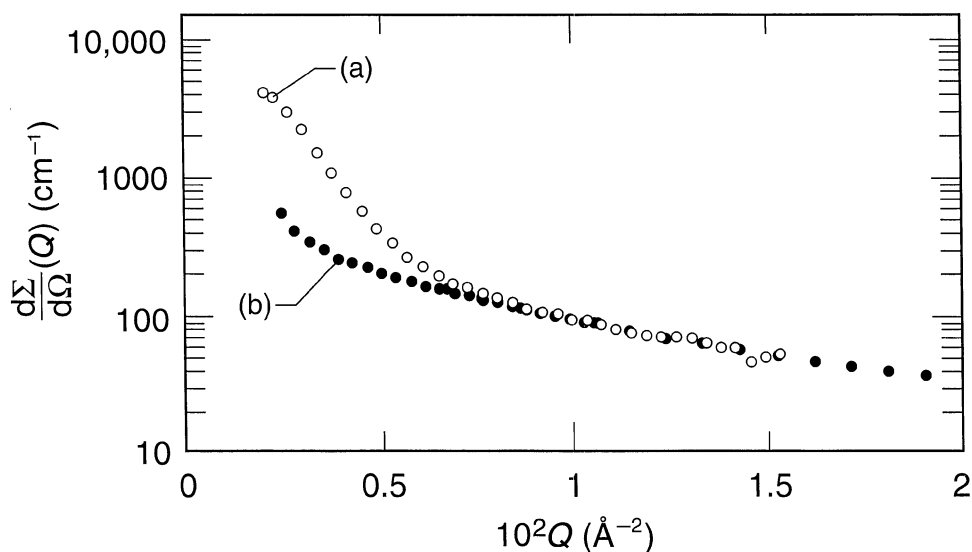


Fig. 7.29. $d\Sigma/d\Omega(Q)$ for (a) a 20/80 blend of HDPE-D and heterogeneous (Ziegler–Natta-catalyzed) ethylene–hexene LLDPE copolymer blend and (b) a 25/75 blend of HDPE-D with a metallocene-based copolymer. (Reproduced with permission from [191]. Copyright 2002 American Chemical Society.)

investigations [96, 189] using a Bonse–Hart USANS instrument increased the spatial resolution by a factor of ~ 30 , as explained in Section 7.4.2, and revealed particle sizes of up to $2\text{--}7\text{ }\mu\text{m}$ (fig. 7.18). This substantially improved the estimate of the volume fraction of the disperse phase by filling in the previously inaccessible range of the SANS data below the resolution limit of pinhole SANS and illustrates the utility of USANS to complement pinhole-SANS techniques.

As explained above, the enormous growth in the use of SANS to determine the miscibility of various macromolecules is based on the RPA [115], which in turn is based on the assumption that the dimensions of polymer chains remain unchanged on mixing and retain the unperturbed radius of gyration $R_g(\Theta)$, as in a melt or in a polymer solution at the theta temperature. However, several experimental results [161, 174] have suggested that this assumption might not hold universally and that R_g may shrink or expand with temperature or concentration. As explained in Section 7.1.2, it is known from studies of polymers in organic solvents that the dimensions depend on the sign and magnitude of the interactions between the chain segments and the molecules of surrounding liquid. In good solvents, the *intra*-chain repulsion or excluded volume between the segments works to expand the polymer dimensions, as does the solvent–solute interaction. In less-favorable solvents, however, the solvent–solute and solute–solute interactions have opposite signs, and, when they are balanced, the chain dimensions are independent both of segment–segment

and of solvent–solute interactions. This phenomenon occurs at the theta temperature (T_Θ), at which R_g corresponds to the dimension of a non-interacting polymer coil, unperturbed by excluded-volume effects. Considering a polymer blend as a special case of a polymer solution with a high molecular weight solvent [196], one might expect that the RPA should be strictly valid only for “ideal” blends of non-interacting polymers with $\chi = 0$. To the author’s knowledge, Brereton and Vilgis [197] were the first to suggest that the RPA may break down if the quality of the polymeric solvent becomes sufficiently poor or good. Subsequently, Melnichenko and *et al.* [162] used SANS to demonstrate that macromolecules in miscible polymer blends may behave as poor, theta and good polymeric solvents for each other and constructed a conceptual phase diagram, indicating the range of validity of the RPA, outside of which molecules contract or expand beyond their unperturbed dimensions. However, it was shown that polymers retain their unperturbed dimensions over most of the phase diagram for the majority of blends studied by SANS.

7.6.2.2 Phase-separated blends and composite materials

The scattering from phase-separated systems has been treated by Koberstein [198], who showed how to separate the domain structure from the molecular configuration and such experiments have been performed for polymer blends, interpenetrating polymer networks (IPNs) and block copolymers [37, 66, 199–203]. An instructive example of how SAXS and SANS may be used in combination to provide detailed insight into the morphologies of phase separated blends has been given by Russell *et al.* [173] for PMMA–PEO mixtures. In the amorphous (one-phase) state, the interaction parameter may be measured as a function of composition (Fig. 7.27) and temperature. When the system is annealed, PEO commences to crystallize and (atactic) PMMA is excluded from the lamellae. If the phase boundaries are sharp, the scattering should follow a Q^{-4} dependence at high Q , corresponding to Porod’s law (see below). Deviations from this exponent indicate the presence of less-sharp or diffuse interfaces and may be analyzed to give the thickness of the phase boundary [173], as shown in Fig. 7.30 for semicrystalline blends of protonated PEO and deuterated PMMA. Interestingly, the results suggest that the interface between crystalline and amorphous regions exhibits different characteristics, depending on the radiation used. The interface appears to be quite sharp for SANS, with a thickness of $E_{\text{SANS}} \sim 5 \text{ \AA}$, whereas for SAXS a diffuse interface is observed ($E_{\text{SAXS}} \sim 20 \text{ \AA}$). Figure 7.31 illustrates schematically how such results may be explained using the concept of an interfacial region on the surface of polymer crystals proposed by Mandelkern [152] and co-workers (see Section 7.6.1 and Chapter 4). Proceeding along the normal to the lamellae, the electron density falls on going from the crystal to the amorphous region as the order is dissipated. After sufficient order has been

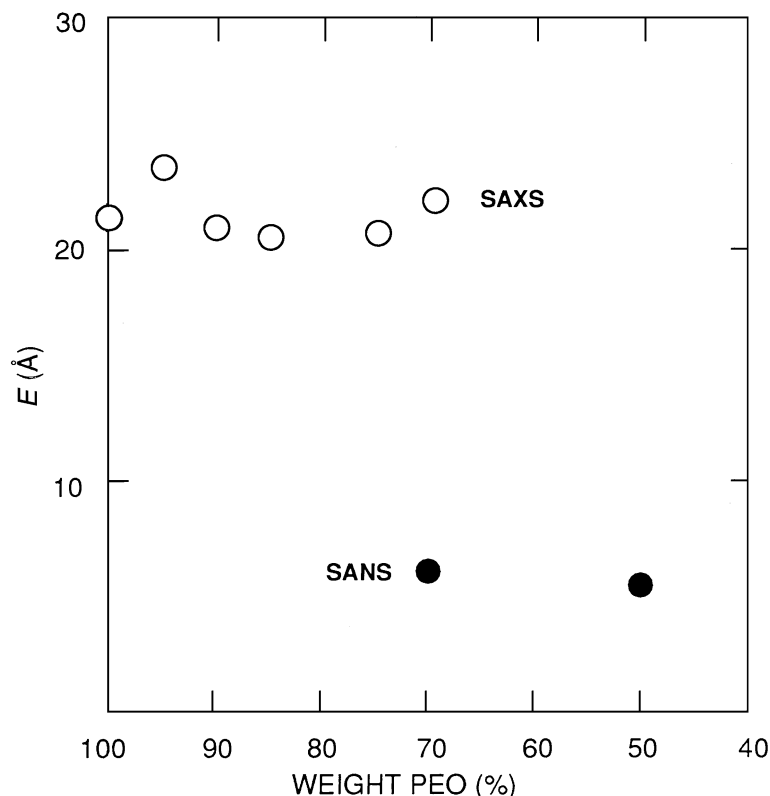


Fig. 7.30. The thickness of the diffuse phase boundary as a function of composition measured by SAXS and SANS. The values remain constant as the composition is varied; however, there is a difference ($\sim 15 \text{ \AA}$) between the two. (Reproduced with permission from [66]. Copyright 1993 American Chemical Society.)

lost ($\sim 15 \text{ \AA}$), PMMA begins to mix with the amorphous PEO, forming a mixture between the lamellae. In terms of the neutron scattering length density (SLD) the situation is quite different, because the PEO is protonated and the PMMA is deuterated. Thus the SLD for PEO is small, due to the mutual cancelation of the scattering lengths of hydrogen and the other atoms (see Table 7.1). As the deuterated PMMA mixes with the amorphous PEO, the SLD increases dramatically over a distance of $\sim 5 \text{ \AA}$, and the slight differences between crystalline and amorphous PEO are negligible compared with the SLD of the mixture of (protonated) PEO and (deuterated) PMMA. Thus the effective interfaces measured by SAXS and SANS are different, as indicated in Fig. 7.31, and this supports the idea that there is an interfacial region at the surface of the PEO crystals representing the distance over which the order is lost and from which the PMMA is excluded.

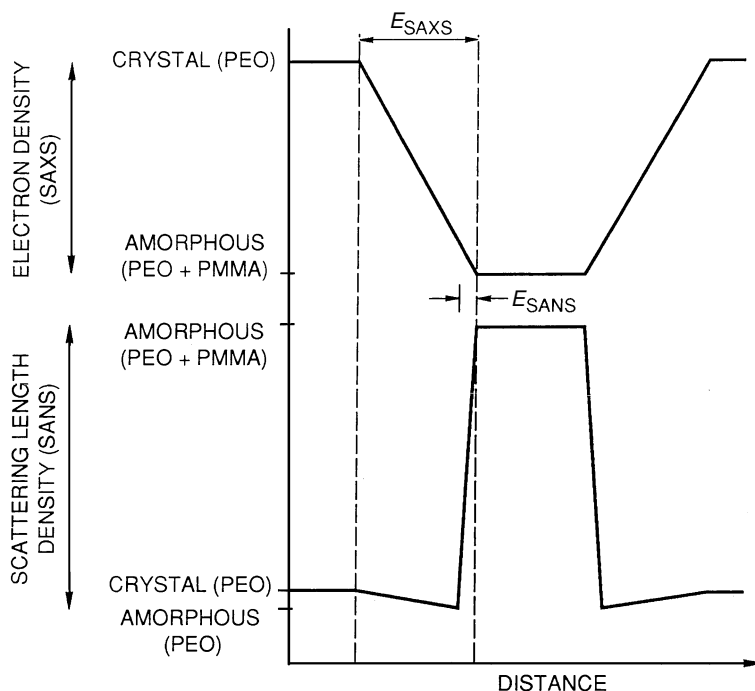


Fig. 7.31. A schematic diagram of the electron density (upper) and the neutron SLD (lower) as functions of distance in the direction normal to the surface of the lamellae. The area between the dashed lines represents the transition zone between the crystalline lamellae and the homogeneous amorphous mixture. E_{SAXS} and E_{SANS} are the thicknesses of the interface measured by SAXS and SANS for PMMA–PEO. (Reproduced with permission from [66]. Copyright 1993 American Chemical Society.)

As described above (Section 7.6.2.1), results of SANS experiments indicate that HDPE–LDPE blends are homogeneous in the melt, though the components may separate on slow cooling due to the difference between the melting points of the species [185, 190]. In these experiments, the HDPE molecules were fully deuterated, and, for such two-phase systems, it was shown [185] that the Debye–Bueche (DB) model [202] was appropriate, with a cross section of the form

$$\frac{d\Sigma}{d\Omega}(Q) = \frac{8\pi a^3 \varphi_A \varphi_B (\rho_{nA} - \rho_{nB})^2}{(1 + Q^2 a^2)^2} \quad (7.29)$$

where a is a length characterizing the spatial dimensions, φ_A and φ_B are the volume fractions, and ρ_{nA} and ρ_{nB} are the SLDs of the two phases [202].

Figure 7.32 shows a DB plot of the data for a 50/50 blend after slow cooling from the melt. The extrapolated cross section ($d\Sigma/d\Omega(0) = 24.5 \times 10^3 \text{ cm}^{-1}$) is

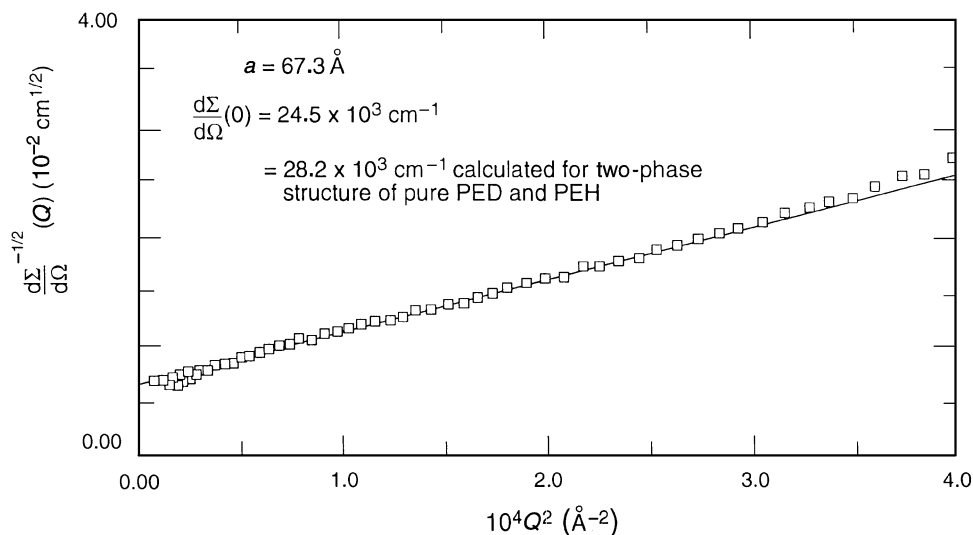


Fig. 7.32. A Debye–Bueche plot for a phase-separated blend of deuterated HDPE and protonated LDPE slowly cooled from the melt. (Reproduced with permission from [184]. Copyright 1994 American Chemical Society.)

well over an order of magnitude higher than that for the melt, indicating that the components have undergone phase separation on cooling [184]. The correlation length (a) is derived from the ratio of the slope and intercept [69, 185] and, assuming that complete separation of the ^1H - and ^2D -labeled species has occurred, Eq. (7.29) gives $d\Sigma/d\Omega(0) = 28.2 \times 10^3 \text{ cm}^{-1}$ [69, 185]. In view of the fact that the data were independently calibrated with no arbitrary fitting factors in the intensity scale, the agreement with the absolute cross section calculated from the DB model is excellent.

SAXS can also provide similar information to SANS wherever there is sufficient electron-density contrast, as demonstrated by Blundell [203] for polyurethane–PMMA composites. Whenever the electron-density contrast is insufficient for SAXS (e.g. for polyolefins), strong SANS contrast may be created by deuterating one phase [199]. Figure 7.33 shows DB plots of SANS data from interpenetrating polystyrene–polybutadiene polymer networks [200]. Assuming that complete segregation of the components occurs, $d\Sigma/d\Omega(0)$ may be calculated from Eq. (7.29) as described above via the measured correlation lengths and the SLDs (Table 7.3). For the data from the samples shown in Fig. 7.33, this leads to calculated values of $17.2 \times 10^3 \text{ cm}^{-1}$ and $2.7 \times 10^3 \text{ cm}^{-1}$, compared with experimental determinations of $21.6 \times 10^3 \text{ cm}^{-1}$ and $2.0 \times 10^3 \text{ cm}^{-1}$. The discrepancies are not unreasonable in view of the strong dependence of the cross section on the domain dimensions, which is a general feature of absolute-intensity comparisons. However, this

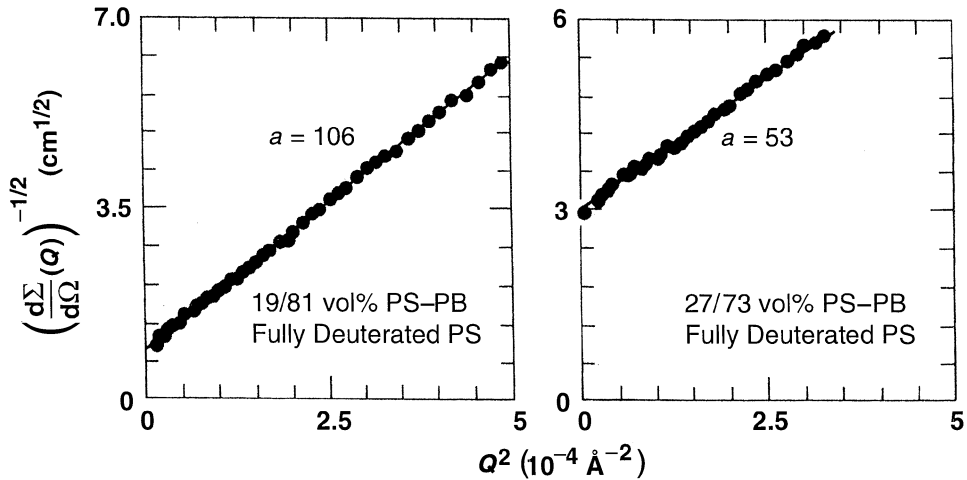


Fig. 7.33. Debye–Bueche plots for two phase-separated blends of polystyrene and polybutadiene. (Reproduced with permission from [66]. Copyright 1993 American Chemical Society.)

illustrates the point made earlier that even an approximate ($\pm 25\%$) absolute calibration is sufficient to test the assumption of complete phase separation of the blend components.

In the limit $Qa \gg 1$, Eq. (7.29) reduces to $d\Sigma/d\Omega \sim PQ^{-4}$,

$$P = 2\pi(\rho_{n1} - \rho_{n2})^2 S_V \quad (7.30)$$

where P is the Porod constant, which may be used to yield the specific surface (i.e. the total inter-phase surface area per unit sample volume, S_V), provided that the data are calibrated in absolute units [204]. By comparison of Eqs. (7.29) and (7.30)

$$S_V = 4\phi_1\phi_2/a \quad (7.31)$$

For the data shown in Fig. 7.33, Eq. (7.31) leads to specific surface values in the range $(58\text{--}150) \times 10^4 \text{ cm}^{-1}$ [69, 200] or $58\text{--}150 \text{ m}^2 \text{ gm}^{-1}$ ($\rho \simeq 1.0 \text{ g cm}^{-3}$).

7.6.2.3 Filled polymers and composite materials

Other multiphase systems involving polymers include composite materials produced by mixing polymers with filler particles in order to modify their mechanical properties or conductivity. Typical additives include carbon black, clay, silica, and glass beads/fiber and understanding the interactions between the filler and the polymer matrix has implications for the performance of such materials. For example, carbon black has been used extensively as a reinforcing filler in a number of applications such as automotive tires and can also be blended with insulators such as semicrystalline PE to produce conductive composites used in electrical products.

When the concentration of carbon black at room temperature is above the percolation threshold, the composite is conducting. However, at higher current loading, the system heats and expands the PE matrix, and, when this approaches the percolation threshold, it becomes highly resistive [205]. This results in a lower current and the device cools to its original state, so a mixture of carbon black and polyethylene acts as a resettable fuse [206].

The electrical properties of the composites are affected by the microstructures formed during processing, which can lead to significant variations in the morphology and changes in the electrical performance. The ability to characterize these systems is therefore important for the design of these materials, though determining the morphology by optical methods is not feasible, due to the absorption of visible light by carbon black. For materials with particle sizes in the range ~ 10 – 1000 Å, both SANS and SAXS may be used to explore the morphology and a combination of these techniques can provide greater insight than can either technique in isolation. For example, results of combined SAXS/SANS studies of carbon–PE composites [205] suggested the presence of a third phase (voids) and subsequent experiments using the contrast options available from deuterium labeling of the PE matrix were designed to quantify the void fraction and its variation with temperature.

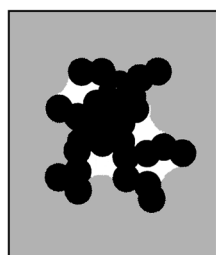
Figure 7.34 illustrates schematically the contrast options available from the combination of SAXS/SANS and deuterium labeling in the study of the three-phase system (polymer, carbon black and voids), and makes it clear that one cannot resolve void morphology solely with SAXS. However, if one examines a normal protonated composite via SANS, the sample is essentially a two-phase material because the neutron SLDs of PE and voids are virtually identical (see Table 7.5). If one blends carbon black with deuterated polyethylene, however, the presence of voids is highlighted within the carbon-black–deuterated-polyethylene matrix. Through a combination of these experiments, one can extract quantitative information about the size and quantity of voids [206] using the theoretical formalism developed by Wu [207] to model microvoids (cracks) in composite materials. Typical concentrations of ~ 2 vol% of voids 400 – 500 Å in size were measured at room temperature in composite materials containing 30–40 vol% carbon. The concentration of these voids decreases significantly during the melting transition, however, dropping by an order of magnitude to ~ 0.2 vol%. This decrease might be expected and suggests that the PE domains grow at the expense of the voids as the temperature is brought above the melting point.

7.6.3 Block copolymers

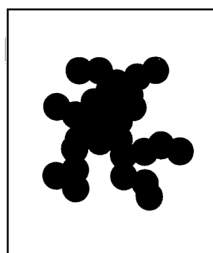
Block copolymers are produced by joining two or more chemically distinct polymer blocks that may be thermodynamically incompatible. Segregation on the molecular

Table 7.5. Neutron and X-ray (photon) SLDs of various polymers and components of carbon–polymer composite materials

Species	Density, ρ (g cm ⁻³)	X-ray SLD, ρ_x (10 ¹⁰ cm ⁻²)	Neutron SLD, ρ_n (10 ¹⁰ cm ⁻²)
Carbon black	1.92	16.2	6.4
Voids	0.0	0.0	0.0
Polyethylene	0.95	9.12	-0.34
Polyethylene-d ₄	1.08	9.12	8.13
Polyisoprene	0.91	8.57	0.27
Poly(vinylmethyl ether)	1.05	9.74	0.36
Polystyrene	1.05	9.53	1.41
Polystyrene-d ₈	1.13	9.53	6.47



SAXS contains contributions from all three phases



SANS from carbon in H-PE gives structure of carbon alone



SANS from carbon in D-PE gives structure of voids alone

Fig. 7.34. Contrast options for SAXS and SANS studies of carbon–polyethylene composite materials.

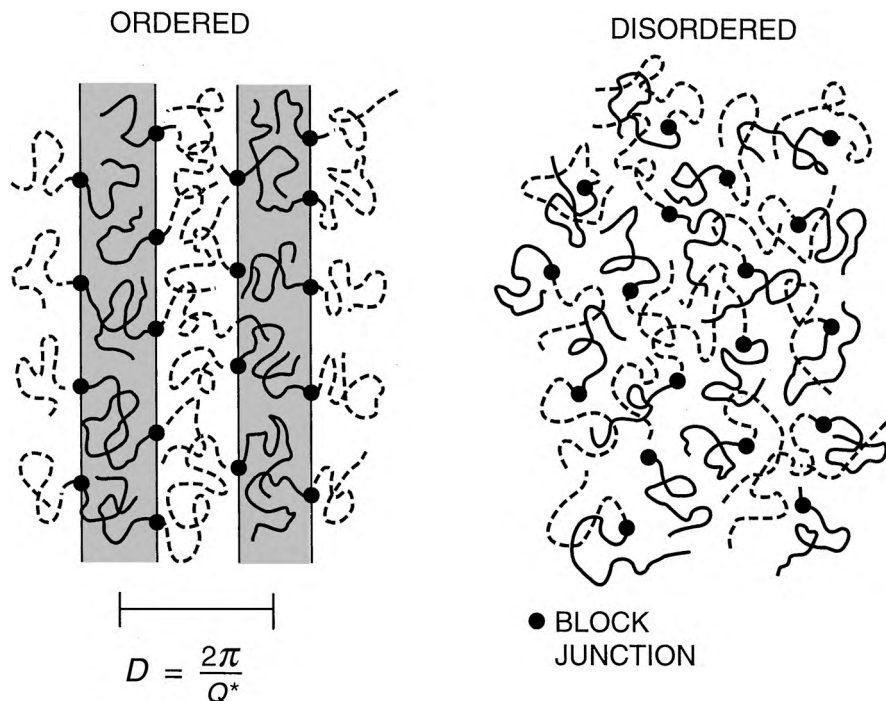


Fig. 7.35. A schematic illustration of the speculated real-space morphology of a symmetric ($f = \frac{1}{2}$) diblock-copolymer melt.

scale (10^1 – 10^3 Å) produces complex nanostructures by self-assembly. Two competing effects govern the structure and, at high temperatures (T), the chains are mixed homogeneously. As T is reduced, incompatible blocks tend to segregate due to the different chemical affinities of the components, though the bond between polymer blocks constrains intra-chain block separation to a length-scale of the order of the overall chain R_g . In recent years, the rich variety of ordered microdomain morphologies of multiblock polymers has attracted wide interest, and such systems now account for important segments of the plastics and rubber industries.

The simplest molecular architecture is obtained by connecting a block of type-A repeat units end to end with a block of type-B units to make a diblock copolymer. The phase behavior is determined by the segment–segment-interaction parameter, the overall degree of polymerization ($N = N_A + N_B$) and the composition, $f = N_A/N$. At equilibrium, a block copolymer will be arranged such that the overall free energy is minimized. Decreasing temperature (i.e. increasing χ) favors a decrease in number of A–B segment contacts. If the degree of polymerization (N) is sufficiently large, this may be accomplished by local compositional ordering, as illustrated in Fig. 7.35 for the symmetric case $f = 0.5$, for which a lamellar morphology is observed.

Alternatively, if either χ or the chain length (N) is decreased enough, entropic factors will dominate, leading to formation of a compositionally disordered phase. The transition between the ordered and disordered phases was treated by Leibler [208], who showed that an order–disorder transition (ODT) occurs when $\chi N \sim 10$. Below this limit the melt is disordered, though the connectivity of the two blocks leads to a correlation hole [208], which is manifested in small-angle scattering measurements as a peak corresponding to a fluctuation length $D \sim R_g$. Above the limit, the system is ordered and D corresponds to the lamellar spacing. The first theories of the ODT [208, 209] were based on the assumption that the A–B interactions are sufficiently weak that the coils remain Gaussian throughout the transition and thus the microdomain period scales as the square root of the degree of polymerization ($D \sim N^{1/2}$). This is referred to as the weak-segregation limit and the second limiting regime occurs for $\chi N \gg 10$, for which narrow interfaces separate well-developed, nearly pure microdomains [210]. Because the block joint is located at the domain interface, and A blocks are excluded from the B phase (and vice versa), the blocks are constrained to adopt more extended configurations than for a Gaussian coil. Equilibrium is established by minimizing the total interfacial area under the entropic penalty of stretched configurations necessitated by the constraint of incompressibility. Thus the microdomain period will scale with a higher exponent than that observed for Gaussian coils, and is predicted to vary as $D \sim N^{2/3}$ [210, 211].

The validity of the assumptions underlying the theories of the ODT may be checked via small-angle scattering measurements of the peak position ($Q^* = 2\pi/D$). The shape of the peak in the disordered region is a function of the interaction parameter and it was proposed by Leibler [208] that χ could be determined by fitting the theory to the scattering data. Similarly, the variation of Q^* with chain length could be used to test the predicted scaling behavior and such experiments have been performed by Bates and Hartney [212], who showed that the Leibler theory gave a reasonable description of the peak shape for model 1,2–1,4-polybutadiene block copolymers. It was also observed that, when the phase transition was approached by lowering the temperature ($\chi \sim T^{-1}$), the position of the peak shifted systematically, though such an effect is not accounted for by theory, which assumes that Gaussian statistics apply, so the dimensions, and hence the position of the peak (Q^*), are determined by the degree of polymerization (N). Since the peak shifted to lower Q -values, this indicated that the chain dimensions were stretching ($D \sim Q^{-1}$) as the ODT was approached, contrary to the assumptions of the theory. Experiments to quantify the degree of stretching near the ODT were performed on model poly(ethylene–propylene)–poly(ethylethylene) (PEP–PEE) block copolymers by Almdal *et al.* [213], who measured the position of the peak as a function of the polymerization index by SANS. Because $Q^* = 2\pi/D$, the scaling exponent (δ) may be measured via the variation of Q^* with $N(Q^* \sim N^{-\delta})$. The results

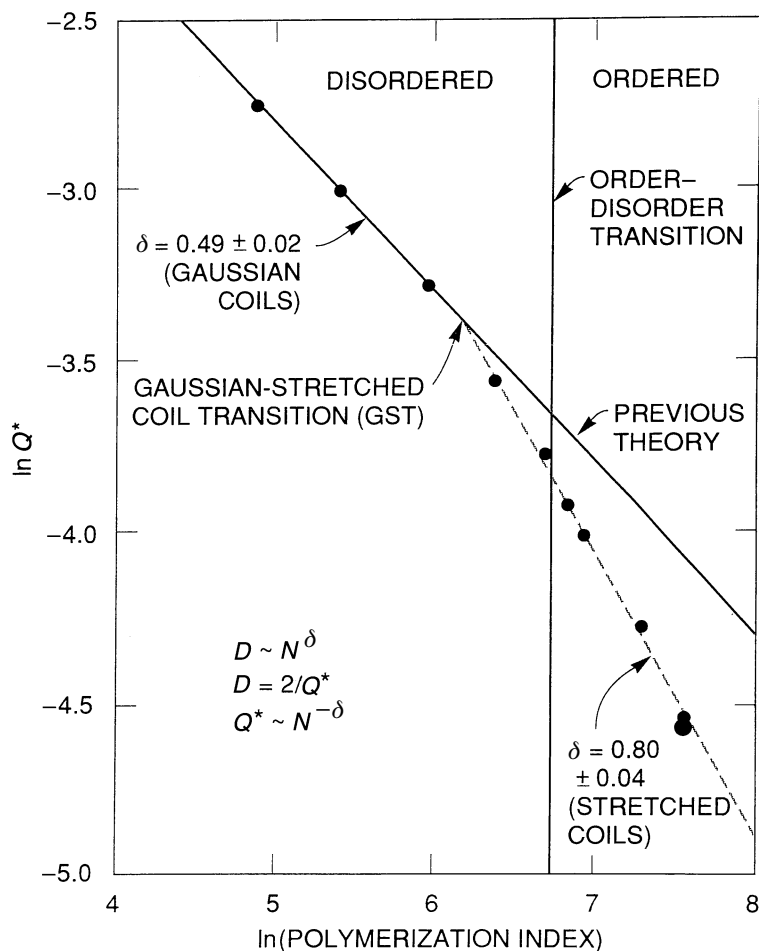


Fig. 7.36. Gaussian-stretched coil transition for PEP-PEE block copolymers as a function of the polymerization index. (Reproduced with permission from [213]. Copyright 1990 American Physical Society.)

(Fig. 7.36) indicate that departures from Gaussian statistics ($\delta = 0.5$) are observed both in the ordered phase and in the disordered phase. This is consistent with the shift in position of the peak as the ODT is approached [212] and shows that the coils undergo a Gaussian-stretched coil transition in the disordered state, where $\delta = 0.8 \pm 0.04$. Such data have indicated the deficiencies of the original theory [208] and have subsequently been used as the basis for new theoretical developments [214–218]. This study indicates the close interaction between theory and experiment which has often been stimulated by the information provided by SANS over the past two decades. The possibility of measuring previously inaccessible parameters has stimulated theoretical developments, which have led to new experiments (e.g. Fig. 7.36), which have in turn prompted improvements in theory.

As explained above, the nanostructure of a typical AB diblock copolymer is controlled by the overall degree of polymerization ($N = N_A + N_B$), the composition $f = N_A/N$, and the Flory–Huggins segment–segment-interaction parameter χ_{AB} . Adding a third chemically distinct block introduces the following complications. The number of χ parameters triples (i.e. χ_{AB} , χ_{BC} , and χ_{AC}), the number of composition variables doubles (i.e. f_A and f_B , with $f_C = 1 - (f_A + f_B)$), and three distinct block sequences become possible (i.e. ABC, ACB, and CAB). There are four known equilibrium diblock morphologies (spheres, cylinders, lamellae, and the gyroid [219]) and, assuming that the number of phases is governed by a simple combinatorial relationship, then linear ABC triblock copolymers would be expected to exhibit literally hundreds of distinct morphologies [219]. Thus, a seemingly unlimited array of ordered block-copolymer phases can be obtained by adding additional chemically distinct blocks to the traditional two-monomer pallet in linear and branched configurations. This presents a daunting challenge to the practitioner interested in designing a specific morphology and the use of theoretical [220], small-angle scattering [221], and other experimental techniques to elucidate and predict triblock and multiblock morphologies is only just beginning.

Another illustrative example of the extra information that may be obtained via the combined use of SANS and SAXS, coupled with deuterium labeling, has been given by Hashimoto and co-workers [222, 223] in studies of the phase transitions of a triblock terpolymer, polyisoprene (PI)–poly(deuterated styrene) (DPS)–poly(vinylmethyl ether) (PVME). The temperature dependence of the SAXS and SANS profiles exhibits intriguing features, as shown in Fig. 7.37, where the D -spacing estimated from the scattering vector, Q_m , of the first-order maximum ($D = 2\pi/Q_m$) is plotted as a function of the inverse temperature for SAXS and SANS. For $T < 140^\circ\text{C}$, the D -values have similar temperature dependences for SAXS and SANS, whereas for $T > 140^\circ\text{C}$, the trends are opposite for the two techniques. Moreover, the SAXS profile exhibits a double spacing, though the SANS data do not. Table 7.5 gives the neutron and X-ray SLDs of the various components. Noting that the SANS SLDs of PI and PVME are approximately equal (but much less than that of DPS), and that the SAXS SLDs of DPS and PVME are similar (but greater than that of PI), the striking T -dependence of D can be interpreted by assuming that, at temperatures below 140°C , spherical microdomains of PI block are dispersed in the matrix of mixed DPS and PVME blocks. Conversely, for $T > 140^\circ\text{C}$, the PVME blocks undergo microphase separation from the matrix of mixed DPS and PVME, so that the spheres of PI and those of PVME coexist. A plausible explanation of the striking differences between SAXS and SANS for $T > 140^\circ\text{C}$ is that SAXS “sees” only the PI spheres, whereas the SANS “sees” both PI and PVME. Moreover, microphase separation of PVME spheres occurs as a result of segregation of PVME blocks from the DPS chains anchored by the PI spheres [222, 223].

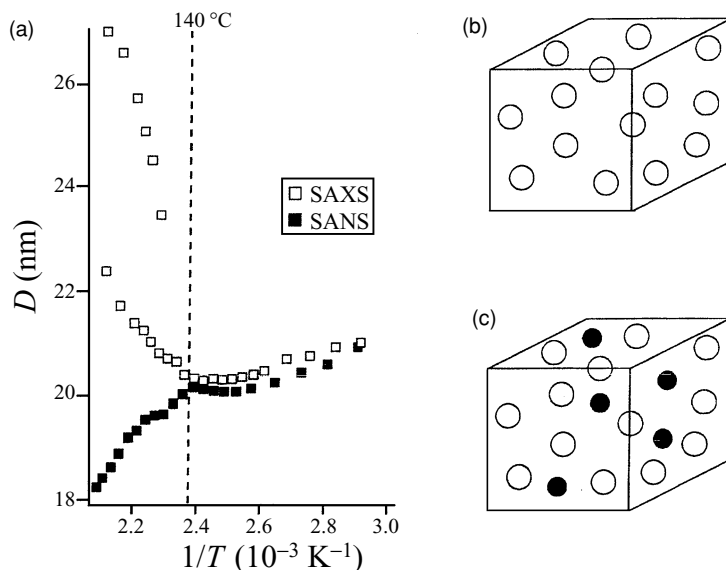


Fig. 7.37. (a) The temperature dependence of the domain spacing D calculated from the first-order scattering maxima for SAXS ($\square$) and SANS ($\blacksquare$) from a PI-b-DPS-b-PVME triblock terpolymer, and schematic models for the domain structure at (b) $T < 140^\circ\text{C}$ and (c) $T > 140^\circ\text{C}$. The spheres shown as open ($\circ$) and filled ($\bullet$) circles represent domains composed of PI and PVME blocks, respectively. (Reproduced with permission from [255]. Copyright 2002, Wiley-VCH, Weinheim.)

Thus, the complementary information provided by SANS and SAXS helps to characterize the structure and transitions in a way that neither technique alone could do, and is a possible argument in favor of locating neutron- and X-ray-scattering sources at the same site.

7.6.4 Dilute, semidilute, and concentrated polymer solutions

SANS measurements of polymers in dilute solution (i.e. below the overlap concentration, at which molecules start to interpenetrate) offer basically the same information as that from LS light and X-ray-scattering techniques, which permit the elucidation of chain dimensions via the electron-density contrast between a macromolecule and solvent. A greater signal-to-noise ratio may be obtained with the neutron technique since it is less sensitive to dust particles [44] and also because of the larger contrast possible with a deuterated polymer (or solvent). However, the main impact of SANS has been in the area of semidilute and concentrated systems. The technique has provided a wealth of new information previously unobtainable by LS or SAXS, for which intermolecular interference effects had restricted

measurements to the dilute regime. These effects may be overcome at higher polymer concentrations by SANS measurements on systems in which a fraction of the solute is isotopically labeled. As in the case of bulk polymers, this type of measurement was initiated on the assumption that the labeled component should be dilute, though it was subsequently demonstrated that measurements may be conducted at high levels of labeling [41, 224-241], thus increasing the experimental signal-to-noise ratio as in the case of bulk polymers.

As explained previously, the R_g of polymer chains in organic solvents depends on the sign and magnitude of the interactions between the chain segments and the molecules of the surrounding liquid. The attractive and repulsive interactions compensate at the “theta temperature” (T_Θ), at which $A_2 = 0$, and R_g corresponds to the dimension of a volume-less polymer coil. Similarly, as the concentration of polymer increases, excluded-volume effects are screened and diminished, and, in the limit of the bulk polymer, the conformation of a single chain can be described as an unperturbed random walk, as originally predicted by Flory [11], and one of the first applications of SANS was to confirm this prediction for the condensed amorphous state (see Section 7.1.2).

In the poor-solvent regime ($T < T_\Theta$, $A_2 < 0$), the attractive interactions between segments work to compress the molecules into compact globules, and, in dilute solution, the widely separated chains collapse as $T \rightarrow T_C$, where T_C is the critical phase-demixing temperature [234]. SANS has also been used to study semidilute solutions, in which, according to de Gennes’ concept, the chains do not interpenetrate significantly in the critical region ($T \sim T_C$), and thus should be collapsed (i.e. $R_g(T_C) < R_g(T_\Theta)$) as in the dilute-concentration regime. However, experiments [235] on polystyrene in cyclohexane (Fig. 7.38) and acetone [236] have shown that the predicted decrease in R_g is not observed. Instead, diverging fluctuations in concentration near T_C lead to the formation of distinct microdomains of strongly interpenetrating molecules, which prevent the expected collapse. The coherent cross section of a mixture of identical protonated and deuterated polymer chains dissolved in a solvent is given by

$$d\Sigma/d\Omega(Q, X) = I_s(Q, X) + I_t(Q, X) \quad (7.32)$$

$$I_s(Q, X) = (a_H - a_D)^2 X(1 - X) N_V N^2 P(Q, R_g) \quad (7.33)$$

$$I_t(Q, X) = [a_H X + (1 - X)a_D - a_s]^2 N_V N^2 S_t(Q) \quad (7.34)$$

where the subscripts “s” and “t” correspond to scattering from a single chain and total scattering, X is the mole fraction of protonated chains and N_V and N are the number density and degree of polymerization. As before, a_H and a_D are the scattering lengths of the ^1H - and ^2D -labeled segments of the polymer chain, and

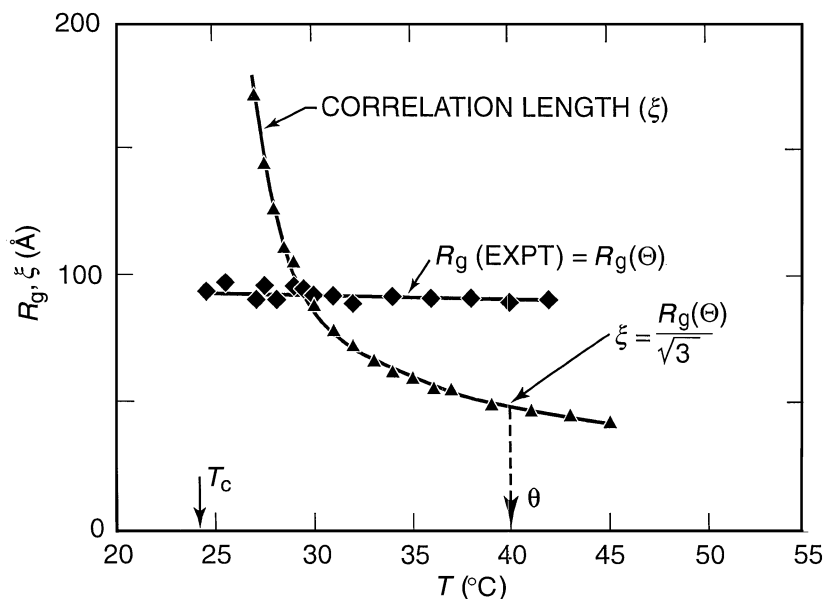


Fig. 7.38. Semidilute solutions of polystyrene in cyclohexane. The condition $\xi(\Theta) = R_g(T_\Theta)/\sqrt{3}$ may be used to locate the theta temperature. (Reproduced with permission from [235]. Copyright 1997 American Physical Society.)

a_s is the scattering length of a solvent molecule, normalized with respect to the same specific volume. $P(Q, R_g)$ is the single-chain structure factor, containing information on the intramolecular R_g , and the total scattering structure factor $S_t(Q)$ embodies both intramolecular and intermolecular correlations between segments.

The prefactor in Eq. (7.34) controls the “total” scattering contribution and it has been shown [235, 236] that, for isotopic mixtures of PS dissolved in deuterated acetone it is zero at $X = 0.214$. Similarly, for PDMS in CO_2 , an isotopic ratio of $X = 0.512$ gives a zero prefactor at a solvent density of $\rho_{\text{CO}_2} = 0.95 \text{ g cm}^3$. This is the *zero-averaged contrast condition*, under which the SLD of the solvent matches the average SLD of the polymer molecules (summed over the deuterated and protonated species). Thus, the “total” scattering of the polymer molecules disappears in much the same way as the glass wool in Fig. 7.12 is no longer “visible” when its refractive index matches that of the solvent in which it is suspended. This leaves only the scattering arising from the contrast of the individual isotopic polymer species with the solvent, described by Eq. 7.33, from which the intramolecular scattering function and R_g may be obtained directly. For systems (e.g. PS in deuterated cyclohexane) for which there is no isotopic ratio X that makes the prefactor of Eq. (7.34) zero, $d\Sigma/d\Omega$ always contains a contribution from the total (intermolecular) scattering, which must be minimized and subtracted in order to extract

R_g . If all chains are all protonated ($X = 1$), the prefactor in Eq. (7.33) is zero and $d\Sigma/d\Omega \sim S_t(Q)$. Thus, the size of the concentration fluctuations, which are characterized via the composition-fluctuation correlation length (ξ), may be measured via the Ornstein–Zernike formalism (Eq. (7.27)).

Figure 7.38 shows the temperature variation of R_g for PS in deuterated cyclohexane at the critical concentration and it may be seen that the chains do not collapse as $T \rightarrow T_C$, as is observed in dilute solutions. Instead, they maintain their unperturbed dimensions in accordance with the theoretical predictions of Muthukumar [237] and Raos and Alegra [238]. The size of the concentration fluctuations increases dramatically near the critical point and stabilizes the chain dimensions. So effective is this mechanism that it has been shown that, even for solutions that never leave the poor solvent domain, and cannot reach the Θ -domain (e.g. PS in acetone), the molecules are always “stabilized” to exhibit the “theta dimensions” over wide ranges of pressure and temperature [236]. As indicated in Fig. 7.38, the condition $\xi(\Theta) = R_g(T_\Theta)/\sqrt{3}$ may be used to locate the theta temperature. Thus, if the unperturbed R_g of the polymer coils is known, the advent of the Θ -condition is indicated when the correlation length reaches $R_g/\sqrt{3}$, as shown in Fig. 7.38, where $T_\Theta \simeq 40^\circ\text{C}$ for PS in cyclohexane. This relationship is particularly useful for supercritical solutions (e.g. PDMS in CO_2), for which the boundaries of the Θ -region are less well known than is the case for organic solvents (see below).

In addition to studying the solubilization of CO_2 -insoluble polymers by means of emulsifying agents [25], as described in Section 7.1.3, SANS has also been used to study CO_2 -soluble systems such as fluoropolymers and PDMS [24]. In particular, Melnichenko *et al.* [239] have studied the dimensions of PDMS molecules in CO_2 in order to test the prediction of Kiran and Sen [240] that they will adopt “ideal” configurations, unperturbed by excluded-volume effects, at a critical “theta pressure” (P_Θ) as they do in polymer solutions at the theta temperature (T_Θ). Results of experiments on PDMS in CO_2 (Figs. 7.39 and 7.40) confirm that the system exhibits both of these phenomena at $P_\Theta \sim 540$ bar and $T_\Theta \sim 55^\circ\text{C}$.

For $P > P_\Theta$ and $T > T_\Theta$, the system exhibits a “good-solvent” domain, where in the polymer molecules expand beyond the unperturbed R_g measured in the condensed (solid) state. However, for $T < T_\Theta$, and $P < P_\Theta$, the chains do not collapse as expected (Figs. 7.39 and 7.40). Instead, they maintain their unperturbed dimensions, as observed in organic solvents (Fig. 7.39). Thus, the deterioration of the solvent quality again leads to the formation of microdomains, consisting of interpenetrating polymer coils. Near T_c , the growth of the polymer concentration fluctuations brings together the initially diluted chains, which adopt the unperturbed dimensions, as in highly concentrated systems [233] and in the condensed state (see Section 7.1.2). Thus, the stabilization of the molecular dimensions in

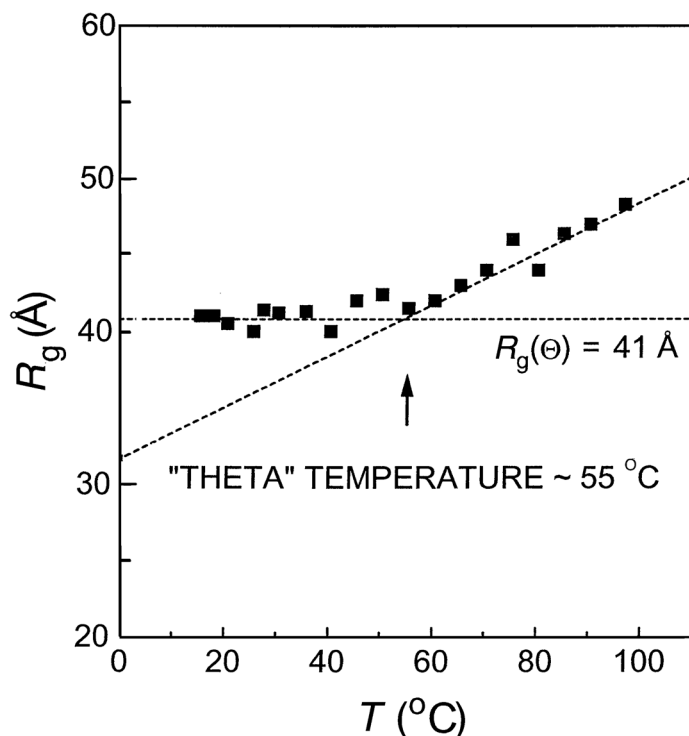


Fig. 7.39. Expansion of polydimethylsiloxane (PDMS) in supercritical CO_2 above the theta temperature ($T_\Theta \sim 55^\circ\text{C}$). Below T_Θ , diverging fluctuations in concentration prevent the coil collapse observed in organic (e.g. cyclohexane; see Fig. 7.38) solvents. (Reproduced with permission from [239]. Copyright 1999 American Chemical Society.)

the poor-solvent domain by diverging concentration fluctuations is a universal phenomenon, which is observed not only in “classical” polymer solutions, such as polystyrene in CH, but also in supercritical fluids (SCFs), and there is a close similarity between the behavior of polymer molecules in organic solvents and that in CO_2 . However, a unique attribute of SCFs is that the solvent strength is tunable with changes in density of the system, offering significant control over the solubility. Thus, for PDMS, CO_2 becomes a “theta” solvent at $P_\Theta \sim 447$ bar and $T_\Theta \sim 55^\circ\text{C}$, whereas it behaves as a “good” solvent for $P > P_\Theta$ and $T > T_\Theta$. However, for solutions in CO_2 , the system may be driven through this transition as a function of pressure in addition to temperature. Understanding the solubility mechanisms is a necessary condition for the development of CO_2 -based technologies and SANS has been shown to give the same level of insight into polymers in supercritical media [24] as that which it has provided for the condensed state and organic solvents [3].

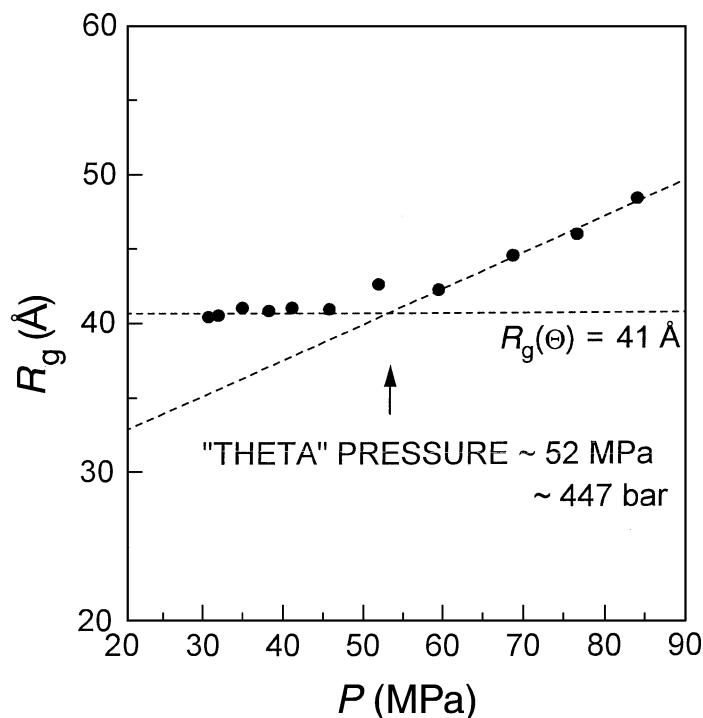


Fig. 7.40. Observation of the “theta pressure” in supercritical CO_2 . As is observed for organic solvents (see Fig. 7.38), the chains do not collapse below T_Θ . (Reproduced with permission from [239]. Copyright 1999 American Chemical Society.)

The correlation length (ξ) in PDMS– CO_2 solutions at constant density is shown in Fig. 7.41 as a function of temperature. ξ diverges as T approaches the critical temperature of phase demixing, T_c , and the temperature variation of the size of the concentration fluctuations in supercritical media (i.e. PDMS in CO_2 (lower)) and organic solvents (i.e. PS in CH (upper)) is similar. The critical index ν of the scaling law for the correlation length $\xi \sim (T - T_c)^{-\nu}$ exhibits a sharp crossover from the mean-field value ($\nu = 0.5$) far from the critical point to the Ising-model value ($\nu = 0.63$) in the critical region around T_c . The crossover takes place when the correlation length becomes equal to the radius of gyration of the polymer, and thus reproduces the main features of the crossover observed in solutions of PS in CH [242, 243].

These observations delineate an intrinsic analogy among the temperature behaviors of polymers in organic solvents, supercritical fluids, and polymer blends in which similar crossover phenomena are observed (see Section 7.6.2.1). Using the scaling variable $\tau^* = (T - T_c)/(\Theta - T_c)$, which accounts for the distances of the temperature both from T_Θ and from T_c , and normalizing the correlation

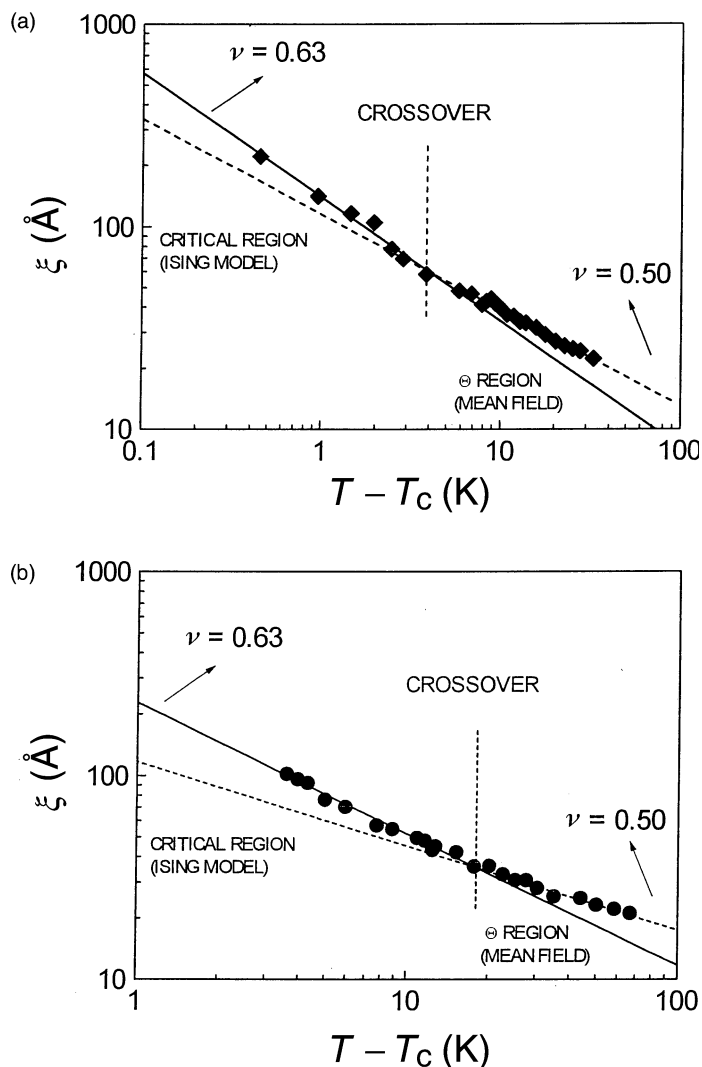


Fig. 7.41. The variation of the correlation length, ξ , as a function of $T - T_c$ for polystyrene in cyclohexane (a) and PDMS in supercritical CO_2 (b). The slopes give the values of the critical index, ν . (Reproduced with permission from [239]. Copyright 1999 American Chemical Society.)

length with respect to the value at the theta temperature, $\xi(\Theta)$, Fig. 7.41, shows that $\xi/\xi(\Theta)$ collapses onto a master curve over wide ranges of molecular weight (2500–400 000), theta temperature ($65^\circ\text{C} < T_\Theta < 484^\circ\text{C}$), and critical temperature ($-40^\circ\text{C} < T_c < 160^\circ\text{C}$). This demonstrates the universality of the structure and thermodynamic properties of polymer molecules in polymeric, liquid, and supercritical solvents [162, 244].

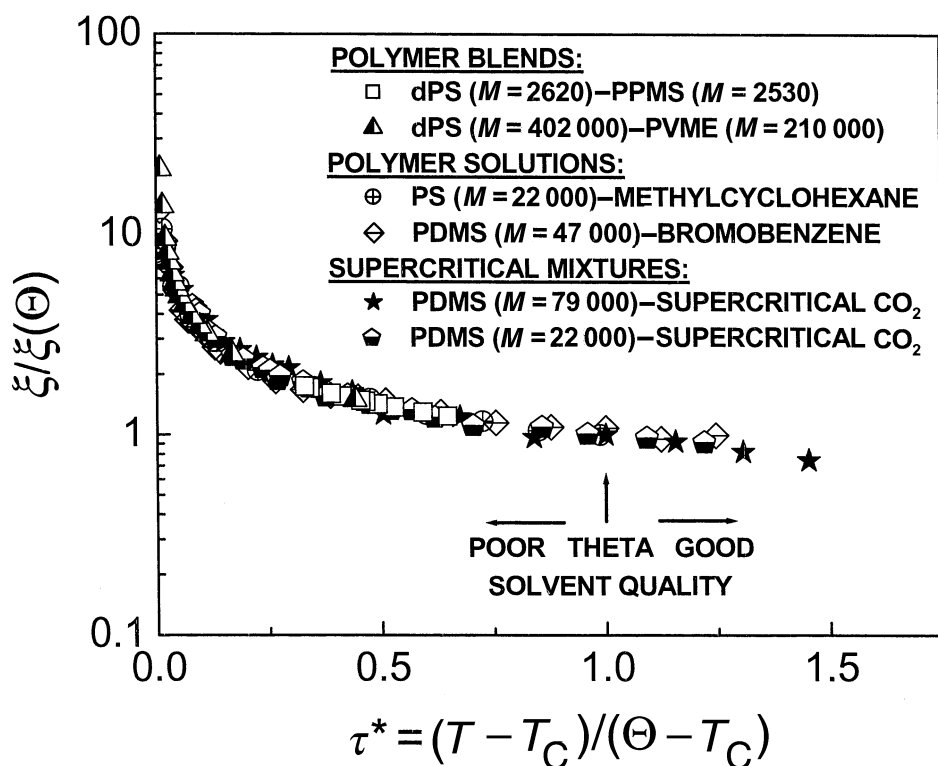
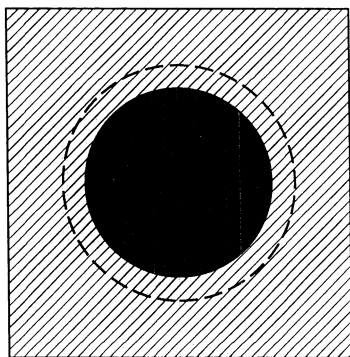


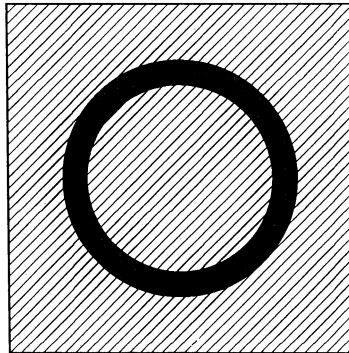
Fig. 7.42. The master curve for polymers in polymer blends, organic solvents, and supercritical solvents. (Reproduced with permission from [244]. Copyright 2002 American Physical Society.)

7.6.5 Polymer latexes

Latexes constitute one of the most important forms of polymers and are widely used in the coating industries as well as in engineering applications. Many properties of latex polymers originate from the molecular conformation and structure of the polymer chains inside the latex particles, though there has been considerable discussion of the actual structure of the latex. Because the latex interacts with its environment through its surfaces, understanding and control of the surface properties are particularly important. Grancio and Williams [245] postulated a polymer-rich spherical core surrounded by a monomer-rich shell that serves as the major locus of polymerization, thus giving rise to a core-shell morphology. This model, in which the first-formed polymer constitutes the core and the second-formed polymer makes up the shell, has been the subject of extensive debate [37]. In order to resolve such differences unequivocally, characterization techniques that probe the internal structure of latex particles are required. With latex-particle diameters of $\sim 10^3$ Å, LS and SAXS may be used to measure intraparticle dimensions and SANS



WHEN THE SLD OF THE SOLVENT MATCHES THE OUTER SHELL, SANS GIVES THE CORE DIMENSIONS VIA THE SPHERE SCATTERING (BESSEL) FUNCTION



WHEN THE SOLVENT SLD MATCHES THE CORE, SANS GIVES THE SHELL MORPHOLOGY VIA THE HOLLOW-SPHERE SCATTERING FUNCTION

Fig. 7.43. SANS studies of polymer-latex particles in H_2O – D_2O mixtures.

has been used in combination with contrast-variation methods to isotopically label particular chains generated at specific points during the process of polymerization. The scattering contrast between normal (^1H -labeled) and deuterated (^2D -labeled) molecules allows their locations and dimensions to be determined and Fig. 7.43 illustrates schematically how the core-shell hypothesis may be tested via SANS. The morphology of the latex core may be characterized by measurements in D_2O , which gives strong contrast with the protonated polymer. For a homogeneous particle, the neutron-scattering cross section is given by

$$\frac{d\Sigma}{d\Omega}(Q) = (\rho_m - \rho_p)^2 N_p V_p^2 P(Q) \quad (7.35)$$

where ρ_m and ρ_p are the SLDs of the medium and the particle, respectively, N_p is the number of particles per unit volume, and V_p and $P(Q)$ are the particle volume and form factor, respectively ($P(0) = 1$). For a solid sphere of uniform radius, R , $P(Q)$ is given by [250, 251]

$$P(Q) = \frac{9[\sin(QR) - QR \cos(QR)]^2}{(QR)^6} \quad (7.36)$$

According to Grancio and Williams [245], polymerization takes place in a surface shell and thus, if the monomer feed is changed from protonated to deuterated material, this will result in a predominantly D-labeled shell. When such a sample is examined by SANS in an H_2O – D_2O mixture that matches the SLD of the protonated

core (Fig. 7.43), the scattering will arise from a hollow sphere with a particle form factor [250, 251] given by

$$P(Q) = \frac{9[\sin(QR_{\text{shell}}) - \sin(lQR_{\text{shell}}) - QR_{\text{shell}} \cos(QR_{\text{shell}}) + lQR_{\text{shell}} \cos(lQR_{\text{shell}})]^2}{Q^6 R_{\text{shell}}^6 (1-l)^6} \quad (7.37)$$

where $l = R_{\text{core}}/R_{\text{shell}}$, and R_{core} and R_{shell} are the outer and inner radii, respectively⁸. For $l = 0$, Eq. (7.37) reduces to the solid-sphere scattering function (Eq. (7.36)) with $R_{\text{core}} = R_{\text{shell}} = R$. Thus the core-shell hypothesis can be tested by comparing SANS data both for cores and for shells (Fig. 7.43) with the model predictions (Eqs. (7.36) and (7.37)).

Such experiments have been undertaken by Fisher *et al.* [74], who studied PMMA latexes with deuterated shells of PMMA-D or PSD polymerized on the surface. Similar experiments on a partially deuterated PMMA shell polymerized on cores consisting of random PMMA-PS copolymers have been performed by Wai and Gelman [75]. The scattering both from cores and from shells exhibits sharp maxima and minima for monodisperse particles, though in practice these sharp features are smeared by the finite experimental resolution. As described in Section 7.5.3, desmearing procedures using IFT methods developed by Glatter [125] and Moore [126], were used to remove these instrumental effects, which led to a pattern showing the expected sharp minima with good agreement between the core radii determined by SANS and independently by LS [74, 75].

In addition to instrumental-resolution effects, the data can also be smeared by integrating over the finite range of particle radii, if the samples are not monodisperse. Such particle-size distributions may be described by a zeroth-order logarithmic distribution (ZOLD) [74, 75]. For this distribution, the prevalence of particles of radius R is a function of the average size and the standard deviation, σ . Figure 7.44 shows desmeared SANS data for the copolymer core compared with the solid-sphere scattering function (Eq. (7.36)), using the ZOLD with an average diameter $D = 1008 \text{ \AA}$ and $\sigma = 92 \text{ \AA}$. Figure 7.45 shows a similar comparison for the core-shell latex. In addition to the shape of the scattering envelope, the scattering intensity provides an independent check on the model if the concentration of particles and the SLD are known. The absolute intensity at zero scattering angle is given by Eq. (7.35) with $P(0) = 1$ and, for the core, V_p is the volume of the latex particle in solution. For the shells, a core-shell structure was assumed (Eq. (7.37)) and for the absolute-intensity calculations V_p was taken to be the volume of the labeled polymer in the

⁸ We may note that, although the term “contrast-matched” is often used, it is actually the SLDs that are matched and thus the contrast is zero.

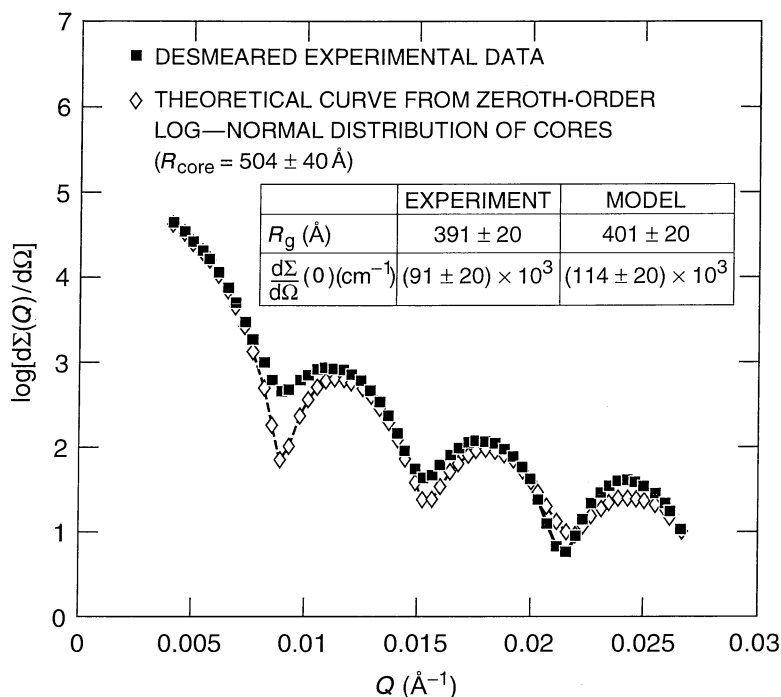


Fig. 7.44. A comparison of experimental SANS data and theoretical values of the scattering function for PS-PMMA core latexes in D_2O . (Reproduced with permission from [66]. Copyright 1993 American Chemical Society.)

shell. The SLDs of core and solvent were matched (i.e. the contrast for the core was zero) and the measured absolute intensities and R_g s are shown in Figs. 7.44 and 7.45, together with those calculated from the latex dimensions determined independently by LS and transmission electron microscopy (TEM). Both the dimensions (R_g) and the cross sections agree with the model to within the experimental error both for homopolymer [74] and for copolymer [75] cores and shells, thus illustrating the importance of absolute calibration (see Section 7.5.2) and supporting the core-shell hypothesis for polymerization under monomer-starved conditions.

Other studies of polymer latexes have been undertaken by Goodwin and Ottewill [246], who used SANS to measure the kinetics of swelling of PS latexes in their monomer (styrene). These experiments were also performed with low volume fractions of the dispersed latexes, whereby particle-particle interactions were minimized. At higher concentrations the mutual arrangement of the particles is reflected in a structure factor, $S(Q)$, from which a latex-latex radial distribution function may be obtained via Fourier transformation. Experiments along these lines have been performed by Alexander *et al.* [247] and Cebula *et al.* [248], and comparison

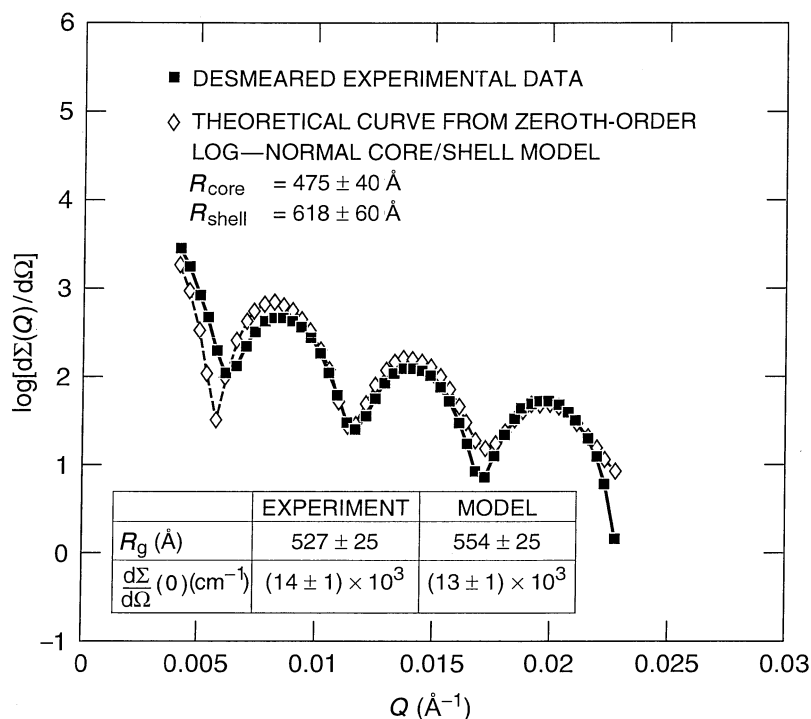


Fig. 7.45. A comparison of experimental SANS data and theoretical values of the scattering function for a PS-PMMA-H core latex with a PMMA-D3 shell; the core SLD was matched to a 25/75 solution of $\text{D}_2\text{O}/\text{H}_2\text{O}$. (Reproduced with permission from [66]. Copyright 1993 American Chemical Society.)

with theoretical models gives information on the interparticle interactions. These techniques are relevant to a wide variety of polymeric, colloidal, and biochemical systems, and reviews of their application to the structures of micellar solutions have been given by Hayter [4, 26, 72], Magid [27], and Chen [42, 251].

Information on the stabilization of non-aqueous dispersions of polymer particles by block copolymers may be obtained by SANS and the possibility of deuterating one of the block lengths allows the determination of the state of dispersion of each block in the particle or on the surface. Such experiments have been performed on non-aqueous dispersions of PMMA and polystyrene particles stabilized by PS-polydimethylsiloxane block copolymers by Higgins *et al.* [249]. More recently, O'Reilly *et al.* [252] have used SANS to investigate the internal structure of amorphous nanoparticles of photographic couplers precipitated from basic solutions in the presence of surfactants and dispersed in aqueous media. In a photographic film, a coupler (dye precursor) reacts with oxidized developer to produce the image dye. The efficiency of image-dye formation depends on the reactivity of the coupler and

the state of dispersion. The colloidal stability of these dispersions is in large part maintained by charge stabilization through the anionic surfactants employed in their preparation. Typical particle sizes were shown to be in the range 50–250 Å and, at higher concentrations, interparticle interactions manifested by a peak, as opposed to a monotonic fall off in the scattering, were observed. For these data, the interparticle scattering function, $S(Q)$, was calculated using the mean-sphere approximation [4], which was used to extract the aggregation number, surface charge, and inner and outer radii of the particle. Such colloidal dispersions are widely used in many other industrial products, such as pharmaceutical, personal-care, and agricultural formulations, and, in view of the contrast-variation options that are available for aqueous dispersions, this methodology has a wide potential application in many practical systems.

7.7 Future directions

At the time of writing there were over 40 neutron sources around the world operating as user facilities [253]. Of these sources, 36 are reactor facilities, but two-thirds of them were commissioned more than 30 years ago and consequently now have increasingly finite lifetimes. Many of these institutions operate SANS facilities, though several of these instruments are no longer operational due to reactor shut-downs, and this trend can be expected to continue. A forward survey [254] estimated that, over the next two decades, the installed capacity of neutron beams for research could decrease substantially. Fortunately, the expected decline in the availability of reactor-based SANS instruments has been offset by two competing trends. First, several new reactors are under construction worldwide [255], together with upgrades to existing sources (e.g. at the ILL in the mid 1990s, the National Institute for Standards and Technology (1995–2002) and Oak Ridge National Laboratory (2000–2005)). In addition, various accelerator-based SANS instruments have been developed over the past 15 years, and, in particular, a “next-generation” Spallation Neutron Source is under construction at Oak Ridge [256]. Similarly, the planned [257] European Spallation Source (ESS) would do much to offset and even reverse the predicted decline in the availability of SANS facilities.

Unlike reactor sources, where fission neutrons are produced in the core, which is surrounded by a moderator (see Section 7.4.1), the spallation process involves bombarding a heavy metal (e.g. Ta, W, or Hg) target with high-energy protons, which trigger an intranuclear cascade, placing those nuclei into a highly excited state. These lose energy by “evaporating” nucleons, and, in the case of a tungsten target, each proton results in the production of ~ 15 neutrons. The protons are usually accelerated in pulses and so neutron production also occurs in pulses, which

allows the use of time-of-flight (TOF) techniques. Shorter-wavelength neutrons travel faster and arrive at a detector earlier than do longer-wavelength neutrons, so there is thus no need to employ a velocity selector to monochromate the incident beam. Another benefit of the TOF approach is that any given point on a detector corresponds to several different Q -values, determined by the wavelength of the neutrons arriving there. Hence, a greater range of Q -values can be measured with any given configuration of the instrument. Pulsed-source SANS instruments therefore have a greater dynamic range in Q than do reactor-source instruments [258], though the range of the latter can be increased by moving the detector “off axis” [259].

As the main applications of the SANS technique have been undertaken on reactor sources, these instruments have been optimized over the past several decades, and the flux of instruments planned for new or upgraded reactor sources will either be less than or equal to that of the current state-of-the-art instruments (e.g. the D22 instrument at the ILL [260]). However, this is not the case for pulsed facilities, which have not yet begun to reach their full potential, so we can still expect order-of-magnitude gains over the current facilities, via the ESS, SNS, etc. Thus, it seems likely that pulsed sources will make a greater contribution to SANS studies of polymers in future than they have in the past.

New high-flux sources will also provide the polymer community with an opportunity to design novel classes of non-equilibrium time-resolved studies and shear-induced phenomena [255]. Processing is a key issue in allowing new materials and technology to reach the market place, and deformation leads to changes in morphology that must be studied under actual conditions. The need for analyzing systems close to actual processing conditions has been recognized previously [261], and new high-flux sources offer the prospect of finally performing structural studies under conditions similar to those used in industry. In this respect, neutrons have a unique advantage since they can penetrate macroscopic extruders and flow devices. Other categories of measurement should also be possible, for example using higher flux to improve the temporal-resolution of kinetic measurements such as *in situ* polymerizations. We may also envision studies of progressively more dilute systems and the routine use of smaller sample volumes (~ 1 mg) or smaller beam sizes (~ 1 mm).

For reactor-based instruments, we may also expect that further improvements in the field of USANS along the lines described in Section 7.4.2 will be made and should make it routinely possible to overlap SANS experiments and LS techniques. To the author’s knowledge, USANS instrumentation has not yet been developed for pulsed-source facilities, and this will be a stimulating challenge for taking advantage of the new high-flux sources that are under construction [256] or planned [257, 262].

Finally, it may be worth re-emphasizing a point made in the “Neutron Scattering in the ’Nineties” Symposium [44] as follows:

The greatest limitation for SANS experimentalists is the securing of suitable samples. To take full advantage of the power of SANS, samples should be selectively deuterated in designated places. The investment in SANS experiments is great enough that samples should be well characterized for M , tacticity, etc.

In view of the planned large investments in new sources, upgrades, and instrumentation, the commitment of a small fraction of this amount to a synthetic program could dramatically increase the overall impact and productivity of future research on polymers, as is planned, for example, at the ORNL Center for Nanophase Materials Sciences to complement current developments in instrumentation [263].

Acknowledgments

This review is dedicated to the memory of John B. Hayter, who was one of the pioneers of the SANS technique both in Europe (at the ILL) and also in the USA (at ORNL). He worked for many years as Scientific Director of the Advanced Neutron Source Project and it is a measure of his tenacity and resilience that, shortly after it was canceled, he proposed a major upgrade of the HFIR facilities. The fact that this project is now nearing completion, and includes two new world-class SANS facilities, is a tribute to John’s dedication to the goal of bringing state-of-the-art instrumentation to the worldwide neutron-user community in general, and to US scientists in particular. The author would like to thank D. M. Engelmann and T. Hashimoto, who provided Figs. 7.12 and 7.37, respectively, and also his many co-workers, for permission to include data from their individual and joint publications, particularly M. M. Agamalian, R. G. Alamo, F. S. Bates, J. M. DeSimone, L. Mandelkern, D. W. Marr, Y. B. Melnichenko, T. P. Russell, J. Schelten, L. H. Sperling, M. P. Wai, and W. L. Wu. The research was supported by the Divisions of Advanced Energy Projects, Materials and Chemical Sciences, US Department of Energy under contract DEAC0500OR22725 with the ORNL, managed by UTBattelle, LLC.

References

- [1] R. M. Moon, *Physica B*, **267–268** (1999), 1.
- [2] T. E. Mason, *et al.*, *Mater. Res. Soc. Bull.*, December, **24** (1999), 14.
- [3] J. S. Higgins and H. Benoit, *Polymers and Neutron Scattering* (Clarendon Press, Oxford, 1994).
- [4] J. B. Hayter and J. Penfold, *Coll. Polym. Sci.*, **261** (1983), 1022.
- [5] P. G. de Gennes, *Fragile Objects: Soft Matter, Hard Science, and the Thrill of Discovery* (Copernicus Books, Springer-Verlag, New York, 1996), p. 89.
- [6] C. W. Bunn, *Trans. Faraday Soc.*, **35** (1939), 482.
- [7] R. G. Kirste, *Jahresber. Sonderforschungsbereiches*, **41** (1970), 547.

- [8] G. D. Wignall, Memorandum PPR G19 (Imperial Chemical Industries, Runcorn, 1970), p. 1.
- [9] J. Schelten, *et al.*, *Coll. Polym. Sci.*, **252** (1974), 749.
- [10] G. Lieser, E. W. Fischer, and K. Ibel, *J. Polym. Sci.*, **13** (1975), 29.
- [11] P. J. Flory, *J. Chem. Phys.*, **17** (1949), 303.
- [12] G. D. Wignall, D. G. H. Ballard, and J. Schelten, *Eur. Polym. J.*, **20** (1974), 861.
- [13] B. H. Zimm, *J. Chem. Phys.*, **16** (1948), 157.
- [14] H. Benoit, *et al.*, *Nature*, **245** (1973), 23.
- [15] R. G. Kirste, W. A. Kruse, and K. Ibel, *Polymer*, **16** (1975), 120.
- [16] P. Debye, *J. Appl. Phys.*, **15** (1944), 338; P. J. Flory, *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, New York, 1969), p. 295.
- [17] D. Yoon and P. J. Flory, *Macromolecules*, **9** (1976), 294.
- [18] M. Rawiso, R. Duplessix, and C. Picot, *Macromolecules*, **20** (1987), 630.
- [19] J. M. O'Reilly, D. M. Teegarden, and G. D. Wignall, *Macromolecules*, **18** (1985), 2747.
- [20] D. Y. Yoon and P. J. Flory, *Polymer*, **16** (1975), 645.
- [21] D. Y. Yoon and P. J. Flory, *Polym. Bull.*, **4** (1981), 692; P. J. Flory, *Pure Appl. Chem.*, **56** (1984), 305.
- [22] J. Schelten, *et al.*, *Polymer*, **27** (1976), 751.
- [23] H. Hayashi, P. J. Flory, and G. D. Wignall, *Macromolecules*, **16** (1983), 1328.
- [24] G. D. Wignall, *J. Condens. Matter*, **11** (1999), R157.
- [25] J. M. DeSimone, *et al.*, *Science*, **257** (1992), 945.
- [26] J. B. Hayter, *Physics of Amphiphiles, Micelles, Vesicles and Microemulsions*, edited by V. de Giorgio and M. Corti (North Holland, Amsterdam, 1985).
- [27] L. J. Magid, *Coll. Surf.*, **19** (1986), 129.
- [28] E. J. Beckman, *Science*, **271** (1996), 613.
- [29] M. Rouhi, *Chem. Eng. News*, February, **5** (1996), 8.
- [30] J. B. McClain, *et al.*, *Science*, **274** (1996), 2049.
- [31] J. D. Londono, *et al.*, *Appl. Crystallogr.*, **30** (1997), 690.
- [32] J. L. Fulton, *et al.*, *Langmuir*, **11** (1995), 4241.
- [33] K. P. Johnston, *et al.*, *Science*, **271** (1996), 624.
- [34] E. Caponetti and R. Triolo, *Adv. Coll. Interf. Sci.*, **32** (1990), 235.
- [35] F. Triolo, *et al.*, *Langmuir*, **16** (2000), 416.
- [36] P. Lindner and T. Zemb (eds.), *Neutron, X-Ray and Light Scattering* (Elsevier Publishers, New York, 1991).
- [37] G. D. Wignall, in *Encyclopedia of Polymer Science and Engineering*, 2nd edition, Vol. 10, edited by M. Grayson and J. Kroschwitz (Wiley, New York, 1987), p. 112.
- [38] J. P. Cotton, *et al.*, *Macromolecules*, **7** (1974), 863.
- [39] J. P. Cotton, *et al.*, *J. Chem. Phys.*, **57** (1972), 290.
- [40] M. Daoud, *et al.*, *Macromolecules*, **8** (1975), 804.
- [41] J. S. King, *et al.*, *Macromolecules*, **18** (1985), 709.
- [42] S. H. Chen, *Ann. Rev. Phys. Chem.*, **37** (1986), 351.
- [43] E. Caponetti, *et al.*, *Langmuir*, **11** (1995), 2464.
- [44] R. S. Stein, *Neutron Scattering in the Nineties*, IAEA, Vienna, CN-46, 335 (1985).
- [45] J. S. Higgins and R. S. Stein, *J. Appl. Crystallogr.*, **11** (1978), 346.
- [46] D. E. Groom, *et al.*, *Eur. Phys J. C* **15** (2000), 1; see <http://pdg.lbl.gov/>.
- [47] W. Schmatz, T. Springer, and J. Schelten, *J. Appl. Crystallogr.*, **7** (1974), 96.
- [48] L. E. Alexander, *X-Ray Diffraction Methods in Polymer Science* (Krieger Publishing Co. Inc., London, 1969).

- [49] J. Brandrup and E. H. Immergut (eds.), *Polymer Handbook* (Wiley Interscience, New York, 1975), ch. IV, p. 1.
- [50] C. H. Macgillavry and G. D. Rieck (eds.), *International Tables for X-ray Crystallography* (Kynoch Press, Birmingham, 1968).
- [51] A. Avitabile, *et al.*, *Polym. Lett. Ed.*, **13** (1975), 351.
- [52] M. Stamm, *J. Polym. Sci.: Polym. Phys. Ed.*, **20** (1982), 235; M. Stamm, *et al.*, *Discuss. Faraday Soc.*, **68** (1979), 263.
- [53] G. D. Wignall, in *Applied Fiber Science*, edited by F. W. Happey (Academic Press, London, 1978), p. 181.
- [54] G. Allen and J. S. Higgins, *Rep. Prog. Phys.*, **36** (1973), 1073.
- [55] K. Nicholson, *Contemp. Phys.*, **22** (1981), 451.
- [56] J. S. Higgins and A. Maconnachie, in *Neutron Scattering*, edited by K. Skold and D. L. Price (Academic Press, New York, 1987), p. 287.
- [57] A. Guinier and G. Fournet, *Small-Angle Scattering of X-Rays* (John Wiley, New York, 1955).
- [58] O. Glatter and O. Kratky, *Small-Angle X-Ray Scattering* (Academic Press, London, 1982).
- [59] R.-J. Roe, *Methods of X-Ray and Neutron Scattering in Polymer Science* (Oxford University Press, Oxford, 2000).
- [60] B. J. Gabrys (ed.), *Applications of Neutron Scattering to Soft Condensed Matter* (Gordon and Breach Science Publishers, New York, 2000).
- [61] M. G. Huglin, *Light Scattering from Polymer Solutions* (Academic Press, London, 1982).
- [62] W. Marshall and S. W. Lovesey, *Theory of Thermal Neutron Scattering* (Clarendon Press, Oxford, 1971).
- [63] G. E. Bacon, *Neutron Diffraction* (Clarendon Press, Oxford, 1971).
- [64] G. D. Wignall, in *Scattering, Deformation and Fracture in Polymers*, edited by G. D. Wignall, B. Crist, T. P. Russell, and E. L. Thomas (Materials Research Society, Pittsburgh, 1987), p. 27.
- [65] R. W. James, *The Optical Principles of the Diffraction of X-rays* (Bell, London, 1958).
- [66] G. D. Wignall, in *The Physical Properties of Polymers*, edited by J. E. Mark (ACS Books, Washington, 1993).
- [67] A. Maconnachie, *Polymer*, **25** (1984), 1068.
- [68] L. D. Coyne and W. Wu, *Polym. Commun.*, **30** (1989), 312.
- [69] G. D. Wignall, *Polymer Properties Handbook*, edited by J. E. Mark (American Institute of Physics, New York, 1996), p. 299.
- [70] W. S. Dubner, J. M. Schultz, and G. D. Wignall, *J. Appl. Crystallogr.*, **23** (1990), 469.
- [71] M. Von Laue, *Ann. Phys.*, **56** (1918), 497.
- [72] J. B. Hayter, in *Proceedings of Enrico Fermi School of Physics Course XC*, edited by V. Degiorgio and M. Corti (North Holland, Amsterdam, 1985), p. 59.
- [73] H. Hayashi, F. Hamada, and A. Nakajima, *Macromolecules*, **9** (1976), 543.
- [74] L. W. Fisher, *et al.*, *J. Coll. Interf. Sci.*, **123** (1988), 24.
- [75] M. P. Wai, *et al.*, *Polymer*, **28** (1987), 918.
- [76] G. D. Wignall, *et al.*, *Mol. Cryst. Liq. Cryst.*, **180A** (1990), 25.
- [77] T. P. Russell, *et al.*, *J. Appl. Crystallogr.*, **21** (1988), 629.
- [78] J. Schelten, *Kerntechik*, **14** (1972), 86.
- [79] J. Schelten, in *Scattering Techniques Applied to Supramolecular and Nonequilibrium Systems*, edited by S. H. Chen, B. Chu, and R. Nossal (Plenum Press, New York, 1981), p. 75.

- [80] K. Ibel, *J. Appl. Crystallogr.*, **9** (1976), 196.
- [81] P. Lindner, R. P. May, and P. A. Timmins, *Physica B*, **180–181** (1992), 967.
- [82] *Neutronenstreuexperimente am FRJ2 in Jülich* (1997). (English and German texts are available from the Forschungszentrum, Jülich.)
- [83] H. Maier-Leibnitz and T. Springer, *Ann. Rev. Nucl. Sci.*, **16** (1966), 207.
- [84] W. C. Koehler, *Physica B*, **137** (1986), 320.
- [85] J. B. Hayter and H. Mook, *J. Appl. Crystallogr.*, **22** (1989), 35.
- [86] R. K. Abele, *et al.*, *IEEE Trans. Nucl. Sci.*, **NS-28** (1981), 811.
- [87] P. Lindner, F. Leclercq, and P. Damay, *Physica B*, **291** (2000) 152.
- [88] M. M. Agamalian, G. D. Wignall, and R. Triolo, *Neutron News*, **9** (2) (1998), 24.
- [89] A. Miksovsky, *et al.*, *Phys. Stat. Sol. (a)*, **130** (1992), 365.
- [90] D. Schwahn, *et al.*, *Nucl. Instrum. Methods A*, **239** (1985), 229.
- [91] A. Hempel and F. Eichhorn, *BENSC Experimental Report*, HM1-B525, 350 (1995).
- [92] K. Aizawa and H. Tomimitsu, *Physica B*, **213–214** (1995), 884.
- [93] T. Takahashi and M. Hashimoto, *Phys. Lett. A*, **200** (1995), 73.
- [94] A. R. Drews, *et al.*, *Physica B*, **241–243** (1998), 189.
- [95] Agamalian, G. D. Wignall, and R. Triolo, *J. Appl. Crystallogr.*, **30** (1997), 345.
- [96] M. M. Agamalian, *et al.*, *Macromolecules*, **32** (1999), 3093.
- [97] *Institut Laue–Langevin Annual Report for 2000*, (ILL, Geneva, 2000), p. 95.
- [98] U. Bonse and M. Hart, *Appl. Phys. Lett.*, **7** (1965), 238.
- [99] H. Matsuoka, *Chemtracts – Macromol. Chem.*, **4** (1993), 59.
- [100] D. K. Christen, *et al.*, *Phys. Rev. B*, **15** (1977), 4506.
- [101] B. Alefeld, D. Schwahn, and T. Springer, *Nucl. Instrum. Methods A*, **274** (1989), 210.
- [102] B. Alefeld, *et al.*, *Physica B*, **236** (1989), 1052.
- [103] J. Schelten, *et al.*, *Polymer*, **18** (1977), 111.
- [104] C. Strazielle and H. Benoit, *Macromolecules*, **8** (1975), 203.
- [105] H. Yang, G. Hadziioannou, and R. S. Stein, *J. Polym. Sci.: Polym. Phys. Ed.*, **21** (1983), 159.
- [106] A. B. Buckingham and H. G. E. Hentschel, *J. Polym. Sci.: Polym. Phys. Ed.*, **18** (1984), 853.
- [107] F. S. Bates, G. D. Wignall, and W. C. Koehler, *Phys. Rev. Lett.*, **55** (1985), 2425.
- [108] F. S. Bates and G. D. Wignall, *Macromolecules*, **19** (1986), 932.
- [109] F. S. Bates, *et al.*, *Macromolecules*, **89** (1988), 535; *Macromolecules*, **21** (1988), 1086.
- [110] D. Schwahn, *et al.*, *J. Chem. Phys.*, **93** (1989), 8383.
- [111] A. Lapp, C. Picot, and H. Benoit, *Macromolecules*, **18** (1985), 2437.
- [112] F. S. Bates and G. D. Wignall, *Phys. Rev. Lett.*, **57** (1986), 1429.
- [113] F. S. Bates, S. B. Dierker, and G. D. Wignall, *Macromolecules*, **19** (1986), 1938.
- [114] J. D. Londono, *et al.*, *Macromolecules*, **27** (1994), 2864.
- [115] P. G. de Gennes, in *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, New York, 1979), Chapter 5.
- [116] V. F. Turchin, *Slow Neutrons* (Sivan Press, Jerusalem, 1965), p. 16.
- [117] G. D. Wignall and F. S. Bates, *J. Appl. Crystallogr.*, **20** (1987), 28.
- [118] G. E. Bacon, *Neutron Scattering* (Clarendon Press, Oxford, 1975), p. 48.
- [119] J. Schelten, private communication (1973).
- [120] B. Jacrot, *Rep. Prog. Phys.*, **39** (1976), 911; B. Jacrot and G. Zaccai, *Biopolymers*, **20** (1981), 2413.
- [121] J. R. D. Copley, *J. Appl. Crystallogr.*, **21** (1988), 639.
- [122] W. Boyer and J. S. King, *J. Appl. Crystallogr.*, **21** (1988), 818.

- [123] R. P. May, K. Ibel, and J. Haas, *J. Appl. Crystallog.*, **15** (1982), 15.
- [124] G. D. Wignall, D. K. Christen, and V. Ramakrishnan, *J. Appl. Crystallog.*, **21** (1988), 438.
- [125] O. Glatter, *J. Appl. Crystallog.*, **10** (1977), 415.
- [126] P. B. Moore, *J. Appl. Crystallog.*, **13** (1980), 168.
- [127] O. Glatter, *Small-Angle X-ray Scattering*, edited by O. Glatter and O. Kratky (Academic Press, London, 1982), p. 131.
- [128] V. Ramakrishnan, *J. Appl. Crystallog.*, **18** (1985), 42.
- [129] P. W. Schmidt, *J. Appl. Crystallog.*, **3** (1988), 137; *J. Appl. Crystallog.*, **21** (1970), 602.
- [130] G. D. Wignall, *J. Appl. Crystallog.*, **24** (1991), 479.
- [131] J. S. Pederson, D. Posselt, and K. Mortensen, *J. Appl. Crystallog.*, **23** (1990), 321.
- [132] P. S. Goyal, J. S. King, and G. C. Summerfield, *Polymer*, **24** (1983), 131.
- [133] J. Schelten and W. Schmatz, *J. Appl. Crystallog.*, **13** (1980), 385.
- [134] P. J. Flory, *J. Am. Chem. Soc.*, **84** (1962), 2857.
- [135] M. Stamm, *et al.*, *Discuss. Faraday Soc.*, **68** (1979), 263.
- [136] C. G. Summerfield, J. S. King, and R. Ullman, *J. Appl. Crystallog.*, **11** (1978), 548.
- [137] D. Y. Yoon and P. J. Flory, *Polymer*, **18** (1977), 509.
- [138] D. Y. Yoon and P. J. Flory, *Discuss. Faraday Soc.*, **68** (1979), 288.
- [139] D. Y. Yoon and P. J. Flory, *Polym. Bull.*, **4** (1981), 693.
- [140] P. J. Flory, *Pure and Appl. Chem.*, **56** (1984), 305.
- [141] M. Guttman, *et al.*, *Discuss. Faraday Soc.*, **68** (1979), 297.
- [142] J. D. Hoffman, *et al.*, *Discuss. Faraday Soc.*, **68** (1979), 177.
- [143] D. M. Sadler, in *The Structure of Crystalline Polymers*, edited by I. Hall (Applied Science, New York, 1983), p. 125.
- [144] G. D. Wignall, *et al.*, *J. Polym. Sci.*, **20** (1982), 245.
- [145] M. Stamm, *J. Polym. Sci.: Polym. Phys. Ed.*, **20** (1982), 235.
- [146] P. J. Flory, *et al.*, *Macromolecules*, **17** (1984), 862.
- [147] D. Y. Yoon and P. J. Flory, *Macromolecules*, **17** (1984), 868.
- [148] D. M. Sadler and A. Keller, *Science*, **19** (1979), 263.
- [149] D. M. Sadler and A. Keller, *Macromolecules*, **10** (1977), 1128.
- [150] G. D. Wignall, *Encyclopedia of Materials Science and Technology* (Elsevier Science Limited, Amsterdam, 2001), p. 8412.
- [151] S. J. Spells and D. M. Sadler, *Polymer*, **25** (1984), 739; D. M. Sadler and S. J. Spells, *Polymer*, **25** (1984), 1219.
- [152] L. Mandelkern, *Chemtracts – Macromol. Chem.*, **3** (1992), 347.
- [153] D. J. Lohse, *et al.*, *Polym. News* **12** (1986), 8; T. C Chung (ed.), *New Advances in Polyolefins* (Plenum Press, New York, 1993), p. 175.
- [154] S. K. Sinha, D. J. Lohse, and M. Y. Lin, *Physica B*, **213–214** (1995), 1.
- [155] R. G. Kirste and B. R. Lehnen, *Makromol. Chem.*, **177** (1976), 1137; W. A. Kruse, *et al.*, *J. Makromol. Chem.*, **177** (1976), 1145.
- [156] R. P. Kambour, *et al.*, *Polymer*, **21** (1980), 133.
- [157] G. D. Wignall, H. R. Child, and F. Li-Aravena, *Polymer*, **21** (1980), 131.
- [158] M. Warner, J. S. Higgins, and A. J. Carter, *Macromolecules*, **16** (1983), 1931.
- [159] G. Hadzioannou and R. S. Stein, *Macromolecules*, **17** (1984), 567; R. S. Stein and G. Hadzioannou, *Macromolecules*, **17** (1984), 1059.
- [160] D. Schwahn, *et al.*, *J. Chem. Phys.*, **87** (1987), 6078.
- [161] R. M. Briber, B. J. Bauer, and B. Hammouda, *J. Chem. Phys.*, **101** (1994), 2592.
- [162] Y. B. Melnichenko, G. D. Wignall, and D. Schwahn, *Phys. Rev. E*, **65** (2002), 061 802.

- [163] C. Herkt-Maetzky and J. Schelten, *Phys. Rev. Lett.*, **51** (1983), 896.
- [164] J. S. Higgins and D. J. Walsh, *Polym. Eng. Sci.*, **24** (1984), 555; D. J. Walsh, J. S. Higgins, and C. Zhikuan, *Polym. Commun.*, **23** (1982), 336.
- [165] M. G. Brereton, E. W. Fischer, and C. Herkt-Maetzky, *J. Chem. Phys.*, **87** (1997), 6078.
- [166] D. Schwahn, *et al.*, *J. Chem. Phys.*, **87** (1987), 6078.
- [167] C. C. Han, *et al.*, *Polymer*, **29** (1990), 2002.
- [168] S. Sakurai, *et al.*, *Macromolecules*, **23** (1990), 451.
- [169] D. J. Lohse, *Polym. Eng. Sci.*, **26** (1986), 1500.
- [170] A. Maconnachie, *et al.*, *Macromolecules*, **17** (1985), 2645.
- [171] J. Jelenic, *et al.*, *Makromol. Chem.*, **185** (1984), 129.
- [172] H. Shibayama, *et al.*, *Macromolecules*, **18** (1985), 2179.
- [173] T. P. Russell, H. Ito, and G. D. Wignall, *Macromolecules*, **20** (1987), 2213; *Macromolecules*, **21** (1988), 1703.
- [174] J. M. R. Lefebvre, S. Porter, and G. D. Wignall, *Polym. Eng. Sci.*, **27** (1987), 433.
- [175] D. Schwahn, K. Mortensen, and H. Yee-Madeira, *Phys. Rev. Lett.*, **58** (1987), 1544.
- [176] F. S. Bates, *et al.*, *Phys. Rev. Lett.*, **65** (1990), 1893.
- [177] A. Nesarikar and B. Crist, *J. Polym. Sci. B*, **B32** (1994), 641.
- [178] D. J. Lohse, *Rubber Chem. Technol.*, **67** (1994), 367.
- [179] W. W. Graessley, *et al.*, *Macromolecules*, **27** (1994), 3896.
- [180] W. W. Graessley, *et al.*, *Macromolecules*, **26** (1993), 1137.
- [181] K. Tashiro, *et al.*, *Macromolecules*, **28** (1995), 8484.
- [182] J. D. Londono, *et al.*, *Macromolecules*, **27** (1994), 2864.
- [183] R. Krishnamoorti, *et al.*, *Macromolecules*, **27** (1994), 3073.
- [184] R. G. Alamo, *et al.*, *Macromolecules*, **27** (1994), 411.
- [185] G. D. Wignall, *et al.*, *Macromolecules*, **28** (1995), 3156.
- [186] G. D. Wignall, *et al.*, *Macromolecules*, **29** (1996), 5332.
- [187] L. Mandelkern, *et al.*, *Trends Polym. Sci.*, **357** (1996), 377.
- [188] R. G. Alamo, *et al.*, *Macromolecules*, **30** (1997), 561.
- [189] M. M. Agamalian, *et al.*, *J. Appl. Crystallogr.*, **33** (2000), 843.
- [190] G. D. Wignall, *et al.*, *Macromolecules*, **33** (2000), 551.
- [191] G. D. Wignall, *et al.*, *Macromolecules*, **34** (2001), 8160.
- [192] J. C. Nicholson, *et al.*, *Polymer*, **31** (1990), 2287; J. Rhee and B. Crist, *Macromolecules*, **24** (1991), 5665.
- [193] E. Karbasheski, *et al.*, *Appl. Polym. Sci.*, **44** (1992), 425.
- [194] P. Schouteren, *et al.*, *Polymer*, **28** (1987), 2099.
- [195] F. M. Mirabella and E. A. Ford, *J. Polym. Sci.: Polym. Phys. Ed.*, **25** (1987), 777.
- [196] P. J. Flory, *J. Chem. Phys.*, **17** (1949), 303.
- [197] M. G. Brereton and T. A. Vilgis, *J. Physique*, **50** (1989), 245.
- [198] J. T. Koberstein, *J. Polym. Sci.: Polym. Phys. Ed.*, **20** (1982), 593.
- [199] G. D. Wignall, H. R. Child, and R. J. Samuels, *Polymer*, **23** (1982), 957.
- [200] A. M. Fernandez, L. H. Sperling, and G. D. Wignall, *Multicomponent Polymer Materials* (ACS, New York, 1985), p. 153.
- [201] F. S. Bates, *et al.*, *Polymer*, **24** (1983), 519.
- [202] P. Debye and A. M. Bueche, *J. Appl. Phys.*, **20** (1949), 518; P. Debye, H. R. Anderson, and H. Brumberger, *J. Appl. Phys.*, **28** (1957), 679.
- [203] D. J. Blundell, *et al.*, *Polymer*, **15** (1974), 33.
- [204] R. W. Hendricks, J. Schelten, and W. Schmatz, *Phil. Mag.*, **30** (1974), 819.
- [205] G. D. Wignall, N. R. Farrar, and S. Morris, *J. Mater. Sci.*, **25** (1990), 69.

- [206] D. W. Marr, *et al.*, *Macromolecules*, **30** (1997), 2120.
- [207] W.-L. Wu, *Polymer*, **23** (1982), 1907.
- [208] L. Leibler, *Macromolecules*, **13** (1980), 1602.
- [209] G. H. Fredrickson and E. Helfand, *J. Chem. Phys.*, **87** (1987), 697.
- [210] E. Helfand, *Macromolecules*, **8** (1975), 552; E. Helfand and Z. R. Wasserman, *Macromolecules*, **9** (1976), 879.
- [211] A. N. Semenov, *Sov. Phys. JETP*, **61** (1985), 733.
- [212] F. S. Bates and M. A. Hartney, *Macromolecules*, **18** (1985), 2478.
- [213] K. Almdal, *et al.*, *Phys. Rev. Lett.*, **65** (1990), 1112.
- [214] J. L. Barrat and G. H. Fredrickson, *J. Chem. Phys.*, **95** (1991), 1281.
- [215] M. Malenkovitz and M. Muthukumar, *Macromolecules*, **24** (1991), 4199.
- [216] H. Tang and K. F. Freed, *Bull. Am. Phys. Soc.*, **37** (1992), 367.
- [217] M. Olvera de la Cruz, *Phys. Rev. Lett.*, **67** (1991), 85.
- [218] A. M. Mayes, M. Olvera de la Cruz, and B. W. Swift, *Macromolecules*, **25** (1992), 944.
- [219] F. S. Bates and G. H. Fredrickson, *Phys. Today*, **52** (1999), 32.
- [220] F. Drolet and G. Fredrickson, *Phys. Rev. Lett.*, **83** (1999), 4137.
- [221] C. Hardy, *et al.*, *Macromolecules*, **35** (2002), 3189.
- [222] T. Koga, *et al.*, *Phys. Rev. E*, **60** (1999), R3501; *J. Chem. Phys.*, **110** (1999), 11 076.
- [223] K. Yamauchi, H. Hasegawa, and T. Hashimoto, *J. Appl. Crystallogr.*, in press.
- [224] C. E. Williams, *et al.*, *J. Polym. Sci.: Polym. Lett. Ed.*, **17** (1979), 379.
- [225] A. Z. Akcasu, *et al.*, *J. Polym. Sci.*, **18** (1980), 865.
- [226] J. P. Cotton, B. Farnoux, and G. Jannink, *J. Chem. Phys.*, **57** (1972), 290; *Macromolecules*, **7** (1974), 863.
- [227] B. Farnoux, *et al.*, *J. Physique Lett.*, **36** (1975), 35.
- [228] M. Daoud, *et al.*, *Macromolecules*, **8** (1975), 805.
- [229] J. P. Cotton, *et al.*, *J. Chem. Phys.*, **65** (1976), 1101.
- [230] S. N. Jahshan and G. C. Summerfield, *J. Polym. Sci.: Polym. Phys. Ed.*, **18** (1980), 1859.
- [231] G. C. Summerfield, *J. Polym. Sci.: Polym. Phys. Ed.*, **19** (1981), 1011.
- [232] H. Benoit, J. Koberstein, and L. Leibler, *Makromol. Chem. Suppl.*, **4** (1981), 85.
- [233] R. Ullman, H. Benoit, and J. S. King, *Macromolecules*, **19** (1986), 183.
- [234] B. Chu, Q. Ying, and A. Grosberg, *Macromolecules*, **28** (1995), 180.
- [235] Y. B. Melnichenko and G. D. Wignall, *Phys. Rev. Lett.*, **78** (1997), 686.
- [236] Y. B. Melnichenko, *et al.*, *Macromolecules*, **31** (1998), 8436.
- [237] M. Muthukumar, *J. Chem. Phys.*, **85** (1986), 4722.
- [238] G. Raos and G. Alegria, *J. Chem. Phys.*, **104** (1996), 1626.
- [239] Y. B. Melnichenko, *et al.*, *Macromolecules*, **32** (1999), 5344.
- [240] E. Kiran and Y. Sen, in *Supercritical Fluid and Engineering Science* (ACS, New York, 1993), p. 514.
- [241] Y. B. Melnichenko, G. D. Wignall, and W. A. Van Hook, *Polym. Mater. Sci. Eng.*, **79** (1998), 311.
- [242] Y. B. Melnichenko, *et al.*, *Europhys. Lett.*, **19** (1992), 355.
- [243] Y. B. Melnichenko, *et al.*, *Phys. Rev. Lett.*, **79** (1997), 5266.
- [244] Y. B. Melnichenko, G. D. Wignall, and D. Schwahn, *Fluid Phase Equilibria*, **212** (2003), 211.
- [245] M. P. Grancio and D. J. Williams, *J. Polym. Sci. pt A-1*, **8** (1970), 2617.
- [246] J. W. Goodwin, *et al.*, *J. Coll. Polym. Sci.*, **78** (1980), 253; *J. Coll. Interf. Sci.*, **78** (1980), 253.
- [247] K. Alexander, *et al.*, *Coll. Surf.*, **7** (1983), 233.

- [248] D. J. Cebula, *et al.*, *Coll. Polym. Sci.*, **261** (1983), 555; *Discuss. Faraday Soc.*, **76** (1983), 37.
- [249] J. S. Higgins, J. V. Dawkins, and G. Taylor, *Polymer*, **21** (1980), 627.
- [250] Lord Rayleigh, *Proc. R. Soc. London, A*, **84** (1911), 24.
- [251] S. H. Chen and T. L. Lin, *Methods Exp. Phys.*, **23B** (1987), 489.
- [252] J. M. O'Reilly, O. I. Thompson, and G. D. Wignall, *Coll. Surf.*, **A201** (2002), 47.
- [253] T. Riste, *Neutron News*, **6** (4) (1995), 32.
- [254] ESF-OECD Technical Report: "A Twenty Years Look Forward at Neutron Scattering Facilities," http://www.oecd.org/dsti/sti/s_t/ms/prod/scattering.htm (1998).
- [255] G. D. Wignall, H. Benoît, T. Hashimoto, J. S. Higgins, S. King, T. P. Lodge, K. Mortensen, and A. J. Ryan, in *Scattering Methods for the Investigation of Polymers*, edited by J. Kahovec (Wiley-VCH, Weinheim, 2002), p. 185.
- [256] <http://www.sns.gov/>.
- [257] <http://www.ess-europe.de/ess.js/index.html>.
- [258] P. Thiyagarajan, *et al.*, *J. Appl. Crystallogr.*, **30** (1997), 280.
- [259] C. J. Glinka, *et al.*, *J. Appl. Crystallogr.*, **31** (1998), 430.
- [260] <http://www.ill.fr>.
- [261] Report of the European Science Foundation Workshop, *Scientific Prospects for Neutron Scattering with Present and Future Sources*, Autrans, France (1996).
- [262] <http://www.isis.rl.ac.uk/targetstation2/>.
- [263] <http://www.ssd.ornl.gov/CNMS/workshops/>.

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