Macromolecular Physics

Bernhard Wunderlich Volume 3 Crystal Melting

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VOLUME 3

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ACADEMIC PRESS 1980
A Subsidiary of Harcourt Brace Jovanovich, Publishers
New York London Toronto Sydney San Francisco

ACADEMIC PRESS, INC.
111 Fifth Avenue, New York, New York 10003

United Kingdom Edition published by
ACADEMIC PRESS, INC. (LONDON) LTD.
24/28 Oval Road, London NW1 7DX

Library of Congress Cataloging in Publication Data

Wunderlich, Bernhard, Date
Macromolecular physics.

Includes bibliographies and indexes
CONTENTS: v. 1. Crystal structure, morphology, defects.—v. 2. Crystal nucleation, growth, annealing.—v. 3. Crystal melting.
1. Macromolecules. 2. Crystals. I. Title.
QD381.W86 547.7 72-82632
ISBN 0-12-765603-0 (v. 3)

PRINTED IN THE UNITED STATES OF AMERICA

80 81 82 83 9 8 7 6 5 4 3 2 1

Preface

This third volume completes the first part of the project "Macromolecular Physics." The first volume dealt with the description of macromolecular crystals; the second volume dealt with crystal growth; and the third volume summarizes our knowledge of the melting of linear, flexible macromolecules. The discussion in the three volumes goes from reasonably well-established topics, such as the structure, morphology, and defects in crystals, to topics still in flux, such as crystal nucleation, detailed growth mechanisms, and annealing processes, to arrive at the present topics of equilibrium, nonequilibrium, and copolymer melting. Our knowledge is quite limited on many aspects of these latter topics.

For the second part of the project it is planned to discuss topics such as thermodynamics and heat capacities (with H. Baur and A. Mehta) and mechanical properties. Topics such as optical properties and electrical properties are planned in a parallel multivolume treatise edited by R. S. Stein.†

One of the main conclusions reached in writing this part of "Macromolecular Physics" is that equilibrium melting of flexible, linear macromolecules discussed in Chapter VIII is of great general interest (Sect. 8.1) and that the melting parameters can give insight into the nature of molecules and phase structure (Sect. 8.4.7). Only a relatively small group of macromolecules, however, has been analyzed in sufficient detail (see Table VIII.6). The unique properties of flexible, linear macromolecules became apparent in the treatment of changes in the equilibrium melting temperature (Sect. 8.5). Most of the experimental work deals with irreversible melting, described in Chapter IX. New experimental methods

† R. S. Stein (ed.), "Polymer Physics." Vol. 2 (1977); other volumes in preparation. Academic Press, New York.

that fix metastable structures long enough for analysis are reviewed for the first time in Sect. 9.2. The present uncertainty about many aspects of melting and melting temperatures rests with our ignorance about internal parameters determining the irreversible processes. Much of the confusion in the field comes from treating results from irreversible melting experiments as equilibrium data. An effort is made to sort experiments by careful examination of condition. The copolymer melting discussion in Chapter X reveals that here the difficulties are compounded, and practically none of the developed copolymer melting theories can be applied to the experimental data. The wide variety of data collected in this chapter should help dispel some common misconceptions about the melting of copolymers. The major effect in copolymer melting turns out to be most often a crystal size restriction, and much less frequently a mixing effect. Eutectic phase diagrams that are usually used in the description of copolymers are found to be less frequently appropriate than assumed. Partial solubility, comonomer concentration enrichment at interfaces, and varying limiting crystal sizes are often neglected variables. Mixed crystal systems are easier to treat, but to date only one reasonably complete phase diagram has been published (Fig. X.19). Finally, the multidimensional nature of copolymer melting is revealed in the discussion of regular copolymers, block copolymers, and side chain copolymers.

The documentation was done, as in the earlier volumes, by a broad search of the literature, assisted for this volume by a computer search of *Chemical Abstracts* on melting of macromolecules (and polymers), to the end of 1978. Still, many key references were found by checking cross references and by checking journals at random. Thus, the quoted references, although not all-inclusive, should represent a typical cross section.

As was true for the first two volumes, Volume 3 represents an attempt to reach a new level of summary of "Macromolecular Physics," on the basis of which further progress can be achieved.

Acknowledgments

My thanks go to the colleagues and students who have contributed by discussion, preprints, and reading of earlier versions of the various chapters. Especial recognition must be given to my secretary, Ms. McGraw, who typed, retyped, and changed the many versions of the more controversial topics of this book.

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American Chemical Society, Washington (Figs. IX.13 and IX.14).
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Associated Book Publishers Ltd, London (Figs. VIII.31, IX.41, and IX.50).
IPC Business Press Ltd, (Figs. VIII.32, VIII.33, and IX.47).
Marcel Dekker Inc., New York (Fig. VIII.11).
Springer Verlag, Berlin (Fig. IX.53).
Dr. Dietrich Steinkopf Verlag, Darmstadt (Fig. IX.46).
John Wiley and Sons, Inc. New York (Figs. VIII.13, VIII.34, IX.3, IX.5, IX.6, IX.12, IX.36, IX.38a, b, c, d, IX.40, IX.42, IX.48, IX.51, IX.52, and X.7a, b).

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CHAPTER VIII

Equilibrium Melting

8.1 Characterization of Matter through Its Equilibrium Melting Behavior

In Volume 1 of this series of books a characterization of macromolecular crystals through crystal structure, morphology, and defects is given (Chapters II–IV). Volume 2 contains a display of the processes that lead to crystalline macromolecules. Nucleation, growth, and annealing are the stages in the development of a crystalline sample (Chapters V–VII).

To describe the linear macromolecules in the solid state, crystal parameters such as size, morphology, structure, and defects must be given as for any crystal; but for the linear macromolecules, the molecular macroconformation must be specified in addition. Figure III.5 in Volume 1 summarizes the possible macroconformations of linear macromolecules in the solid state. The limiting macroconformations are approximated by the glassy state (metastable, random coil macroconformation, area A in Fig. III.5), the regularly chain-folded crystal (metastable, folded chain macroconformation, area B in Fig. III.5), and the fully extended chain crystal (stable, equilibrium macroconformation, area C in Fig. III.5). The fringed micellar macroconformation, which contains elements of all three limits and has molecules traversing through several ordered and disordered regions, can be thought of as an intermediate state, realized to various degrees in many actual samples (area D in Fig. III.5). This two-level description through crystal parameters and molecular macroconformation is characteristic for linear macromolecules.

In this volume (Chapters VIII–X) the melting of linear macromolecules is discussed. Emphasis will be placed on equilibrium melting (Chapter VIII), irreversible melting (Chapter IX), and the melting of copolymers (Chapter X). The description of the theory of thermal properties (Chapters XI and XII) and a discussion of heat capacity (Chapter XIII) are planned for Volume 4.

8.1.1 Equilibrium Melting of Linear Macromolecules

In this chapter equilibrium melting is discussed. Ubbelohde (1965) places the beginning of serious understanding of melting with the discovery of Black (1762) of the latent heat of fusion and the immediately ensuing calorimetric studies. The thermodynamic arguments on which the idea of the equilibrium of melting is based had their start with the formulation of the second law of thermodynamics (Thomson, 1849) (see also Sect. 11.1.5).

The study of equilibrium melting of crystals of linear macromolecules has been somewhat neglected. The reason for this neglect is illustrated by the statement of Stuart (1955): "Crystallizing high polymers have no sharp melting point. . . . At equal thermal history, the disappearance of the last crystalline portions of spherulites and other regions of order, as observable with the polarizing microscope, is on sufficiently slow heating, however, reasonably sharp, and reproducible to 1°C." This statement holds true for many of the nonequilibrium crystals of linear macromolecules which will be discussed in Chapter IX. Up to about 1960, hardly any linear macromolecular crystals approaching equilibrium, i.e., of extended chain macroconformation and macroscopic size,† had been grown and analyzed with respect to their melting behavior. Because of the lack of demonstrating large crystals, it was thought earlier that flexible, linear macromolecules always end up in a fringed micellar, nonequilibrium crystal. The melting behavior in such crystals must be governed by irreversible effects, recognizable often by broad melting ranges, and leading to melting temperatures that are coupled to given thermal histories. Equilibrium considerations, as are given in Sect. 11.1.5, serve for such nonequilibrium crystals only to set boundaries and define forces for the actual, irreversible processes. Local conformational equilibria, size restrictions, impurities, and sample heterogeneities were thus recognized as the major problems in macromolecular melting, rather than equilibrium properties. The cen-

† Macroscopic size is usually reached if a crystal approaches or exceeds dimensions of 1 μm in all three dimensions.

tral question was whether a sample with a fringed micellar macroconformation is to be treated as a one or a two phase structure, and whether melting is a first or a second order transition (Stuart, 1955). Many of these points will be taken up in more detail in Chapters IX, XI, and XII.

Since the 1960s it has become clear that close to equilibrium crystals of flexible macromolecules can be grown (Sect. 3.9). This permits the discussion of equilibrium melting from an experimental point of view. Furthermore, it was found that many of the metastable, well-crystallized folded chain lamellae (Sect. 3.3.2) represent clearly separate phases with only one small dimension, the fold length, which is usually 50–500 Å. Although these folded chain lamellae are not equilibrium crystals and their crystallinity is less than 1.0, their molecules do not always interconnect different crystals. It was shown by Mehta and Wunderlich (1975) that from well-crystallized samples one can extract practically all amorphous molecules after partial melting. Tie molecules between crystals can clearly be identified by their nonextractability after some of the crystals they interconnected, melted (Mehta and Wunderlich, 1974b). Such tie molecules increase in number as poorer crystallization conditions are chosen and as the molecular weight is increased. Crystallization with large amounts of tie molecules is described in Sect. 6.1.7. From solution, fringed micellar crystallization or poor crystallization is indicated by gelation of the whole sample.

Polymer crystals cover thus a broad range of structures, and care must be taken to identify the type of crystal discussed, before generalizing aspects of melting.

In this chapter, the two phase melting process of crystals at equilibrium will be discussed from the experimental point of view. Usually, macroscopic crystals are meant when talking about equilibrium crystals. Small equilibrium crystals are only possible on mass limitation. In this case the macroconformation must be folded, and shape and size of the crystal become critical parameters (Sect. 3.1.2). The Thomson–Gibbs equation (see Sect. 11.1.5) is usually adequate to treat the deviation from the macroscopic size. Mass limitation is of particular interest for single molecule, single crystals observed on dilute solution crystallization (see Sect. 5.1.2.2) and on annealing of high molecular weight, folded chain crystals (Sects. 5.1.4.1 and 7.2.1). Small equilibrium crystals have also been postulated as an intermediate structure during the crystallization of copolymers (Sect. 6.3.4). The small dimension in the molecular chain direction is in this case caused by the occurrence of noncrystallizable units along the molecular backbone. Deviations from equilibrium take place, however, already so early, that at best an upper end of the crystal distribution can be realized experimentally (see Chapter X).

8.1.2 Equilibrium Melting to Characterize Matter

The melting of large crystals under equilibrium conditions can be used for the general characterization of matter. There is a clear connection between melting and crystal structure (Ubbelohde, 1971). In the following an attempt will be made to characterize crystals of different chemical composition through their melting behavior.

For this purpose it is convenient to distinguish three classes of molecules:

1. rigid macromolecules,†
2. flexible macromolecules, and
3. small molecules.

Rigid macromolecules always lose their molecular integrity on melting (or sublimation). Their strong chemical bonds may extend in one, two, or three dimensions of space. In the melt, the strong bonds between atoms or ions interchange frequently, although at any moment only a small fraction of bonds is actually broken. Since the bonds that set up structure are strong, the melting temperature for all these materials is relatively high. In the solid state, the detailed structure of the rigid macromolecule is of less importance than the knowledge of its crystal or glassy structure, the grain size and shape, the boundary configuration and type, and the defect concentration. Three-dimensional macromolecules are possible with all three types of strong bonding: ionic, metallic, and covalent (see also Sect. 2.3.1). Two-dimensional macromolecules are relatively rare and involve covalent bonding for setting the main molecular plane. The examples that come quickly to mind are graphite, boron nitride, and perhaps mica.‡ These substances show weak bonds at right angles to the molecular plane. The two-dimensional bonding is often directly linked to the characteristic mechanical behavior of these materials. Rigid linear macromolecules, such as SiS_2, are usually fibrous in nature due to the relatively weak forces at right angles to the chain direction. The melting for both two-dimensional and rigid linear macromolecules is not very different from three-dimensional macromolecules. The molecular integrity is in all cases lost on melting (or sublimation).

Small molecules behave quite differently during melting. Their crystal

† For the definition of the term macromolecule see Sect. 1.1. (A macromolecule consists of more than 1000 atoms).

‡ For organic two-dimensional macromolecules, see, for example, the synthetic work of Hurley *et al.* (1972) and Kellman and Marvel (1975). Typical other inorganic, two-dimensional macromolecules are ZrS_2, $NbSe_2$, and MoS_2.

structure is set up by weak forces, so that on melting the molecular integrity is often preserved and the melting temperature is low. Many small molecules can, at somewhat higher temperatures, even be brought into the gaseous state without decomposition. Examples in this class are not only the noble gases and inorganic, small molecules like H_2O, NH_3, and CO_2, but also all organic molecules of less than 1000 atoms.

Flexible macromolecules are intermediate between the molecules of the other two classes. They can often be molten or dissolved without loss of molecular integrity and have an intermediate melting temperature. Since all degrees of molecular rigidity can be produced, linear macromolecules can span melting temperatures from below room temperature, as in *cis*-1,4-polybutadiene, to temperatures close to and above the thermal stability of the C—C— bond.† In order to show sufficient flexibility, the molecules in this class must be more or less linear. The number of possible linear macromolecules that maintain their molecular integrity during melting is practically unlimited, since any number of repeating units can be linked in any number of ways. This multiplicity lies at the root of the importance of macromolecular science, which traditionally deals mainly with flexible linear macromolecules.

8.2 The Equilibrium Melting Process

To understand the melting process, one needs detailed information on the crystalline as well as the molten or dissolved states. For flexible linear macromolecules, knowledge exists about the crystalline state in terms of the macroconformation, the crystal structure and the morphology (Chapters II and III). The molten state is, however, not known in sufficient detail. The macroconformation in the molten state is usually assumed to be that of a random coil (Sect. 1.4), but the structure of the melt and the degree of interpenetration of the molecules is still largely unknown (see, for example, Sects. 5.1 and 6.1.7). Details about the dissolved state are also lacking. The question of interpenetration of the molecules can be eliminated in this case by working with dilute solutions, but correlations between molecular conformations in the crystal and in the solution are needed to describe the dissolution stages. Despite this lack of detailed structure knowledge, much can be said about the melting process when one applies general thermodynamic principles which do not need structure

† Some linear macromolecules with melting temperatures above 500°C are (see Miller, 1975): Poly(*p*-aminobenzoic acid), poly(4,4′-biphenylene terephthalamide), poly(4,4′-ethylene biphenylene), cellulose trinitrate, poly-*p*-phenylene, poly(*p*-phenylene terephthalamide).

information (see Sect. 11.1.5). Adding limited mechanism models may round out the picture. Some of these models for small and macromolecules are summarized in this section.

8.2.1 General Statements about Melting

Early observations of melting revealed that this is a process that always occurs with an increase in disorder, i.e., an increase in entropy. Quantitatively this increase is much less than the increase in entropy on evaporation. Early comparison of the entropies of melting of simple solids that form "monatomic" melts led to the realization that for these

$$\Delta S_f = \Delta H_f/T \approx 7\text{–}14 \quad \text{J/(K mol)} \tag{1}$$

[Richards's rule (Richards, 1897); see also Crompton, 1903]. This entropy increase compares with the molar entropy increase on evaporation of about 90 J/(K mol) for simple liquids [Trouton's rule (Trouton, 1884)].

A second general observation on melting is the change in volume. For most substances the volume increases on melting. Typically, this volume increase is from 1 to 20% with the smaller volume changes (1–5%) occurring mostly for metals. There is, however, a small group of crystals of all types which show a decrease in volume on melting [H_2O, −8%; Sb, −1%; Bi, −3%; Ga, −3%]. Trying to find corresponding state ratios of volume was not very successful, even for relatively similar molecules.

A third parameter of interest is the heat capacity (see Chapter XIII). As in the case of volume changes on melting, there are no general statements that can be made about the heat capacity changes. Perhaps the broadest conclusion is that changes are relatively small. In many cases there is an increase in heat capacity. In metals, typical changes range from −10 to +10%. Ionic solids show more often larger changes (up to +50%). The increase in heat capacity may be caused by a decrease in vibrational frequencies due to weaker interactions and a greater increase in the number of defects with temperature in the liquid. Processes that may cause a decrease in heat capacity include changes of vibrations to rotations or even translations. The balance between the effects causing increases and decreases in heat capacity seems often to lead to little change.

The parameter that changes most from material to material is the heat of fusion. Assuming a largely constant entropy of fusion [Eq. (1)] suggests a higher melting temperature for substances of higher heat of fusion (see Sect. 11.1.5):

$$T_m = \Delta H_f/\Delta S_f \tag{2}$$

Indeed, melting temperatures vary from close to the absolute zero to