CRYSTALLIZATION OF POLYMERS, SECOND EDITION

In *Crystallization of Polymers*, second edition, Leo Mandelkern provides a self-contained, comprehensive, and up-to-date treatment of polymer crystallization. All classes of macromolecules are included and the approach is through the basic disciplines of chemistry and physics. The book discusses the thermodynamics and physical properties that accompany the morphological and structural changes that occur when a collection of molecules of very high molecular weight are transformed from one state to another.

The first edition of *Crystallization of Polymers* was published in 1964. It was regarded as the most authoritative book in the field. The first edition was composed of three major portions. However, due to the huge amount of research activity in the field since publication of the first edition (involving new theoretical concepts and new experimental instrumentation), this second edition has grown to three volumes.

Volume 1 is a presentation of the equilibrium concepts that serve as a basis for the subsequent volumes. In this volume the author shows that knowledge of the equilibrium requirements is vital to understanding all aspects of the polymer crystallization process and the final state that eventually evolves.

This book will be an invaluable reference work for all chemists, physicists and materials scientists who work in the area of polymer crystallization.

LEO MANDELKERN was born in New York City in 1922 and received his bachelors degree from Cornell University in 1942. After serving in the armed forces during World War II, he returned to Cornell, receiving his Ph.D. in 1949. He remained at Cornell in a post-doctoral capacity until 1952.

Professor Mandelkern was a staff member of the National Bureau of Standards from 1952 to 1962 where he conducted research in the physics and chemistry of polymers. During that time he received the Arthur S. Fleming Award from the Washington DC Junior Chamber of Commerce "As one of the outstanding ten young men in the Federal Service".

In January 1962 he was appointed Professor of Chemistry and Biophysics at the Florida State University, Tallahassee, Florida, where he is still in residence.

He is author of *Crystallization of Polymers*, first edition, published by McGraw-Hill in 1964. He is also author of *Introduction to Macromolecules*, first edition 1972, second edition 1983, published by Springer-Verlag.

Besides the Arthur S. Fleming Award he has been the recipient of many other awards from different scientific societies including the American Chemical Society and the Society of Polymer Science, Japan.

Professor Mandelkern is the author of over 300 papers in peer reviewed journals and has served on the editorial boards of many journals, including the *Journal of the American Chemical Society*, the *Journal of Polymer Science* and *Macromolecules.*

CRYSTALLIZATION OF POLYMERS

SECOND EDITION

Volume 1

Equilibrium concepts

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To Berdie, my wife,
and
to my grand-daughter, Sarah,
whose memory will be everlasting

Contents

Preface to second edition

Since the publication in 1964 of the first edition of *Crystallization of Polymers* there has been a vast amount of scientific activity in the study of crystalline polymers. This abundance that we enjoy has ranged from the synthesis of new classes of crystalline polymers to the application of sophisticated experimental techniques, accompanied by significant theoretical advances. Consequently, a large body of literature has resulted. As might be expected, many divergent opinions have been presented. The central problems in this subject were reviewed at a seminal Discussion of the Faraday Society (vol. 68, 1979). At this meeting different points of view were ardently presented. Since that Discussion, which can be considered to be a turning point in the investigation of the crystallization behavior of polymers, a coherent body of work has evolved. Some problems that were posed have been resolved. The differences in many others have been clarified. It appeared to the author that it was an appropriate time to bring together, in a coherent manner, the present status of the field. This was the motivation for the present work. Some aspects of crystalline polymers can be given a definitive analysis. On the other hand, there are still some problems that remain to be resolved. The different points of view will be presented in these cases. A strong effort has been made to present these matters in as an objective and scholarly manner as possible.

There is an extraordinary range of literature dealing with all aspects of the behavior of crystalline polymers. Therefore, no effort has been made here to present an annotated bibliography. Emphasis has been given to the basic, underlying principles that are involved. A considered effort has been made to present as diverse a set of examples as possible, illustrating the principles involved. Some works that should have been included may have been omitted. The author apologizes for this inadvertent error. There is a natural prejudice to select ones own material when appropriate. One hopes that this has not been overdone here. Fundamental principles are emphasized in these volumes. However, it has been the author's experience that these principles can be applied in an effective manner to the control

of both microscopic and macroscopic properties of crystalline polymers. Thus, the book should be helpful in understanding and solving many technological problems involving crystalline polymers.

Students and investigators entering this research field for the first time should find a clear and objective perspective of the existing problems, as well as those that are reasonably well understood. For those who have been carrying out research in crystalline polymers, the problems are defined in a manner so as to indicate the directions that need to be taken to achieve resolution.

It was pointed out in the preface to the first edition, that it was composed of three major portions. These three portions have now grown to three volumes. The first of these is concerned with equilibrium concepts. The second deals with the kinetics and mechanisms of crystallization. Morphology, structure and properties of the crystalline state are discussed in the third volume. There is a strong interconnection between these major subjects.

The author is indebted to several generations of students and post-doctoral research associates, whose dedication, enthusiasm and love of research has sustained and contributed greatly to our research effort. It is also a pleasure to acknowledge a great debt to Mrs. Annette Franklin for her expert typing of the manuscript and preparing it in final form.

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Tallahassee, Florida *Leo Mandelkern*
August, 2001

Preface to first edition

We have been witnessing in recent years an unprecedentedly high degree of scientific activity. A natural consequence of the intensity of this endeavor is an ever-expanding scientific literature, much of which contains information of importance and interest to many diverse disciplines. However, it is a rare scientific investigator indeed who has either the time or the opportunity to digest and analyze critically the abundance we enjoy. Nowhere is this problem more acute than in the studies of the properties and behavior of macromolecular substances. Because of the somewhat belated recognition of its molecular character, this class of substances has been susceptive to quantitative investigations only for the past 30 years. During this period, however, there has developed a very rapidly increasing amount of activity and knowledge, in the realm of pure research as well as in industrial and practical applications. The problems presented have engaged the attention of individuals representing all the major scientific disciplines. In this situation it was inevitable that many subdivisions of polymer science have evolved. It appeared to the author that some of these areas could be subjected to a critical and, in some instances, a definitive analysis. Such endeavors also serve the purpose of acting as connecting links between the different specialities. At the same time they tend to underscore the more general and fundamental aspects of the scientific problems.

The present volume was suggested and stimulated by the aforementioned thoughts. We shall be concerned here with the phenomena and problems associated with the participation of macromolecules in phase transitions. The term crystallization arises from the fact that ordered structures are involved in at least one of the phases. The book is composed of three major portions which, however, are of unequal length. After a deliberately brief introduction into the nature of high polymers, the equilibrium aspects of the subject are treated from the point of view of thermodynamics and statistical mechanics, with recourse to a large amount of experimental observation. The second major topic discussed is the kinetics of crystallization. The treatment is intentionally very formal and allows for the deduction

of the general mechanisms that are involved in the process. The equilibrium properties and the kinetic mechanisms must, in principle, govern the morphological characteristics of the crystalline state, which is the subject matter of the last chapter. The latter topic has been under intensive investigation in recent years. Many new concepts have been introduced which are still in a state of continuous revision. Consequently, a very detailed delineation of morphological structure has not been attempted. Instead, the discussion and interpretation have been restricted to the major features, which find their origin in the subject matter of the previous chapters.

Although many of the problems that fall within the scope of this work appear to be in a reasonable state of comprehension, there are some important ones that are not. It is hoped that these have become at least more clearly defined. Although no effort has been made to present a bibliographic compilation of the literature, care has been taken to avoid the neglect of significant work. Primary emphasis has been placed on principles, and this consideration has been the main guide in choosing the illustrative material. In this selection process a natural prejudice exists for material with which one is more familiar. This partiality, which appears to be an occupational hazard, has not been completely overcome in the present work. A great deal of what has been learned from studies of the simpler polymers can be applied to the properties and function of the more complex polymers of biological interest. Consequently, whenever possible, a unified approach has been taken which encompasses all types and classes of macromolecules, their diverse origin and function notwithstanding.

It was the author's pleasure and very distinct privilege to have the opportunity to be associated with Prof. P. J. Flory's laboratory some years ago. The author owes to him a debt, not only for the introduction to the subject at hand, but also for an understanding of the problems of science in general and polymer science in particular. As will be obvious to the reader, this book leans very heavily on his gifted and inspired teachings and research. However, the responsibility for the contents and the interpretations that are presented rests solely with the author.

The generous assistance of many friends and colleagues is gratefully acknowledged. Dr. N. Bekkedahl read and criticized a major portion of the manuscript and rendered invaluable aid to the author. Criticisms and suggestions on various chapters were received from Drs. T. G. Fox, W. Gratzer, G. Holzworth, H. Markowitz, and D. McIntyre. Dr. R. V. Rice and Mr. A. F. Diorio generously contributed electron micrographs and x-ray diffraction patterns for illustrative purposes.

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Tallahassee, Florida *Leo Mandelkern*
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