

科学版研究生教学丛书

现代高分子化学

影印版

Harry R. Allcock

Frederick W. Lampe

James E. Mark



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科学版研究生教学丛书

现代高分子化学

(影印版)

Contemporary Polymer Chemistry

(Third Edition)

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内 容 简 介

本书作者是高分子化学领域的知名教授。书中全面介绍了现代高分子化学的合成、结构与应用,涵盖了从高分子化学到材料科学的诸方面。本书不仅对高分子科学的基本理论与原则有着系统阐述,而且对高分子科学的最新进展,如生物医学高分子、活性自由基聚合等,也有着精辟反映。全书分5大部分,共24章。每章均附有综合试题和近期参考文献,以测试学生对知识的掌握并提供深入学习的阅读资料。

本书可作为化学、化工及材料等专业的研究生、高年级本科生的教学用书,也可供高分子专业的师生及科技人员参考。

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Preface

This third edition of *Contemporary Polymer Chemistry*, like the two preceding editions, is designed as an introduction to polymers for students of chemistry, physics, chemical engineering, materials science, and biomaterials. It assumes a basic knowledge of subjects taught in university undergraduate programs in the above disciplines. Specifically, the book aims to broaden the perspective of specialists in different technical areas to the point where they can appreciate the scope, importance, and future potential of polymer chemistry and technology. Thus, in writing this book we have kept in mind the individual who has a sound knowledge of basic science but needs to know more about polymers for future academic research or teaching or for entry into the polymer industry. For this reason, many topics that are well-known to practicing polymer scientists are handled here from first principles.

More rigorous and more comprehensive treatments exist for nearly all of the topics discussed in this book. However, few attempts have been made to bring together synthetic, structural, kinetic, thermodynamic, and use-oriented material in one volume. Our aim has been to provide a broad, coherent introduction to modern polymer chemistry and to direct the reader to more detailed sources for advanced study.

This edition has undergone an appreciable expansion compared to the earlier volumes. This reflects the widening scope of the field and the need to include recent advances in polymer synthesis as well as to broaden the treatment of polymer characterization methods and the physics and materials science aspects of the subject. Contributions by new co-author James E. Mark have added considerably to this widened perspective. A number of new topics have also been introduced, including insights into rubberlike elasticity, viscoelasticity, biomimicry, and the materials science of structure-property relationships. The list of references for further reading and the study questions, problems, and solutions have been updated extensively throughout the book.

The book is divided into five parts. *Part I* (Chapters 1–9) provides an introduction to the different classes of polymers and the ways in which they are synthesized and modified. Individual chapters deal with condensation, free-radical, and ionic or coordination polymerization, with photolytic, high energy

radiation, and electrolytic polymerization, polymerization of cyclic compounds, biological macromolecules, with the ways that synthetic polymers can be modified chemically, and with polymers that contain inorganic elements. Several of the chapters in this section have been revised to reflect recent developments. For example, new sections have been included on molecular weight distributions, dendrimers and telechelic polymers, polymer surface chemistry, organometallic-initiated polymerizations, atom transfer radical reactions, polymerizations in supercritical carbon dioxide, and inorganic polymers. Thus, the emphasis in these chapters is on descriptive chemistry, general principles, and synthetic issues. The material in this section should be understandable to students who have taken undergraduate courses in general chemistry, and organic, inorganic, or biological chemistry. These chapters form the groundwork for the sections that follow.

Part II (Chapters 10–13) deals with thermodynamics, equilibria, and polymerization kinetics. Chapter 10 provides an elementary overview of the underlying principles that determine whether a monomer or a cyclic compound will polymerize or if a polymer will depolymerize. Chapters 11, 12, and 13 deal respectively with the kinetics of condensation, free-radical, and ionic polymerizations. A unique feature of these chapters is the full derivation of the kinetic expressions, with every attempt made to explain the underlying principles for each step. This should enable the treatments to be understood by anyone with a basic background of third year undergraduate physical chemistry.

Part III (Chapters 14–19) covers the physical methods that are employed for the characterization of polymers. Individual chapters cover “absolute” molecular weight measurements by osmometry, light scattering and ultracentrifugation; secondary molecular weight methods such as solution viscosity and gel permeation chromatography; thermodynamics of high polymer solutions; polymer morphology; glass transitions and crystallinity; conformational analysis; and X-ray diffraction techniques. The sections on secondary molecular weight methods, thermodynamics of polymer solutions, solid state characterization, X-ray scattering, and other physical methods have been expanded to provide more detail than in the earlier editions. In all these chapters the reader is introduced to the underlying theory and, where appropriate, to the practical approaches used. Each chapter provides the basic groundwork for elementary experimental work in these areas or for further, more detailed, studies.

In *Part IV* (Chapters 20 and 21) we discuss the engineering aspects of polymer science, including the fabrication of polymers and testing techniques. Here too, new sections have been added that deal with polymer chain orientation and materials reinforcement, with the behavior of polymers within fabrication machinery, and a much expanded section on rubberlike materials.

In *Part V* (Chapters 22–24) the emphasis is on the uses of polymers and the ways in which the polymer scientist can correlate molecular structure with properties and applications. Chapter 22 provides an overview of how the practicing chemist intuitively relates molecular structure to polymer properties as a route to the design of new materials. An addition to this chapter is an overview of how

the molecular features of polymers become translated into solid state materials properties. Chapter 22 is one of the most important sections of the book for those who are encountering polymers for the first time. Chapter 23 gives an account of the rapidly expanding field of electroactive and electro-optical polymers, a subject that it likely to be the focus of much research in the future. The treatment in this edition includes electronically conductive materials and their use in devices, ionically conducting polymers and their role in advanced batteries and fuel cells, soft lithography, polymers for lenses and optical waveguides, optically responsive polymers, light-emitting polymers, and polymers for photovoltaic cells. The last chapter (Chapter 24) deals with the biomedical uses of synthetic polymers, a topic that continues to grow in importance year by year, and which accounts for an increasing proportion of the total research effort in polymer science.

Appendix I is a brief review of polymer nomenclature, and Appendix II is a compilation of physical property data and uses for a number of commercially important and research intensive polymers. This latter appendix provides perspective and serves as a reference source as the reader encounters new polymers at different points in the book.

The book may be used in several different ways. We recommend that the reader should follow the sequence outlined above, although specialized topics, such as those discussed in Chapters 10–13, might be absorbed best during a second reading. However, for readers who prefer to approach the subject from the viewpoint of properties and uses, we suggest starting with Chapters 1 and 22–25, and then following the remaining chapters in sequence beginning with Chapter 2.

In writing this new edition we have been helped considerably by a number of individuals. We are especially grateful to the many users of the earlier editions who have made numerous suggestions for improvements and to the reviewers of the manuscript for this edition. Virtually all of their suggestions have been incorporated into this edition, including the availability of a booklet of answers to the numerical questions.

Finally, we are sad to report that Fred Lampe died suddenly while this new edition was being prepared. His death was a serious blow to all who knew him. His engaging personality, good cheer, fairness, common sense, and deep fascination with physical chemistry are severely missed. Most of the sections of this book for which he was mainly responsible have been updated, but have otherwise retained their original character. We believe that his classic and, to a large degree, timeless contributions to this book will constitute a fitting memorial to him.

HARRY R. ALLCOCK
JAMES E. MARK

About the Authors

Harry R. Allcock is Evan Pugh Professor of Chemistry at The Pennsylvania State University. He received his B.Sc. and Ph.D. degrees from the University of London. After holding postdoctoral positions at Purdue University and the National Research Council of Canada, he spent five years as a polymer research scientist in American industry before joining The Pennsylvania State University in 1966. Trained initially as a mechanistic organometallic chemist, his research interests have included the synthesis of new organic and inorganic polymers, the use of inorganic and organometallic compounds as polymerization initiators, radiation-induced polymerizations, ring-chain equilibria, organosilicon compounds, and the structural examination of polymers by X-ray diffraction, NMR, and conformational analysis techniques. A major interest throughout his career has been the design and synthesis of new biomedical materials. He and his coworkers synthesized the first stable polyphosphazenes, and his research group has been responsible for many of the major developments in this field. His pioneering research has been recognized by numerous awards including the American Chemical Society National Awards in Polymer Chemistry and Materials Chemistry, and the A.C.S. Polymer Division Herman Mark Award in Polymer Science. He is also a Guggenheim Fellow and a recipient of the American Institute of Chemists Chemical Pioneer Award. He has held a number of visiting lectureships, has published three research monographs, co-authored three other volumes, and co-edited three additional books. Professor Allcock has authored or co-authored more than 440 research papers and reviews, holds 54 patents, and has trained more than 100 graduate students and postdoctoral students in his laboratory.

Frederick W. Lampe (1927–2000) was a Professor of Chemistry at the Pennsylvania State University. Professor Lampe was born in Chicago. He served in the United States Navy from 1944 to 1946, and later received a B.S. degree from Michigan State University and a Ph.D. degree from Columbia University. He then spent seven years as a research scientist with the Humble Oil and Refining Company in Texas before moving to Penn State in 1960. Professor Lampe was a physical chemist whose polymer interests were in the areas of radiation-induced polymerizations, kinetics of polymerization processes, application of mass spec-

trometry to polymer degradation processes, statistical mechanics, and molecular weight methods. He was also interested in gaseous ion reactions, photochemistry, and the effects of ionizing radiation on materials. He was the author or co-author of over 160 research papers and review articles, and held five patents on polymer chemistry and radiation chemistry. He was also a visiting professor at the University of Freiburg, Germany, and at the Hahn-Meitner Nuclear Research Institute in Berlin. His honors included the Alexander von Humboldt Senior Scientist Award, a National Science Foundation Senior Postdoctoral Fellowship, and a Robert A. Welch Lecturship. Professor Lampe also served for five years as the Head of the Chemistry Department at Penn State.

James E. Mark was born in Wilkes-Barre, Pennsylvania. He received a B.S. degree in Chemistry from Wilkes College and his Ph.D. in Physical Chemistry from the University of Pennsylvania. After serving as a Postdoctoral Fellow at Stanford University with Professor Paul J. Flory, he was an Assistant Professor at the Polytechnic Institute of Brooklyn before moving to the University of Michigan, where he became a Full Professor in 1972. In 1977 he assumed the position of Professor of Chemistry at the University of Cincinnati, where he was Chairman of the Physical Chemistry division and Director of the Polymer Research Center. In 1987 he was named to the first Distinguished Professorship at Cincinnati. Dr. Mark's research interests include the physical chemistry of polymers, elasticity of polymer networks, liquid crystalline polymers, hybrid organic-inorganic composites, and a variety of computer simulations. He has lectured widely on polymer chemistry, is a consultant to industry, and has organized a number of polymer-related short courses. He has published over 600 research papers and has coauthored or coedited eighteen books. Among his awards are the A.C.S Applied Polymer Science Award and the A.C.S. Polymer Division Paul. J. Flory Polymer Education Award, the Whitby Award, and the Charles Goodyear Medal from the A.C.S Rubber Division. He is the founding Editor of the journal *Computational and Theoretical Polymer Science* and serves on the Editorial Boards of a number of other journals. He has also been a Turner Alfrey Visiting Professor and has received the Edward W. Morley Award from the A.C.S. Cleveland Section.

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