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PRINCIPLES OF POLYMERIZATION

F O U R T H E D I T I O N

G E O R G E O D I A N

The new edition of a classic text and reference

The large chains of molecules known as polymers are currently used in everything from "wash and wear" clothing to rubber tires to protective enamels and paints. Yet the practical applications of polymers are only increasing; innovations in polymer chemistry constantly bring both improved and entirely new uses for polymers onto the technological playing field.

Principles of Polymerization, Fourth Edition presents the classic text on polymer synthesis, fully updated to reflect today's state of the art. New and expanded coverage in the *Fourth Edition* includes:

- Metallocene and post-metallocene polymerization catalysts
- Living polymerizations (radical, cationic, anionic)
- Dendrimer, hyperbranched, brush, and other polymer architectures and assemblies
- Graft and block copolymers
- High-temperature polymers
- Inorganic and organometallic polymers
- Conducting polymers
- Ring-opening polymerization
- In vivo and in vitro polymerization

Appropriate for both novice and advanced students as well as professionals, this comprehensive yet accessible resource enables the reader to achieve an advanced, up-to-date understanding of polymer synthesis. Different methods of polymerization, reaction parameters for synthesis, molecular weight, branching and crosslinking, and the chemical and physical structure of polymers all receive ample coverage. A thorough discussion at the elementary level prefaces each topic, with a more advanced treatment following. Yet the language throughout remains straightforward and geared towards the student.

Extensively updated, *Principles of Polymerization, Fourth Edition* provides an excellent textbook for today's students of polymer chemistry, chemical engineering, and materials science, as well as a current reference for the researcher or other practitioner working in these areas.

GEORGE ODIAN received his PhD from Columbia University. He is currently Emeritus Professor of Chemistry at the College of Staten Island of the City University of New York. He has previously served as professor of chemistry and chairman, Division of Pure and Applied Sciences at Richmond College of CUNY, assistant professor at Columbia University, research director of RAI Research Company, and research chemist at Thiokol Chemical Company. He has written over sixty research publications and authored both taped and short courses for the American Chemical Society. He is also the coauthor of four books in general, organic, and biochemistry.

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PRINCIPLES OF
POLYMERIZATION

FOURTH EDITION

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PRINCIPLES OF POLYMERIZATION

Fourth Edition

GEORGE ODIAN

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City University of New York
Staten Island, New York



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PRINCIPLES OF POLYMERIZATION

Fourth Edition

PREFACE

This book describes the physical and organic chemistry of the reactions by which polymer molecules are synthesized. The sequence I have followed is to introduce the reader to the characteristics which distinguish polymers from their much smaller sized homologs (Chap. 1) and then proceed to a detailed consideration of the three types of polymerization reactions—step, chain, and ring-opening polymerizations (Chaps. 2–5, 7). Polymerization reactions are characterized as to their kinetic and thermodynamic features, their scope and utility for the synthesis of different types of polymer structures, and the process conditions which are used to carry them out. Polymer chemistry has advanced to the point where it is often possible to tailor-make a variety of different types of polymers with specified molecular weights and structures. Emphasis is placed throughout the text on understanding the reaction parameters which are important in controlling polymerization rates, polymer molecular weight, and structural features such as branching and crosslinking. It has been my intention to give the reader an appreciation of the versatility which is inherent in polymerization processes and which is available to the synthetic polymer chemist.

The versatility of polymerization resides not only in the different types of reactants which can be polymerized but also in the variations allowed by copolymerization and stereoselective polymerization. Chain copolymerization is the most important kind of copolymerization and is considered separately in Chap. 6. Other copolymerizations are discussed in the appropriate chapters. Chapter 8 describes the stereochemistry of polymerization with emphasis on the synthesis of polymers with stereoregular structures by the appropriate choice of initiators and polymerization conditions. In the last chapter, there is a discussion of the reactions of polymers that are useful for modifying or synthesizing new polymer structures and the use of polymeric reagents, substrates, and catalysts. The literature has been covered through early 2003.

It is intended that this text be useful to chemists with no background in polymers as well as the experienced polymer chemist. The text can serve as a self-educating introduction to polymer synthesis for the former. Each topic is presented with minimal assumptions

regarding the reader's background, except for undergraduate organic and physical chemistry. Additionally, it is intended that the book will serve as a classroom text. With the appropriate selection of materials, the text can be used at either the undergraduate or graduate level. Each chapter contains a selection of problems. A solutions manual for the problems is available directly from the author.

Many colleagues have been helpful in completing this new edition. I am especially indebted to Chong Cheng, Krzysztof Matyjaszewski, and Stephen A. Miller who graciously gave their time to read and comment on portions of the text. Their suggestions for improvements and corrections were most useful. I also thank the many colleagues who generously responded to my inquiries for their advice on various topics: Helmut G. Alt, Jose M. Asua, Lisa S. Baugh, Sabine Beuermann, Vincenzo Busico, Luigi Cavallo, John Chadwick, Geoff Coates, Scott Collins, James V. Crivello, Michael F. Cunningham, Thomas P. Davis, Pieter J. Dijkstra, Rudolf Faust, Hanns Fischer, Michel Fontanille, Robert Gilbert, Alexei Gridnev, Richard A. Gross, Robert H. Grubbs, Howard Haubenstock, Jorge Herrera-Ordonez, Walter Hertler, Hans Heuts, Henry Hsieh, Aubrey Jenkins, Jaroslav Kahovec, Mikiharu Kamachi, Walter Kaminsky, Hans Kricheldorf, Morton Litt, Roberto Olayo, Patrick Lacroix-Desmazes, W. V. Metanomski, Michael J. Monteiro, Timothy E. Patten, Stanislaw Penczek, Peter Plesch, Jorge Puig, Roderic P. Quirk, Anthony K. Rappe, Luigi Resconi, Ezio Rizzardo, Greg Russell, Erling Rytter, Richard R. Schrock, Donald Tomalia, Brigitte Voit, Kenneth Wagener, Robert M. Waymouth, Owen W. Webster, Yen Wei, David G. Westmoreland, Edward S. Wilks, Bernard Witholt, Nan-loh Yang, Masahiro Yasuda, and Adolfo Zambelli. Their helpful and insightful comments enriched and improved the text.

I welcome comments from readers, including notice of typographical, factual, and other errors.

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