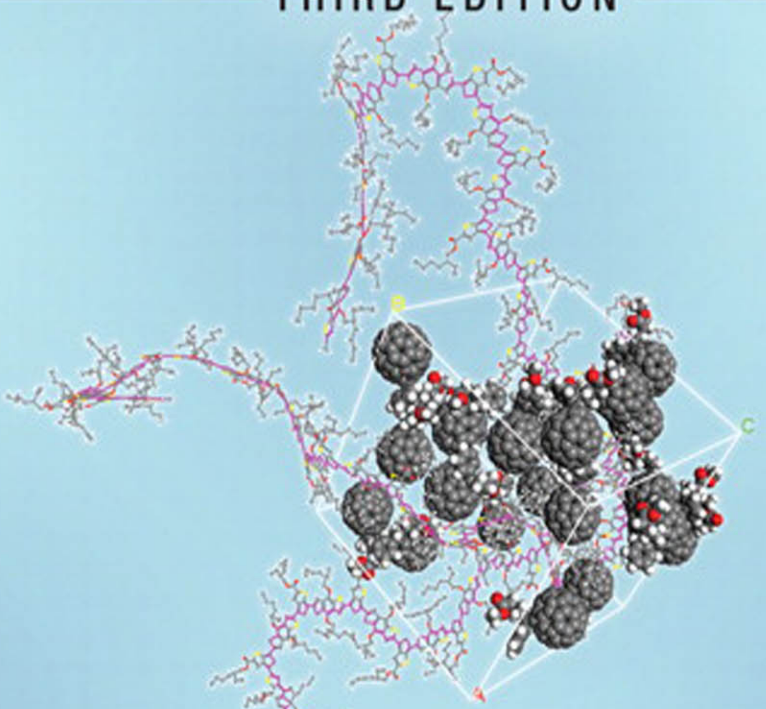
PRENTICE HALL

POLYMER SCIENCE & TECHNOLOGY

THIRD EDITION



JOEL R. FRIED

POLYMER SCIENCE AND TECHNOLOGY

Third Edition

This page intentionally left blank

POLYMER SCIENCE AND TECHNOLOGY

Third Edition

Joel R. Fried

PRENTICE HALL

Upper Saddle River, NJ • Boston • Indianapolis • San Francisco
New York • Toronto • Montreal • London • Munich • Paris • Madrid
Capetown • Sydney • Tokyo • Singapore • Mexico City

For information about buying this title in bulk quantities, or for special sales opportunities (which may include electronic versions; custom cover designs; and content particular to your business, training goals, marketing focus, or branding interests), please contact our corporate sales department at corpsales@pearsoned.com or (800) 382-3419.

For government sales inquiries, please contact governmentsales@pearsoned.com.

For questions about sales outside the U.S., please contact international@pearsoned.com.

Visit us on the Web: informit.com/aw

Library of Congress Cataloging-in-Publication Data
Fried, Joel R.
Polymer science and technology / Joel R. Fried.—Third edition.
pages cm
Includes bibliographical references and index.
ISBN 978-0-13-703955-5 (hardcover : alk. paper)
1. Polymers. 2. Polymerization. I. Title.
QD381.F73 2014
668.9—dc23 2014000967

ISBN-13: 978-0-13-703955-5
ISBN-10: 0-13-703955-7

Text printed in the United States on recycled paper at Courier Corporation in Westford, Massachusetts.
First printing, May 2014

To my parents, who provided the opportunities, support, and guidance, and to my wife, Ava, and sons, Marc and Aaron, for their love, patience, and understanding.

CONTENTS

PREFACE

Polymer Science and Technology, *Third Edition*, provides new and expanded coverage in a number of areas of contemporary interest in polymer science and technology. In particular, Chapter 2 on polymer synthesis provides new coverage of controlled radical polymerization, polymerization in ionic liquids, and the use of click chemistry and green chemistry. Chapter 4, on solid-state properties, includes added coverage on the use of microscopy and scattering methods in solid-state characterization. Chapter 7, on additives, blends, and composites, includes a new section on block copolymers as well as expanded coverage of nanocomposites including the use of buckyballs, carbon nanotubes, graphene, and POSS as nanofillers. Electrospinning has been added to the discussion of fiber-spinning operations in Chapter 8. Coverage of biomedical engineering and drug delivery, solar cells, and sensors has been included in Chapter 12, on polymers for advanced technologies. In addition, an entirely new chapter on correlations and simulation methods in polymer science has been added. This new chapter includes expanded treatment of group-correlation methods to predict polymer properties that has previously appeared in a number of earlier chapters in the second edition. Totally new is the inclusion of topological indices and artificial neural networks to predict properties. For the first time in an introductory polymer textbook, the fundamentals and applications of computational polymer science including the use of molecular dynamics and Monte Carlo methods are presented with a number of examples and exercise problems.

Joel R. Fried
Tallahassee, Florida

About the Cover Illustration

The cover illustration shows a molecular simulation of a blend of 37 wt% of functionalized C_{60} fullerene, PCBM, (space-filling representation) in an amorphous cell containing a thiophene copolymer. This system has been reported to provide attractive photovoltaic properties for polymeric photovoltaic cells. Simulations of polymeric systems are described in Chapter 13 of this third edition.

PREFACE TO THE SECOND EDITION

The second edition provides new and expanded coverage of important topics in polymer science and engineering and includes additional example calculations, homework problems, and bibliographic references. Additional topics in the treatment of polymer synthesis (Chapter 2) include metallocene catalysis, atom transfer radical and plasma polymerization, the genetic engineering of polymers, and the use of supercritical fluids as a polymerization medium. The new field of dynamic calorimetry (temperature-modulated DSC) has been added to the coverage of polymer viscoelasticity in Chapter 5. Chapter 6 provides expanded coverage of biodegradable polymers while Chapter 7 introduces the important new area of nanocomposites. Chapter 8 has been totally revised to include coverage of biopolymers and naturally occurring polymers including chitin and chitosan, while material on commodity thermoplastics has been moved to Chapter 9. In Chapter 10, new engineering and specialty thermoplastics including dendrimers, hyperbranched polymers, and amorphous Teflon are discussed. Examples of polymer-processing modeling have been expanded to include wire-coating operations in Chapter 11. The topic of drag reduction has been moved from Chapter 12 to the coverage of polymer rheology in Chapter 11, which now also includes an introduction to melt instabilities. The discussion of the electrical and optical applications of engineering polymers has been enhanced and new coverage of barrier polymers has been provided in Chapter 12.

Although the intended audience for this text is advanced undergraduates and graduate students in chemical engineering, the coverage of polymer science fundamentals (Chapters 1 through 5) is suitable for a semester course in a materials science or chemistry curriculum. Chapters 6 and 7 discuss more specialized topics such as polymer degradation, recycling, biopolymers, natural polymers, and fibers. Sections from this coverage can be included to supplement the basic coverage provided by the earlier chapters. Chapters 9 and 10 survey the principal categories of polymers—commodity thermoplastics, elastomers, thermosets, and engineering and specialty polymers. Material from these chapters may be included to supplement and reinforce the material presented in the chapters on fundamentals and provides a useful reference source for practicing scientists and engineers in the plastics industry. Polymer engineering principles including rheology and processing operations, introduced in Chapter 11, can be used as the basis of a short course on polymer engineering at the senior undergraduate and graduate level. Chapter 12 describes polymers used in areas of advanced technology including membrane separations, electrolytes for batteries and fuel cells, controlled drug release, nonlinear optical applications, and light-emitting diodes and displays. This coverage may be used as reference material for scientists and engineers and provides a basis for short courses in such areas as membrane science and technology and polymer physics.

Joel R. Fried
Cincinnati, Ohio

PREFACE TO THE FIRST EDITION

At least dozens of good introductory textbooks on polymer science and engineering are now available. Why then has yet another book been written? The decision was based on my belief that none of the available texts fully address the needs of students in chemical engineering. It is not that chemical engineers are a rare breed, but rather that they have special training in areas of thermodynamics and transport phenomena that is seldom challenged by texts designed primarily for students of chemistry or materials science. This has been a frustration of mine and of many of my students for the past 15 years during which I have taught an introductory course, *Polymer Technology*, to some 350 chemical engineering seniors. In response to this perceived need, I had written nine review articles that appeared in the SPE publication *Plastics Engineering* from 1982 to 1984. These served as a hard copy for my students to supplement their classroom notes but fell short of a complete solution.

In writing this text, it was my objective to first provide the basic building blocks of polymer science and engineering by coverage of fundamental polymer chemistry and materials topics given in Chapters 1 and 7. As a supplement to the traditional coverage of polymer thermodynamics, extensive discussion of phase equilibria, equation-of-state theories, and UNIFAC has been included in Chapter 3. Coverage of rheology, including the use of constitutive equations and the modeling of simple flow geometries, and the fundamentals of polymer processing operations are given in Chapter 11. Finally, I wanted to provide information on the exciting new materials now available and the emerging areas of technological growth that could motivate a new generation of scientists and engineers. For this reason, engineering and specialty polymers are surveyed in Chapter 10 and important new applications for polymers in separations (membrane separations), electronics (conducting polymer), biotechnology (controlled drug release), and other specialized areas of engineering are given in Chapter 12. In all, this has been an ambitious undertaking and I hope that I have succeeded in at least some of these goals.

Although the intended audience for this text is advanced undergraduates and graduate students in chemical engineering, the coverage of polymer science fundamentals (Chapters 1 through 7) should be suitable for a semester course in a materials science or chemistry curriculum. Chapters 8 through 10, intended as survey chapters of the principal categories of polymers—commodity thermoplastics and fibers, network polymers (elastomers and thermoplastics), and engineering and specialty polymers—may be included to supplement and reinforce the material presented in the chapters on fundamentals and should serve as a useful reference source for the practicing scientist or engineer in the plastics industry.

Joel R. Fried
Cincinnati, Ohio

ACKNOWLEDGMENTS

This text in its three editions could not have been completed without the help of many colleagues who provided figures and photographs and offered important advice during its preparation. I am particularly indebted to those colleagues who read all or sections of the first edition and offered very helpful advice. These included Professor James E. Mark of the University of Cincinnati, Professor Otto Vogl of the Polytechnic University, Professor Erdogan Kiran of Virginia Polytechnic Institute, Professor Paul Han of the University of Akron, Professor Donald R. Paul of the University of Texas at Austin, and Professor R. P. Danner of Penn State. Appreciation is also extended to many students and colleagues at the University of Cincinnati who have provided important comments over the past few years following the publication of the first edition. These include Professor Michael Greenfield of the University of Rhode Island, Professor Zvi Rigbi of the Technion, Professors U. Sundararaj and Philip Choi of the University of Alberta, Professor Jin Chuk Zjung of Pohang University of Science and Technology, and Professor Carlos Co of the University of Cincinnati. Appreciation is also extended to those who kindly assisted in reviewing portions of the third edition. These include Professors George Odian and Alan Lyons of the College of Staten Island (City University of New York), Dr. Donald Klosterman of the University of Dayton Research Institute, Professor Peng-yu Ren of the University of Texas at Austin, and Professors Rufina Alamo, Daniel Hallinan, and Biwu Ma of Florida State University.

I also wish to thank those colleagues who kindly provided some key illustrations and photos. These include Dr. Roger Kambour of General Electric, Professor Bill Koros of the Georgia Institute of Technology, Professor Paul Philips of the University of Tennessee, Dr. Marty Matsuo of Nippon Zeon (Japan), Dr. Robert

Cieslinski of the Dow Chemical Company, Dr. Richard Baker of Membrane Technology and Research, Inc., Dr. Mostafa Aboulfaraj of Pechiney Centre de Recherches de Voreppe (France), Professor Morton Denn of the City College of New York, Professor David Tirrell of the California Institute of Technology, Dr. Graeme Moad of CSIRO (Australia), Craig Hawker of the University of California, Santa Barbara, and Professor Rufina Alamo of Florida State University.

Joel R. Fried
Tallahassee, Florida

ABOUT THE AUTHOR

Dr. Joel R. Fried is professor and chair of the department of chemical and biomedical engineering at Florida State University. Previously, he was professor and the Wright Brothers Endowed Chair in Nanomaterials at the University of Dayton. He is also professor emeritus of chemical engineering and a fellow of the graduate school at the University of Cincinnati, where he directed the Polymer Research Center and served as head of the Department of Chemical Engineering over a career of 32 years. During this time he has advised more than sixty graduate and postdoctoral students, many of whom are currently in academic positions or have prominent positions in industry. Dr. Fried holds B.S. degrees in biology and chemical engineering, and an M.E. degree in chemical engineering from Rensselaer Polytechnic Institute. He also holds M.S. and Ph.D. degrees in polymer science and engineering from the University of Massachusetts, Amherst. Prior to his academic career, Dr. Fried was a senior engineer at the Monsanto Corporate R&D Center in St. Louis and an associate staff member of the GE Corporate R&D Center near Schenectady, New York. At Monsanto, he was a member of a fundamental research group developing hollow fiber membranes for industrial gas separations.

Dr. Fried is an instructor for the short course on Polymer Science and Technology at the National Meetings of the American Chemical Society and has been a course instructor on extrusion for the Plastics Institute of America. He is the author of more than one hundred and fifty publications, including many book chapters and monographs. Dr. Fried has served as editor of *Polymer Contents* and associate editor of *Computational and Theoretical Polymer Science*, has served on the editorial boards of *Polymer* and *Polymer Engineering*, and is a frequent consultant to industry. Current research interests focus on experimental studies and simulations of ion and small molecule transport through polymeric, biological, and biomimetic membranes for separations, energy, and sensor applications.

This page intentionally left blank