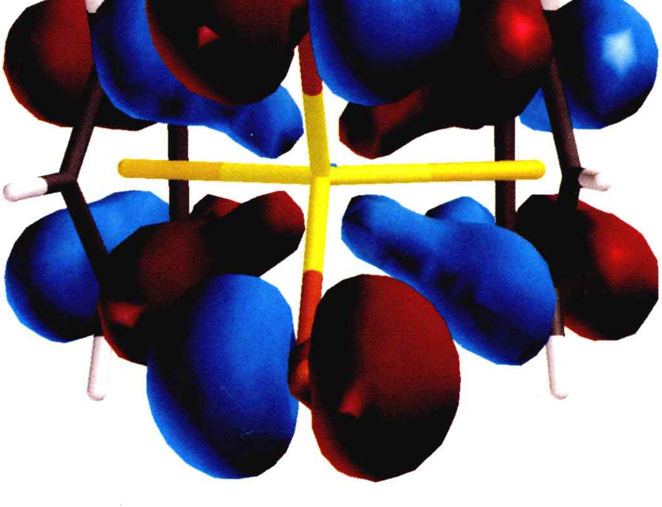
POLYMER SCIENCE & TECHNOLOGY

second edition



JOEL R. FRIED

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Second Edition

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POLYMER SCIENCE AND TECHNOLOGY

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

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PREFACE

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 student 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

About the Cover Art

The cover illustration shows a molecular representation of results of a density functional calculation of bis(cyclopentadienyl)zirconium dichloride, Cp_2ZrCl_2, that can be used to catalyze the polymerization of ethylene and some α-olefins. The important new area of metallocene polymerization is covered in Chapter 2.

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 addresses 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 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 through 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 polymers), 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 thermosets), 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.

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I wish to also thank those colleagues who kindly provided some key illustrations and photos. These are Dr. Roger Kambour of General Electric, Professor Bill Koros of the Georgia Institute of Technology, Professor Paul Han of the University of Akron, Professor John Gilham of Princeton University, 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 & Research, Inc., Dr. Mostafa Aboulfaraj of Pechiney Centre de Recherches de Voreppe (France), Professor Morton Denn of the City College of New York, and Professor David Tirrell of the California Institute of Technology.

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CONTENTS

CHAPTER 1

Introduction to Polymer Science

The word *polymer* is derived from the classical Greek words *poly* meaning "many" and *meres* meaning "parts." Simply stated, a polymer is a long-chain molecule that is composed of a large number of *repeating units* of identical structure. Certain polymers, such as proteins, cellulose, and silk, are found in nature, while many others, including polystyrene, polyethylene, and nylon, are produced only by synthetic routes. In some cases, naturally occurring polymers can also be produced synthetically. An important example is natural (Hevea) rubber, known as polyisoprene in its synthetic form.

Polymers that are capable of high extension under ambient conditions find important applications as elastomers. In addition to natural rubber, there are several important synthetic elastomers including nitrile and butyl rubber. Other polymers may have characteristics that permit their formation into long fibers suitable for textile applications. The synthetic fibers, principally nylon and polyester, are good substitutes for naturally occurring fibers such as cotton, wool, and silk.

In contrast to the usage of the word *polymer*, those commercial materials other than elastomers and fibers that are derived from synthetic polymers are called *plastics*. A typical