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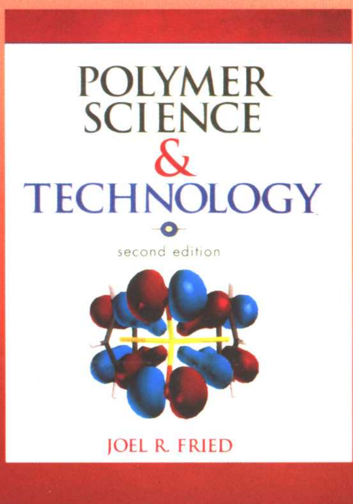
聚合物科学与工程

第二版（英文影印版）

Joel R. Fried



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Second Edition

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Joel R. Fried

化学工业出版社

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［美］**Joel R. Fried** 著

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前 言

随着中国社会主义现代化建设进入新的阶段，以高质量的高等教育培养千百万专门人才，迎接新世纪的挑战，是实现“科教兴国”战略的基础工程，也是完成“十五”计划各项奋斗目标的重要保证。为切实加强高等学校本科教学并提高教学质量，教育部于2001年专门下发文件提出12条意见，对高等学校教学工作从认识、管理、教师队伍到教学方法和教学手段等给予指导。文件强调，按照“教育要面向现代化、面向世界、面向未来”的要求，为适应经济全球化和科技国际化的挑战，本科教育要创造条件使用英语等外语进行公共课和专业课教学。

在文件精神指导下，全国普通高等学校尤其是重点高校中兴起了使用国外教材开展教学活动的潮流。如生物技术与工程、环境科学与工程、材料科学与工程及作为其学科基础理论重要组成部分的化学技术和化学工程技术又是这股潮流中最为活跃的领域之一。在教育部“化工类专业人才培养方案及教学内容体系改革的研究与实践”项目组及“化工类专业创新人才培养模式、教学内容、教学方法和教学技术改革的研究与实践”项目组和“全国本科化学工程与工艺专业教学指导委员会”的指导和支持下，化学工业出版社及时启动了引进国外名校名著的教材工程。

出版社组织编辑人员多次赴国外学习考察，通过国外出版研究机构对国外著名的高等学校进行调查研究，搜集了一大批国际知名院校的现用教材选题。他们还联络国内重点高校的专家学者组建了“国外名校名著评价委员会”，对国外和国内高等本科教学进行比较研究，对教材内容质量进行审查评议，然后决定是否引进。他们与国外许多著名的出版机构建立了联系，有的还建立了长期合作关系，以掌握世界范围内优秀教材的出版动态。

以其化学化工专业领域的优势资源为基础，化学工业出版社的教材引进主要涉及化学、化学工程与工艺、环境科学与工程、生物技术与工程、材料科学与工程、制药工程等专业，对过程装备与控制工程、自动化等传统专业教材的引进也在规划之中。

他们在影印、翻译出版国外教材的过程中，注意学习国外教材出版的经验，提高编辑素质，密切编读联系，整合课程体系，更新教材内容，科学设计版面，提高印装质量，更好地为教育服务。

在化工版“国外名校名著”系列教材即将问世之际，我们不仅感谢化学工业出版社为高等教育所做的努力，更应赞赏他们严谨认真的工作作风。

中国科学院院士，天津大学教授

余国琮

2002年8月

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.

Joel R. Fried
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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.

Joel R. Fried
Cincinnati, Ohio

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 commercial plastic resin may contain two or more polymers in addition to various additives and fillers. These are added to improve a particular property such as processability, thermal or environmental stability, or the modulus of the final product.

The birth of polymer science may be traced back to the mid-19th Century. In the 1830s, Charles Goodyear developed the vulcanization process that transformed the sticky latex of natural rubber to a useful elastomer for tire use. In 1847, Christian F. Schönbein reacted cellulose with nitric acid to produce cellulose nitrate. This was used in the 1860s as the first man-made thermoplastic, celluloid. In 1907, Leo Hendrik Baekeland[1] produced Bakelite (phenol-formaldehyde resin). Glyptal (unsaturated-polyester resin) was developed as a protective coating resin by General Electric in 1912.

By the 1930s, researchers at DuPont in the United States had produced a variety of new polymers including synthetic rubber and more exotic materials such as nylon and Teflon™. In 1938, Dow had produced polystyrene in commercial scale and, in 1939, polyethylene (low-density) was made for the first time by scientists at ICI in England. Efforts to develop new polymeric materials, particularly synthetic rubber, were intensified during World War II when many naturally occurring materials such as Hevea rubber were in short supply. In the 1950s, Karl Ziegler and Giulio Natta independently developed a family of stereospecific transition-metal catalysts that lead to the commercialization of polypropylene as a major commodity plastic. The 1960s and 1970s witnessed the development of a number of high-performance engineering plastics polymers that could compete favorably with more traditional materials, such as metals, for automotive and aerospace applications. These included polycarbonate, poly(phenylene oxide), polysulfones, polyimides, aromatic polyamides such as Kevlar, and other high-temperature rigid-chain polymers. More recently, specialty polymers with electrically conducting, photoconducting, and liquid crystal properties have appeared for a variety of consumer applications.

Today, polymeric materials are used in nearly all areas of daily life and their production and fabrication are major worldwide industries. As indicated by data given in Table 1-1, the annual U.S. production of plastics, fibers, and rubber exceeded 87 billion pounds in 2000. As a group, plastics accounted for the major portion (82%) of this production, while synthetic fibers (12%) and elastomers (6%) made up the rest.

The repeating unit of a common polymer, polystyrene, is illustrated in Figure 1-1. In this example, the repeating unit has the same chemical composition (i.e., C_8H_8) as the low-molecular-weight *monomer*, styrene, from which polystyrene is synthesized. The number of repeating units is indicated by the index n. In the case of commercial grades of polystyrene, the average value of n may be 1,000 or more. Given that the molecular weight of a polystyrene repeating unit is 104, a value of 1,000 for n represents an average molecular weight of 104,000. Molecules with fewer than 10 repeating units are termed *oligomers* and exhibit quite different thermal and mechanical properties compared to the corresponding high-molecular-weight polymer. For example, oligomeric styrene with seven repeating units (i.e., $n = 7$) is a viscous liquid at room temperature while commercial-grade, high-molecular-weight polystyrene is a brittle solid that does not soften until it is heated to above approximately 100°C.