Polymer Chemistry Introduction to an INDISPENSABLE SCIENCE

By David Teegarden





Claire Reinburg, Director J. Andrew Cocke, Associate Editor Judy Cusick, Associate Editor Betty Smith, Associate Editor

ART AND DESIGN Linda Olliver, Director
 PRINTING AND PRODUCTION Catherine Lorrain-Hale, Director
 Nguyet Tran, Assistant Production Manager
 Jack Parker, Desktop Publishing Specialist

NATIONAL SCIENCE TEACHERS ASSOCIATION Gerald F. Wheeler, Executive Director David Beacom, Publisher

Copyright O 2004 by the National Science Teachers Association. All rights reserved. 06 05 04 4 3 2 1

Library of Congress Cataloging-in-Publication Data

Teegarden, David M.
Polymer chemistry : introduction to an indispensable science / by David M. Teegarden.
p. cm.
ISBN 0-87355-221-0
Polymers. 2. Polymerization. I. Title.
QD381.T42 2004
547'.7—dc22
2004003160

NSTA is committed to publishing quality materials that promote the best in inquiry-based science education. However, conditions of actual use may vary, and the safety procedures and practices described in this book are intended to serve only as a guide. Additional precautionary measures may be required. NSTA and the author(s) do not warrant or represent that the procedures and practices in this book meet any safety code or standard or federal, state, or local regulations. NSTA and the author(s) disclaim any liability for personal injury or damage to property arising out of or relating to the use of this book including, any of the recommendations, instructions, or materials contained therein.

Permission is granted in advance for reproduction for purpose of classroom or workshop instruction. To request permission for other uses, send specific requests to: NSTA PRESS, 1840 Wilson Boulevard, Arlington, Virginia 22201-3000. Web site: *www.nsta.org*

Dedicated to the memory of Katharine Morrison Teegarden 1909–2002

whose tolerance, interest in ideas, love of books, and belief in the importance of education have influenced all who knew her.

Contents

xiii xv xvii xxiii	Foreword Preface and Acknowledgments About This Book Notes on Equations and Units
xxiv	Polymer Science Relationships
Section 1	Chapter 1
Introduction 1 3	They're Everywhere!
4	Major Types of Polymers
7	The Increasing Importance of Synthetic Polymers
9	"Just One Word"
11	Less Mass, Yet More
12	There Is No Free Lunch
	References Cited
	Other Reading
	2
	Chapter \angle
13	What Are They?
15	How Big Are They?
16	How Long Is Long Enough?
17	Polymers-Molecules with Unique Properties
19	How Are They Made and How Can
	We Name Them?
23	Summing Up
	References Cited
	Other Reading
	.)
	Chapter J
27	Natural Polymers
28	Proteins
	Protein Synthesis
	Some Specific Types of Proteins
34	Polynucleotides
	Chemical Structure
	Biochemical Function
37	Polysaccharides
	Structure
	Function and Properties
	An Ocean of Polysaccharides

	41 42	Natural Rubber Summing Up References Cited
		Other Reading
		Chapter 4
		A History of Polymers:
	45	The Road to the Plastic Age, and Beyond
	47 50	Before Synthetic Polymers Polymers before World War I Improving Natural Rubber
		Behind the Eight Ball—The First True Plastic The Picture of Things to Come Other Cellulose Derivatives
		The First Synthetic Polymer
	58	Polymer Chemistry Defined by the World Wars What Is a Polymer, Anyway? Call in the Special Forces Hermann Staudinger and Herman Mark: Who's the Father? Wallace Carothers and the First Synthetic Fiber
		From Globs to Fiber Chain-Growth Polymers Polyethylene and the War It's a Stretch
	66	Down the Slippery Slope After the Second World War A Whole New Approach to Chain-Growth Polymers How the Hula Hoop Saved the Day From Polyethylene to Polypropylene—Stereoregularity Other Significant Advances
	78	Chain-Growth Copolymers Conducting Polymers The Need for Polymers in Electronics The Influence of Sputnik Summing Up References Cited Other Reading
		5
Section 7	0.2	Chapter J Delumer Conthesis
Synthesis and	83	Polymer Synthesis
Properties	84 84	How Do They Grow? A Comparison of Step-Growth and Chain-Growth Polymerizations

National Science Teachers Association

	<i>Step-Growth</i>
	Chain-Growth
	Comparison of the Two Reactions
90	Step-Growth Polymerization in More Detail
	Making PET in the Melt
	Interfacial Polycondensation
92	Chain-Growth Polymerization in More Detail
	Free Radical Chain Polymerization
	Going One Step Better: Emulsion Polymerization
	Copolymerization
	Ionic Chain Polymerization
	It Lives!
	Block Copolymerization
	Cationic Polymerization
	Polymer Stereochemistry: Tacticity
	Coordination Polymerization
	Coordination Polymerization of 1,3-Dienes
	Single-Site (or Metallocene) Catalysts
	Living Radical Polymerizations
108	Other Types of Polymerizations, Polymers
	Ring-Opening Polymerization
	Ring-Opening Olefin Metathesis Polymerization (ROMP)
	Dendrimers: Polymers That Look Like Trees
	Silicones
114	Summing Up
	References Cited
	Other Reading
	Chapter ()
117	Polymer Solutions and Dispersions
118	Introduction
118	Polymer Solutions
	Random Coils
	Why Won't This Stuff Dissolve?
	Thick as Molasses—Viscosity
121	Gels
123	Things That Stretch or Flow
124	Non-Newtonian Fluids-Weird Behavior
	Shear-Thinning and Shear-Thickening Fluids
	Viscoelastic Fluids
126	Some Applications of Polymer Solutions and Dispersions
	Films

Polymer Chemistry

	130	Coatings Oil-Based Paints and Varnishes Latexes Summing Up References Cited Other Reading Chapter 7
	133	Physical Properties
	134	The Viscoelastic State
	135	Structure and Thermal Properties
		Amorphous Polymers and the Glass Transition Crystallinity and Melting Density
	142	Mechanical Properties
		Stress-Strain Properties
	144	Ioughness and Impact Strength
	144	Orientation
		Making Really Strong Polymers Tricks for Strengthening Ordinary Polymers Thermoplastic Elastomers
	150	Additives Plasticizers Fillers and Reinforcing Agents; Composites Fibers Impact Modifiers Crosslinking or Vulcanizing Agents
	154	Summing Up References Cited Other Reading
Section $2_{ m ar{b}}$		Chapter δ
Useful 🕽	159	Polymer Processing—Making Useful Materials
Materials	160	Melt-Processing of Polymers
	161	Injection Molding
	162	Injecting Molding Thermoset Polymers; Reaction Injection Molding
	162	Bottles and Other Hollow Objects-Blow Molding
	165	Cast and Blown Films
	167	Thermotorming

168	Foamed Objects
168	Fibers
173	Summing Up
	References Cited
	Other Reading
	Chapter 9
177	Disposal, Degradation, and Recycling; Bioplastics
178	The "Polymer Cycle"
179	The Disposal Phase: What Are Our Options?
	Just Throw It Away!
	Better Yet, Bury It
181	How Degrading!
	A Chain Is No Stronger Than Its
	Getting the Bugs Out—The Promise of Monomers
	from Nature The Pirth of a Pioplastic
190	Polymer Recycling
170	Some Bright Spots: PET Bottles
	Reprocessing PET and Other Polymers: Secondary
	Recycling
	Not Everything Is Easily Recycled
	Back to Basics: Tertiary Recycling
	Recycling by Thermal Decomposition
	Practical Recycling
199	Summing Up
	References Cited
	Other Reading
	Chapter 10
203	A Glimpse of Things to Come
204	How Did We Get Here? Evolution and Revolution
205	A View of the Future: From Inert Polymers to Active Materials
	to Smart Systems
	Active Materials
	Smart Materials
	Materials with a Memory
209	Thinking Smaller and Smaller: Macro, Micro Nano
	Materials on the Nano Scale
	Nanocomposites Smaller and Smaller Devices
	smauer and smauer Devices
1	

Copyright © 2004 NSTA. All rights reserved. For more information, go to www.nsta.org/permissions.

	214 216 218	From Macromolecules to the Supramolecular The Concept of Self-Assembly Summing Up References Cited
Section 🖊		
Demonstrations T	223	Introduction
and	225	Polymer Synthesis
Experiments		Free Radical Polymerization
		Interfacial Step-Growth Polymerization: Synthesis of Nylon
		Step-Growth Polymerization: Synthesis of Polyesters in
		the Melt
		Step-Growth Polymerization: Synthesis of a
		Polyurethane Foam
	238	Studies of Solutions and Gels
		Polymer Precipitation
		Gels from Alginic Acid Salts
	245	Solid State Properties
		Identifying Plastics by their Densities
		Experiments with Films
	252	Sources of Additional Experiments and Demonstrations
	257	Glossary
	265	Index

Foreword

It is a pleasure and a privilege to introduce David Teegarden's beautiful book *Polymer Chemistry: Introduction to an Indispensable Science*. Written in a graceful style, it fills a major gap in the polymer literature. It clearly explains the connection between structure and physical properties and therefore the uses to which polymers are put in everyday life. The various types of polymerization reactions required to synthesize those polymers are also clearly explained.

David takes us through the spectacular growth of polymer chemistry over the past seven decades. These accomplishments were carried out by creative individuals who rose to the challenge and opportunity. This book will, I hope, reach younger scientists and help them to realize that they, too, can contribute.

He brings us to the present situation, where ecological concerns are increasingly important. Current research frontiers such as nanotechnology are included. Of course the recent decoding of the human Genome is ranked as a landmark of polymer chemistry, and the continuing evolution of proteomics is an exercise in structural polyamide chemistry.

David takes the reader in hand on a congenial stroll through this wonderland. He emphasizes that polymers are organic molecules differing only in size from those familiar to us in organic chemistry. He also correctly identifies viscosity, resulting from "spaghetti-like" entanglements of those long molecules, as the key difference in physical properties from those of small molecules.

David's extensive background in academia and in industrial research makes him amply qualified to present this subject. I predict that it will appeal to a wide spectrum of readers, from the technical specialist to the citizen interested in the science of the world around him or her.

> H. K. Hall, Jr. Chemistry Department University of Arizona Tucson, Arizona

Copyright © 2004 NSTA. All rights reserved. For more information, go to www.nsta.org/permissions.

Preface

This is a book of many subjects. Although "chemistry" is in the title, the operative word is "polymers," a subject that transcends a range of disciplines. Chemistry is included because polymers comprise molecules, many of which are synthesized by humans. As a result, polymer properties are dictated by the same laws that govern smaller, more familiar molecules. We need to understand something about the properties of these huge molecules to appreciate the extremely wide range of useful properties they possess.

Chemistry, and chemists, are only part of the story, however, as the Venn diagram on page xxiv attempts to convey. Without engineers and materials scientists, we would have interesting molecules but few useful materials. Finally, we need the skills of design engineers, architects, fiber specialists, packaging engineers, and a host of other product designers to figure out how to produce the tremendous assortment of objects fabricated with polymers. The knowledge and creativity of people in these fields and others combines to provide the materials that define our way of life and that we tend to take for granted. Although we have a long way to go, scientists and manufacturers are making significant progress in producing these materials more efficiently from natural resources, improving our ability to reuse and recycle them, and lessening the impact on important environmental issues such as ozone depletion and global warming.

Ironically, the field of polymers, so central to each of our lives, is woefully neglected in our science curricula at all levels. High school and college chemistry textbooks often tuck a token section or chapter near the back. Rarely are polymeric molecules presented as examples during the coverage of the usual topics. Most students, science majors or not, have an extremely poor understanding of the many essential ways polymers affect their lives.

The primary purpose of this book is to provide a resource that helps teachers introduce polymer concepts in their classes. Basic principles are developed and compared to "small-molecule" fundamentals where possible. The subject matter of this book assumes some background in general and organic chemistry, although much of the coverage is quite general and descriptive. Chapter 4 provides a general history of polymers and could be used in a number of different classes. Chapter 9 discusses the disposal and recycling of polymers, topics that fit nicely in environmental science curricula. Elizabeth Dabrowski's insightful "About This Book" provides a teacher's perspective on how to use the text.

We have been living in the Polymer Age for quite some time. My fervent belief, shared by my many colleagues, is that we must increase everyone's awareness of these essential materials, not just that of the chemists and engineers who will be working with them professionally. I hope this book will facilitate that educational process in some small way.

Polymer Chemistry

Copyright © 2004 NSTA. All rights reserved. For more information, go to www.nsta.org/permissions.

Industrial workers who are beginning to work with polymers should also find this book a useful introduction to the subject. Laboratory technicians, technical staff, and managers in many organizations can learn the vocabulary quickly and begin to gain an appreciation for the field of polymers and its many facets.

Acknowledgments

The author expresses his warm thanks to Wayne T. Ferrar, Adam Freeman, Christine Landry-Coltrain, and Dennis J. Massa, all stimulating industrial research colleagues for many years. Each is a patient teacher with the gift of explaining difficult concepts in understandable terms. Henry K. Hall, Jr., Emeritus Professor of Chemistry at The University of Arizona, has provided the author valuable assistance, insight, and encouragement for more decades than either of us wishes to acknowledge. His many scientific contributions have helped shape the Polymer Age. His love of polymers and passion for teaching have influenced generations of students. Lynn M. O'Brien, Professor of Chemistry at Nazareth College of Rochester, provided many helpful suggestions on the treatment on natural polymers. All of these individuals read the manuscript carefully, offering valuable suggestions and critical comments that have resulted in a more accurate and readable text. Their enthusiasm for the project has been very encouraging.

James Shannon, Mendon High School, Pittsford, New York, and Aileen Svereika are gifted and dedicated high school chemistry teachers who offered many helpful suggestions. Debbie Liana, SUNY-Buffalo, and Paul Wesson, Northwestern University, provided valuable comments from the students' perspective. I thank all of these people for their enthusiasm, skill, and willingness to somehow squeeze this task into their extremely busy schedules.

I am grateful for the encouragement and support of Ed Schofield and the management of the Research Laboratories at Eastman Kodak Company. I also thank Ellen Dietterick for her valuable assistance with literature searches. In addition, I am grateful to Stephen Teegarden for his assistance in drawing some of the figures.

Betty Smith and Claire Reinburg of the NSTA Press have been extremely helpful and just terrific to work with. Thank you for supporting me in this project and for your patience!

Finally, I express a special gratitude to my wife, Carole. Her many comments on the manuscript were extremely beneficial and helped clarify a number of confusing passages. In addition, her love, patience, and encouragement during the manuscript preparation were invaluable.

> David Teegarden January 2004

About This Book

How often do your students ask you, "What does this have to do with real life?" Probably every day in every class. Students voice this concern so often that the school at which I teach made "Connecting Learning to Life" a school improvement goal. Similarly, with this book, you have in your hands a way to answer that question and achieve that connection by saying, "It is all about polymers, and polymers are all around us today."

Polymer chemistry is definitely a growth industry, but most chemistry teachers have had few polymer chemistry or materials science courses even at the college level. This textbook gives a teacher a thorough introduction to the chemistry of polymers, both synthetic and natural. Moreover, it is easy to understand and enjoyable to read.

I would like to suggest ways in which you can use this book in the classroom. An obvious way is that you can use this textbook as just that—a textbook in an elective polymer chemistry course. You could us it as a textbook in an advanced placement chemistry course during those weeks between the AP examination and the end of school.

Polymer of the Week

But there are also ways you can use this textbook to introduce students to the fascinating subject of polymers in a regular high school chemistry course. Some books on the market encourage teachers to teach their classes about a different element, compound, or demonstration each day or week. Why not apply that idea to polymers? Each week choose a different polymer, such as nylon or acrylic or DNA (deoxyribonucleic acid). Each day devote about five minutes of class time to the "Polymer of the Week." Here's how you then could proceed:

- On Monday, have students discuss where they might find the polymer of the week. Is it found in nature or what consumer products or medical products are made with that polymer?
- On Tuesday, introduce a discussion on the type of polymer—elastomer, chaingrowth, step-growth, fiber, or copolymer—and introduce some of the actual chemistry of polymers.
- On Wednesday, use Chapter 4 and its excellent history of polymers to discuss the development of the polymer of the week.
- On Thursday, discuss how the products that were mentioned in the class discussion on Monday are produced, such as the forming of bottles through blow molding.
- On Friday, use Chapters 1 and 9 for a risk-benefit analysis of the Polymer of the Week.

Polymer Chemistry

Copyright © 2004 NSTA. All rights reserved. For more information, go to www.nsta.org/permissions.

Using Each Chapter

Yet another way to use this textbook is to use polymers as the examples for discussions or explanation of concepts covered in a chemistry course. Chapter 1 can be used in conjunction with the first chapter of any textbook where a discussion of "What is chemistry?" occurs. A teacher wants students to know the importance of chemistry in their everyday lives and the good things that have been the result of chemistry, but it is also necessary to discuss some of the problems that have arisen because of the careless use of chemistry. (You can also refer to Chapter 9, "Disposal, Degradation, And Recycling; Bioplastics," for another angle on responsible chemistry.)

With Chapter 2, "What Are They?" you can use a long list of covalent molecules to explain covalent bonding in the context of something as ubiquitous as a plastic grocery bag. You can also use polymer reactions as examples of composition reactions.

Across the Disciplines

Chapter 3, "Natural Polymers," might not find use in the regular curriculum of a high school-level chemistry course, but would be excellent in a biology course at any level. The explanation of natural polymers is very clear and introduces the chemistry of these biomolecules in an easy-to-understand fashion that could be used in even an introductory high school biology course.

Chapter 4, "The History of Polymers," offers a chance to do an interdisciplinary activity with a social studies teacher. Students can learn how the development of polymers is an integral part of the economic development of the twentieth century. Students can gain an appreciation of how conflicts were often the reason for the development of synthetic polymers to replace natural ones or ones that required monomers that were no longer accessible. In the chemistry course, students can learn more about the companies discussed in the history of polymers and what products they market in the twenty-first century.

Elementary and Advanced Chemistry

Chapter 5, "Polymer Synthesis," is probably most useful in a second-year chemistry course that touches on the topics of stereochemistry and some organic chemistry.

Density, a topic that is taught in the early weeks of a chemistry course, is introduced in Chapter 6, "Polymer Solutions and Dispersions." Why not use some plastic samples for density experiments? Have the students identify the plastic from its density. This will enforce the concept that density is an intensive property of matter. The discussion of viscosity can also fit into a presentation on H-bonding. The explanation of polymer viscosity is very useful for a teacher using the "Chemistry in the Community" curriculum. It is an excellent reference for the experiment that has the students determining viscosity by timing the rate of fall of a plastic bead in various organic liquids.

Chapter 7, "Physical Properties," provides examples of intermolecular forces and how they affect the state of matter and the physical properties of familiar compounds.

Chapter 8, "Polymer Processing," can be introduced on those days when you don't have enough time to begin a new concept before a vacation or a free day. If you gather some photographs or computer images of the machines mentioned in this chapter, students can learn about the manufacturing of chemicals. Those photographs are also a good start for a discussion of the differences and similarities of careers as chemists vis-a-vis chemical engineers or materials scientists. They are also useful for a discussion of the development of a new "product" from the research laboratory bench to the pilot plant to the actual manufacturing plant.

Chapter 9, "Disposal, Degradation, and Recycling," can be used for a class project for Earth Day. Students have sent projects on the effects of the environment on plastics out into space on the International Space Station. Classes can do a similar project on a smaller scale by studying the effects of the weather on some plastic samples kept outside the classroom window.

Writing across the curriculum is being strongly encouraged in many schools. Chapter 10, "A Glimpse of Things to Come," can be the source of ideas for a student essay. Ask students to write about the future. Ask them to suggest new uses for current polymers or uses of existing polymers that might require the invention of totally new polymers. These ideas do not have to be currently feasible. This could be a bit of science fiction writing, but it could also encourage a great deal of creative thinking from students. These essays should find their way out onto a bulletin board so that other students and teachers could see how learning is being connected to life in the chemistry classroom.

Experiments

If you have been highlighting a polymer a week, the first four experiments in Section 4—"Free Radical Polymerization," "Synthesis of Nylon," "Synthesis of Polyesters in the Melt," and "Synthesis of a Polyurethane Foam"—are excellent demonstrations to intersperse with the content as it is presented. If you want your students to actually perform the experiments, it might be best to wait until the end of a first-year chemistry course when the students have developed their laboratory techniques to the greatest extent. Another use for the four experiments would be to introduce a different one each quarter and discuss the polymer produced in the experiment. This is a good way to use the information on polymer chemistry if time does not permit the presentation of a Polymer of the Week.

One of these four experiments can find a special use. "Step-Growth Polymerization: Synthesis of a Polyurethane Foam" can be a special part of a study of stoichiometry. Although it does not deal with molar ratios, it does ask the students to calculate how much of each reactant is needed to produce an object of a desired volume. This reviews concepts such as unit conversions and volume.

You can use "Polymer Precipitation" at the beginning of the school year as a safety demonstration. Compare what happens when an egg is cooked to what happens when a concentrated acid is added to a raw egg. The students will observe a very similar denaturing of the protein. This can be a lesson on why students must

Polymer Chemistry

wear safety goggles in the laboratory and can also be used during a presentation on the dangers of acids and bases.

"Gels from Alginic Acid Salts" teaches two areas of chemistry simultaneously. In addition to introducing polymer chemistry to a class, it also shows periodic trends. The experiment looks at the reactions of a sodium alginate solution in the presence of divalent metallic cations. Ions that are suggested for use include those of calcium, magnesium, iron, cobalt, nickel, copper, and zinc. Students can compare main group ions and transition metal ions. Students can also compare a divalent ion to a trivalent ion by observing the reactions with magnesium and aluminum ions. Students can compare the trends in reactions down a group on the periodic table by observing the results of the reactions with calcium and magnesium. Several of the period four transition metals are used in the experiment, and students can observe the colors of the beads formed based on the different ions used to form the beads. The experiment also introduces some coordination chemistry, especially in the reaction of the copper bead with ammonia solution.

Density is always introduced sometime in the early weeks of the first-year chemistry course. Traditional laboratory experiments have students determining the density of water or ethanol. Teachers usually set up a density column with various liquids and solids to demonstrate differences in density. Why not substitute "Densities" for this experiment? It has directions on setting up a "polymer density column," and the students can use part one of the experiment to understand the concept of density. This can be a second density experiment after the traditional experiment. The students can be presented with the solutions of various densities and several samples of known polymers and an unknown polymer. (Some scientific supply companies sell polymer samples to be used for specific gravity experiments. Used in density experiments, they eliminate the problems of floating or air bubbles.) Ask students how density would be used to sort the polymer samples. This can be a more open-ended experiment and may prove somewhat challenging but would be excellent, especially for honors students.

"Experiments with Films" is an application of some practical chemistry. While it involves some very simple techniques of stretching and tearing, it illustrates a very critical aspect of the testing of polymers in physical testing laboratories. The fabric used in the escape slides of airplanes is tested by stretching it taut and then repeatedly hitting it with a pointed metal probe. What is the point of this test? Airline passengers are told to take off shoes, jewelry, and even glasses if they must use the escape slide but often they do not. Women have been known to keep on high-heeled shoes. The puncture test is a way of seeing if the polymer can withstand a pair of high heels. Students can discuss the direction of the lines in a garbage bag and why they are oriented in that direction. (Yard waste can puncture the bag, but when you lift it up, you don't want it to tear and leave the bottom of the bag of garbage on the floor or sidewalk.) Use this experiment to illustrate the difference in strength between covalent bonds and intermolecular forces. If students pull along the transverse direction (samples marked TD or B), some covalent bonds are actually being broken, and this increases the difficulty in tearing the sample. If students pull along the machine direction (samples marked MD or A), intermolecular forces are merely being overcome. The experiment recommends looking through the polymer at a light source as it is being stretched. If possible, use a set of polarizing filters to look at the polymer as it is being stretched and the areas of strain and stress are colorfully evident. Containers from cassette tapes or adhesive tape can be observed between polarizing filters. The colors observed show the areas of strain put on the plastics during the forming of the object. These ideas can even be introduced in a study of spectra during a presentation on the atomic theory to show how light can be used to determine the structure of materials. A more sophisticated version of "Experiments with Films" could use a strain gauge probe for the calculator or computer so that the actual force needed to tear the sample could be determined. This would give the students a greater appreciation of actual techniques used in the research laboratory.

These are just a few of the methods you can use with this text. As you continue working with the book, you will discover more ways to help your students learn about the fascinating and pervasive subject of polymers.

Elizabeth Dabrowski Magnificat High School, Rocky River, Ohio

About the Author

David Teegarden is a research scientist with Eastman Kodak Company in Rochester, New York. He earned an A.B. in chemistry at Ohio Wesleyan University and an M.S. and Ph.D. in organic chemistry at the University of Michigan. He spent 17 years as a college professor, teaching primarily courses in organic and polymer chemistry. He has spent more than 18 years in industrial research and development, working on the synthesis of specialty polymers for various imaging applications.

Teegarden makes frequent presentations to science teachers' workshops and conventions, including the National Science Teachers Association national convention, and has written extensively for polymer chemistry journals and other science publications. He is involved with the American Chemical Society Polymeric Materials Science and Engineering Division, the Science Teachers Association of New York State, and NSTA.

Chemistry is the mother of all technologies. E. A. Rietman

Chapter 1 They're Everywhere!

Major Types of Polymers The Increasing Importance of Synthetic Polymers "Just One Word" Less Mass, Yet More There Is No Free Lunch References Cited

Other Reading

s we begin to study polymers and their properties, let's consider why they literally surround us. Why are they so important and so pervasive? Why are so many of the things we buy, eat, wear, consume, and discard polymers? As we look around, we see very few objects that do not contain polymers. In fact, our bodies are mostly polymeric: our bones, muscle, DNA, enzymes, skin, and hair, to name just a few parts. Much of what we eat, too, is polymeric or contains polymers: meat (protein), potatoes and pasta (starch), milk (protein), and green vegetables (cellulose). Many of our processed foods have been modified by adding polymers-for example, instant soups, ice cream, milk shakes, cheese, sausage, jams and jellies, and whipped "cream." Consider the materials that package our foods, to protect them physically, to keep water out (or in), to protect them from microorganisms-most of these materials are polymers. Our clothes are all made up of polymers, either natural (cotton, linen, wool, silk) or synthetic (polyester, nylon, rayon). We depend upon many synthetic polymers for medical applications, including sterile packaging, surgical garments, blood bags, drug delivery devices, artificial organs and joints, replacement blood vessels, and skin grafts for burn patients.

Our houses are built of wood (cellulose and lignin), sheathed with particleboard (wood chips pressed with plastic resin), wrapped with plastic sheeting, clad with siding (vinyl), and decorated with plastic shutters. Buildings with wood siding are covered with paint. Inside, water flows through plastic pipes, the floors are covered with tiles (vinyl) or carpeting (polyester, nylon), the walls are covered with wallpaper (vinyl) or painted (acrylics), and the

Polymer Chemistry

bathtubs, shower stalls, kitchen counters, and sinks are fabricated from synthetic polymers (acrylics and polyesters). For the past 50 years or so, our automobiles have contained increasing amounts of polymers, primarily to reduce mass. Originally, plastic parts replaced metal in and around the dashboard and in trim pieces. Seat coil springs were replaced with foam (polyurethane). Under the hood, polymers became increasingly common in heating ducts, fan housings, and electrical and electronic components. Outside, fenders, grilles, lamp housings, and wheel covers are no longer made of metal. An increasing number of automobile bodies are now molded from polymers rather than stamped from metal. Toys are made of tough plastics; boats, personal watercraft, and snowmobiles are molded with fiberglass-filled resins; downhill skis, bobsleds, and bulletproof vests contain extremely strong synthetic polymer fibers.

When we shop, we often pay with "plastic." We talk with our friends on cell phones, listen to CDs on our personal stereos, watch TV, and surf the Net on our computers. All of these devices consist mostly of plastics. The list truly seems endless.

Major Types of Polymers

Let's start by developing an overview of the major types of polymers. We can categorize polymers in a number of ways. We will develop chemical as well as structural classifications later in the text when we learn about their synthesis and properties. However, to begin, we will divide them on the basis of origin and function. We have already alluded to two different types: natural and synthetic. Table 1-1 lists several types of *natural* polymers and provides examples of each. As their name implies, natural polymers occur in nature.

Туре	Examples
polysaccharides	
structural	cellulose (wood, cotton, flax, hemp)
reserve	amyloses, amylopectins (starches [potato, corn, tapioca], glycogen, dextrans)
gel-forming	gums, mucopolysaccharides
proteins	egg white, gelatin, enzymes, muscle, collagen, elastin, silk, wool
polynucleotides	DNA, RNA
polyisoprenes	natural rubber, gutta-percha, chicle
polyesters	poly(3-hydroxybutyrate), cork
lignins	binder for cellulose fibers, cell walls

Table 1-1. The major types of natural polymers.

National Science Teachers Association

Also referred to as biopolymers, they are synthesized in the cells of all organisms. It is interesting to note that two of the most prevalent types, polysaccharides and proteins, each contain diverse compounds with extremely different properties, structures, and uses. For example, the protein in egg white (albumin) serves a much different function (nutrition) from that in silk or wool (structural). Likewise, the properties of starch and cellulose could hardly be more different. Although each is made up of polymers based on the condensation of glucose, the final molecular structures differ dramatically. Both sustain life, but in completely different ways. We will discuss natural polymers in more detail in Chapter 3.

However interesting natural polymers are, the focus of this book will be on synthetic or man-made polymers. The reasons for this emphasis will become obvious as we increase our understanding of polymer science. For now, however, let the following two statements suffice:

- Although nature provides us with a huge variety of materials for specific uses, it doesn't give us polymers that can be easily molded (i.e. are plastics).
- Natural polymers are very difficult to synthesize in the laboratory.

In Chapter 4, we will discover that the field of polymer science essentially began when scientists chemically modified natural polymers to prepare new materials with improved properties. Some of these reactions are still commercially important today. However, the specificity in the structures of most biopolymers themselves makes their laboratory synthesis extremely difficult.

So what do we mean by *synthetic* polymers? Simply put, these are compounds that are synthesized or made by man using known chemical reactions and processes. The distinction for polymers is exactly the same as that between natural and synthetic small-molecule organic compounds. In fact, most synthetic polymers are made from organic starting materials and are themselves (very large) organic compounds. Almost all of the starting materials come from petroleum. Inorganic polymers (e.g., silicones) are both known and important, but are far fewer in number compared to their organic cousins. We will explore the properties of silicone rubbers in Chapters 5 and 7.

Consider Figure 1-1, which shows the conversion of crude oil into petrochemicals and fuel. The process of producing organic compounds from petroleum is called refining. Less than 10% of petroleum that is refined is converted into petrochemicals, almost all of it being converted into gasoline, diesel or jet fuel, or heating oils. Petrochemicals are converted into a variety of organic compounds, including solvents, organic compounds such as dyes,

Polymer Chemistry



Figure 1-1. The small fraction of petroleum that is converted to polymers.

fertilizers, drugs, and food additives, and into monomers, the starting materials for making polymers.

Table 1-2 separates synthetic polymers into broad categories that describe their ultimate function or property. We are familiar with some of these terms.

- Plastics are materials that can be heated and then molded or shaped into useful objects. More specifically, thermoplastics can be processed more than once by reheating, while thermoset resins react chemically during initial heating and molding to form a permanent network. The term plastic is often loosely used to describe all polymers, sometimes in an unfavorable way. As we can see in Table 1-2, however, several other categories of polymers exist, each with its own set of properties.
- Fibers are polymers with high strength in one dimension that can be processed into long strands. The range of strength for fibers is truly impressive, from those used for textiles (clothing, carpets; relatively weak), to commercial monofilament fishing line up to 130 km long (80 land miles!), to materials that can be woven into bulletproof vests (aramids).

Туре	Examples	Typical Uses
plastics	polystyrene, poly (methyl methacrylate), poly(vinyl chloride)	bottles, toys, automobiles, seemingly everything
fibers	nylon, polyesters, polyaramids	clothing, disposable diapers, tennis racquets, carpets, fishing line
films	polyethylene, polyesters	packaging, grocery and garbage bags, paints, photographic films
elastomers	polybutadiene, polyisoprene	tires, golf balls, condoms, latex gloves, rubber bands
adhesives	epoxies, poly(vinyl alcohol), polycyanoacrylates	white glue, epoxy cement, "instant" glue

Table 1-2. Examples of synthetic polymers.

- Films have two-dimensional strength and can be processed into flexible thin sheets. Grocery, garbage, and dry-cleaning bags, food wrap, and photographic film are common examples. *Coatings* (e.g., paints) can be included in the category of films that adhere to the surface of other materials.
- *Elastomers* are rubbery polymers with varying ability to stretch.
- Adhesives include glues and sealants and may be rubbery or hard after drying or setting.

Although this list covers the majority of polymer types, additional classes of polymers exist, including some specialized ones that we will take up later in the text. Also, some polymers fall into more than one category depending upon application. For example, some of the polymers formulated into paint have excellent adhesive properties, for obvious reasons.

The Increasing Importance of Synthetic Polymers

We understand something of the importance of natural polymers. Cellulose is relatively stiff and allows trees and plants to grow toward the sun. Starch is an efficient molecule for storing energy. Proteins such as enzymes catalyze biological reactions. DNA (deoxyribonucleic acid) and RNA (ribonucleic acid) are responsible for the storage and transmission of genetic information. But why do we find so many synthetic polymers in our lives?

The first reason is the most obvious: *replacement*. Because most synthetic polymers are organic, their densities are quite low compared to metals and ceramics. Consider an object as simple as a drinking tumbler to be used by a major airline.

Common glass has a density of approximately 2.6 g/cm³, while the density of polystyrene used by the airline is 1.0. Also, the polystyrene tumbler can be less than one-half as thick as the glass because the polymer is

Polymer Chemistry

stronger and less brittle. Therefore, the plastic tumbler has a mass only about 10% to 20% of the mass of the glass one. Advantage number one.

- Assuming the item could be molded with an inexpensive plastic (polystyrene is a cheap commodity plastic), the cost for the plastic tumbler would be significantly lower. And for about the same price, it will also have the airline's symbol printed on the side. Advantage number two.
- Someone is going to drop a tumbler from time to time. The plastic one is much less likely to break, and, if it does, it will not shatter. Advantage number three.
- The tumbler made out of glass is expensive enough that it will have to be returned, washed, and reused. The cheap plastic one will simply be thrown out. Advantage number four.

You can see that using polystyrene tumblers saves the airlines time and money. And that is why only first-class passengers receive their beverages in glass tumblers!

Repeat this scenario with just about any common object you can think of, and you begin to understand why polymers are so common. Plastics come in an extremely wide range of compositions, with different physical and mechanical properties, chemical resistance, and cost. They can be molded, blowmolded, extruded, and shaped into an infinite variety of one-, two-, and threedimensional shapes and objects. They can be made optically clear, translucent, opaque, textured, and multicolored. They have made available to all of us household items that were once enjoyed only by the extremely wealthy (Wascher 1988). Thus the evolution of what many call the *Plastic Age* was inevitable.

The packaging industry provides many excellent examples for the substitution of plastics for older, traditional materials. For example, plastic beverage containers have become increasingly common, replacing aluminum, steel, glass, and paper for many types of drinks. Mass is one factor, obviously. In addition, as shown in Table 1-3a, the cost of the energy required to produce a kilogram of each material varies dramatically. These are average numbers for generating *virgin* (new) material and do not take into account recycling.

Table 1-3b takes the message one step further. What is the energy cost for producing a given container? Again, because the density of most plastics is so low, the low bulk energy cost (Table 1-3a), coupled with the low mass of the container, results in a per container cost at least one-tenth that for aluminum or glass. How could food and beverage manufacturers ignore such dramatic economic figures?

Much of the food we buy, either in the grocery store or in fast-food restaurants, is wrapped in some form of plastic. Some of this is for convenience and marketing (e.g., trendy prepackaged snacks with separate compartments and wrappings for each type of food), while some packaging is used to retard spoilage. Obviously, decisions about what foods to encase in plastic, and what plastics to use, depend upon economic, marketing, and technical (polymer science and plastics engineering) considerations. **Table 1-3.** Energy requirements for beverage packaging material (adapted from Guillet 1997, courtesy of Wiley-VCH).

1-3a. Thermal energy required to produce 1 kg of material.

Material	(J/kg) (x10⁻⁵)*	
aluminum	26.7	
steel	5.0	
glass	2.9	
paper	2.5	
plastic	1.1	

1-3b. Energy per container

Container	Volume	E Mass (g)	nergy/Container (J) (x10 ⁻⁶)*
aluminum Pepsi can	12 oz (355 mL)	14.0	3.7
returnable glass beer bottle	12 oz (355 mL)	238.8	6.8
paper milk carton	1 pint/16 oz (473 mL)	26.1	0.66
plastic milk bottle (HD polyethylene)	1 pint/16 oz (473 mL)	30.9	0.34
plastic Grower's Pride OJ (PET)	1 pint/16 oz (473 mL)	45.6	0.50
plastic Pepsi bottle (PET)	20 oz (591 mL)	27.4	0.30

* J = joule

"Just One Word"

Mr. McGuire:	I just want to say one word to you. Just one word.
Ben:	Yes, sir.
Mr. McGuire:	Are you listening?
Ben:	Yes, sir, I am.
Mr. McGuire:	Plastics!

(The Graduate, 1967)

This scene was particularly funny in 1967 when Mr. McGuire advised recent college graduate Ben to pursue a career in plastics. A then-young Dustin Hoffman as Ben tried to answer politely, but the dismay and bewilderment of his reaction made this scene one of the most memorable in film history. (If you aren't familiar with this classic movie, talk to someone older—they will be.) The replacement of conventional materials with polymers that began in

Polymer Chemistry

earnest during and following World War II initially resulted in plastic products notably inferior to the quality of the originals. The terms *plastic* and *synthetic* took on the meaning of cheap and impermanent imitations. Being part of an industry that seemed only to turn out an increasing number of such items was not what Ben or many other college graduates dreamed of.

But the replacements have continued unabated ever since, and advances in polymer science coupled with improvements in processing soon brought about higher quality and more sophisticated products. By 1976, plastics surpassed steel to become the most consumed synthetic material in the United States (Wascher 1988). New polymers, as well as new uses for old polymers, continue to find niches in consumer applications with ever-increasing volume. Not surprisingly, the use of plastics has exploded since their first introduction in the midtwentieth century. This is shown for plastics in Figure 1-2. The reasons behind the dramatic growth of this new industry and the ways it has changed our lives will be the underlying theme of this book.

Figure 1-2. Worldwide consumption of plastics from 1950 to 2010 (Szabo 2002, reprinted courtesy of Rapra Technology, Ltd.).



Sometimes the replacement of a traditional item with a simple plastic one can provide a huge improvement in quality of life. In many parts of Africa, people must walk long distances to obtain water. Traditionally this job fell to the women, who carried the water on their heads in ceramic vats. Children couldn't carry a heavy, breakable vat, which could be a family's most valuable possession. Many families could not afford more than one. Enter the plastic bucket. Light, inexpensive, and not very fragile, it enabled the children to assume some responsibility for obtaining water, thus freeing women for other tasks (Fenichell 1996).

Less Mass, Yet More

If the simple replacement of "conventional" materials with polymers constituted the whole story, a study of polymers would be far less interesting than it actually is. The second major reason for the prevalence of so many polymers in our society results from the possibility of *unique properties*. The study of polymers, polymer science, encompasses several disciplines, including chemistry, physics, and engineering. The range of properties one can obtain with macromolecules is extremely broad and truly fascinating. In addition, we see an ever-increasing demand for more sophisticated materials. Thus, industrial corporations as well as government agencies have long funded research in the synthesis and processing of new polymers, resulting in a wide range of commercial products with properties that are not possible with other materials. Such materials have resulted in the development of entirely new technologies, such as space travel, integrated circuits, computers, optical fiber, water-based paints, artificial organs, and automobile tires that last 60,000 miles or more.

Polymers can be made that are electrically insulating, semiconducting, conducting, or magnetic. When subjected to electrical fields, exposed to light or changes in temperature, some polymers change color or switch from transparent to opaque (e.g., liquid crystals). Some polymers change shape when subjected to an input of energy, while others cause solutions to become more or less viscous or to form a gel when it is desirable to do so. Many materials do not consist solely of polymers, but are *composites* containing substances called *fillers*. Some fillers are inexpensive inorganic materials such as glass, minerals, or carbon black. Alternatively, fibrous or platelike particles can be used as fillers to reinforce a polymer, making the composite material stronger than the polymer alone. Examples of *reinforcing agents* include glass fiber, carbon fiber, and other polymers (e.g., aramid or nylon fibers). We will discuss some of the technological applications of composites in more detail in Chapters 8 and 10.

How far we have come since the period of cheap imitations! Consider for a moment the lowly automobile bumper. Until fairly recently, bumpers were constructed of steel and electroplated with chromium to make them shiny. Even minor accidents usually necessitated the replacement of a steel bumper, whose job was to protect the automobile body from damage. Now, most cars have plastic bumpers that offer a number of advantages. Not only are they much lighter, they are also very tough, meaning they are able to withstand significantly greater impact before undergoing damage. In addition, they can be molded in complex shapes so they become integrated into

Polymer Chemistry

the overall design of the automobile. The plastic can be colored, either the same as the rest of the car or as a complement. The colorant is not just on the surface, so minor scrapes and bumps are hardly noticeable. And finally, they do not rust.

There Is No Free Lunch

Not surprisingly, in addition to the many advantages of polymers comes the inevitability of some disadvantages. The plastic tumbler discussed above doesn't have the "heft and feel" of a glass one. It isn't as classy. And significantly, the disposal of an increasing number of these and many other plastic items causes sometimes alarming increases in the volume of municipal waste entering our landfills. Extremely few of these materials are biodegradable, and many cannot be directly reused.

So how do we balance the increasing pressure to introduce even more plastic objects into our lives while minimizing the impact on our environment? This is an extremely important question, one that we will address when we discuss issues surrounding the recycling and disposal of polymers in Chapter 9.

Meanwhile, let's continue to build our understanding of polymers. So far, we have talked briefly *about* polymers and why they are so prevalent in our lives. We have distinguished natural polymers from synthetic ones and have classified the latter based on properties. We have also suggested the promise of making materials with very interesting and unusual properties. In the next chapter we will explore exactly what polymers are and will probe the origin of their unusual properties. We will begin to understand polymers as chemical molecules similar to, but very different from, small organic molecules.

References Cited

- Fenichell, S. 1996. *Plastic: The making of a synthetic century*. 9-10. New York, NY: HarperBusiness.
- Guillet, J. 1997. Environmental aspects of photodegradable plastics. *Macromolecular Symposia*, 123: 209–24.
- Szabo, F. 2002. The world plastic industry. International Polymer Science and Technology 29(6): T71–T77.

Wascher, U. S. 1988. GE plastics materials strategy. Polymer News 13: 194-98.

Other Reading

Elias, H-G. 1987. Mega molecules. New York, NY: Springer-Verlag.

- Emsley, J. 1998. *Molecules at an exhibition: Portraits of intriguing materials in everyday life*. Gallery 5. New York, NY: Oxford University Press.
- Seymour, R. B., and C. E. Carraher. 1990. *Giant molecules: Essential materials for* everyday living and problem solving. New York, NY: Wiley Interscience.