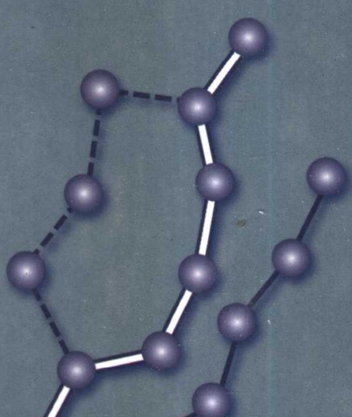
THE ELEMENTS OF

Polymer Science and Engineering

Second Edition

An Introductory Text and Reference for Engineers and Chemists



ALFRED RUDIN

THE ELEMENTS OF

Polymer Science and Engineering

Second Edition

An Introductory Text and Reference
for Engineers and Chemists

Alfred Rudin
University of Waterloo

ACADEMIC PRESS

San Diego London Boston
New York Sydney Tokyo Toronto

This book is printed on acid-free paper. ∞

ACADEMIC PRESS
a division of Harcourt Brace & Company
525 B Street, Suite 1900, San Diego, CA 92101-4495, USA
http://www.apnet.com

ACADEMIC PRESS
24–28 Oval Road, London NW1 7DX, UK
http://www.hbuk.co.uk/ap/

Library of Congress Cataloging-in-Publication Data
Rudin, Alfred
The elements of polymer science and engineering /Alfred Rudin.—2nd ed.
p. cm.
Includes bibliographical references and index.
ISBN 0-12-601685-2 (acid-free paper)
1. Polymers. 2. Polymerization.
QD381.R8 1998
547′.7—dc21
98-11623
CIP

Printed in the United States of America
98 99 00 01 02 MV 9 8 7 6 5 4 3 2 1

Preface

Unprovided with original learning, uninformed in the habits of thinking, unskilled in the arts of composition, I resolved to write a book.

—Edward Gibbon

This introductory text is intended as the basis for a two- or three-semester course in synthetic polymers. It can also serve as a self-instruction guide for engineers and scientists without formal training in the subject who find themselves working with polymers. For this reason, the material covered begins with basic concepts and proceeds to current practice, where appropriate.

Space does not permit any attempt to be comprehensive in a volume of reasonable size. I have tried, instead, to focus on those elements of polymer science and technology that are somewhat different from the lines of thought in regular chemistry and chemical engineering and in which a student may need some initial help. Few of the ideas dealt with in this text are difficult, but some involve a mental changing of gears to accommodate the differences between macro- and micromolecules. If this text serves it purpose, it will prepare the reader to learn further from more specialized books and from the research and technological literature.

An active, developing technology flourishes in synthetic polymers because of the great commercial importance of these materials. This technology teaches much that is of value in understanding the basic science and engineering of macromolecules, and the examples in this text are taken from industrial practice.

Polymer molecular weight distributions and averages seem to me to be widely quoted and little understood, even though there is nothing particularly difficult in the topic. This may be because many textbooks present the basic equations for

$\overline{M}_n$, $\overline{M}_w$, and so on with no explanation of their origin or significance. It is regrettable that much good effort is defeated because a worker has an incorrect or imperfect understanding of the meaning and limitations of the molecular weight information at his or her disposal. Chapter 3 focuses on the fundamentals of molecular weight statistics and the measurement of molecular weight averages. It will be more use to a reader who is actively engaged in such experimentation than to a beginning student, and some instructors may wish to treat the material in this chapter very lightly.

I have included an introduction to rubber elasticity in Chapter 4 because it follows logically from considerations of conformational changes in polymers. This material need not be taught in the sequence presented, however, and this topic, or all of Chapter 4, can be introduced at any point that seems best to the instructor. Chapters 5 through 7 are quite orthodox in their plans. I have, however, taken the opportunity to present alkyd calculations as an example of practice in the coatings industry and formulating thermosetting materials.

Chapter 7 deals with free radical copolymerizations. This area has been considerably "worked over" for some years. Recent developments have shown, however, that many of our concepts in this area need reexamination, and I have tried to provide a critical introductory picture of the state of this field. Emulsion polymerization, which is dealt with in Chapter 8, is in an intense state of fermentation, spurred by technological advances and mechanistic insights. I have dispensed with the neat mathematical description of the Smith–Ewart emulsion polymerization model that was given in the first edition of this text, because this theory no longer reflects modern thinking. Newer understanding of this important process can be expressed mathematically, but I believe that would be dauntingly complex for novice students and practitioners. Instead, this chapter is mainly a "how-to" primer, with the object of introducing the reader to the many opportunities that are offered by this versatile technique. The material in this chapter may not be very useful to students who will not be in a position to try the polymerization and some instructors may wish to treat this topic very lightly. I have updated Chapter 9, with particular attention paid to metallocene catalysis, because of the great current importance and potential of this subject.

Chapter 10 is a modest attempt to introduce polymerization reaction engineering. I would hope that this subject will be interesting and useful not just to engineers but to scientists as well, because it is always informative to see how basic concepts are applied in practice. In this connection, the student and practitioner should realize that there are lessons to be learned not only in industrial versions of laboratory-scale reactions but also in how and why some processes are not used. Computer modeling of polymerization processes has not been included in this chapter because of space limitations.

Chapter 11 treats the basic elements of the mechanical properties of polymeric solids and melts. Topics such as fracture mechanics and rheology are touched on lightly, because of their importance to polymer applications. Some instructors may prefer to skip this material, depending on the orientation of their classes. Polymer mixtures, which are of great commercial importance, are treated in Chapter 12. There are two main schools of thought in this area: the scientists who study the statistical thermodynamics of polymer mixtures and the technologists who make and use blends. Neither pays much attention to the other; I have tried to introduce some basic elements of both viewpoints in this chapter to show that each can benefit from the other.

The only references included here are those dealing with particular concepts in greater detail than this text. This omission is not meant to imply that the ideas that are not referenced are my own, any more than the concepts in a general chemistry textbook are those of the author of that book. I lay full claim to the mistakes, however.

The units in this book are not solely in SI terms, although almost all the quantities used are given in both SI and older units. Many active practitioners have developed intuitive understandings of the meanings and magnitudes of certain quantities in non-SI units, and it seems to be a needless annoyance to change these parameters completely and abruptly.

The problems at the end of each chapter are intended to illustrate and expand the text material. A student who understands the material in the chapter should not find these problems time consuming. The problems have been formulated to require numerical rather than essay-type answers, as far as possible, since "hand-waving" does not constitute good engineering or science. The instructor may find an incidental advantage in that answers to such problems can be graded relatively rapidly with the aid of the *Solutions Manual.*

My thanks go to all the students who have endured this course before and after the writing of the first edition, to the scientists and engineers whose ideas and insights form the sum of our understanding of synthetic polymers, and to the users who kindly pointed out errors in the first edition.

Alfred Rudin

Contents

Chapter 2 **Basic Principles of Polymer Molecular Weights**

Chapter 3 **Practical Aspects of Molecular Weight Measurements**

Chapter 4 Effects of Polymer Isomerism and Conformational Changes

Chapter 5 Step-Growth Polymerizations

Chapter 11 **Mechanical Properties of Polymer Solids and Liquids**

Chapter 12 **Polymer Mixtures**

Chapter 1

Introductory Concepts and Definitions

Knowledge is a treasure, but practice is the key to it.
—Thomas Fuller, *Gnomologia*

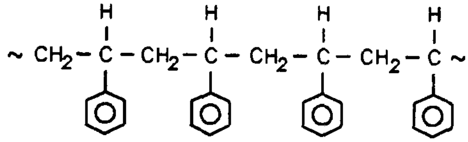
1.1 SOME DEFINITIONS

Some basic concepts and definitions of terms used in the polymer literature are reviewed in this chapter. Much of the terminology in current use in polymer science has technological origins, and some meanings may therefore be understood by convention as well as by definition. Some of these terms are included in this chapter since a full appreciation of the behavior and potential of polymeric materials requires acquaintance with technical developments as well as with the more academic fundamentals of the field. An aim of this book is to provide the reader with the basic understanding and vocabulary for further independent study in both areas.

Polymer technology is quite old compared to polymer science. For example, natural rubber was first masticated to render it suitable for dissolution or spreading on cloth in 1820, and the first patents on vulcanization appeared some twenty years later. About another one hundred years were to elapse, however, before it was generally accepted that natural rubber and other polymers are composed of giant covalently bonded molecules that differ from "ordinary" molecules primarily only in size. (The historical development of modern ideas of polymer constitution is traced by Flory in his classical book on polymer chemistry [1], while Brydson [2] reviews the history of polymer technology.) Since some of the terms we are going to review derive from technology, they are less precisely defined than those the reader may have learned in other branches of science. This should not be cause for alarm, since all the more important definitions that follow are clear in the contexts in which they are normally used.

1.1.1 Polymer

Polymer means "many parts" and designates a large molecule made up of smaller repeating units. Thus the structure of polystyrene can be written

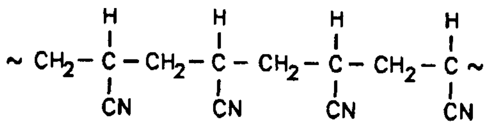


1-1

Polymers generally have molecular weights greater than about 5000 but no firm lower limit need be defined since the meaning of the word is nearly always clear from its use. The word *macromolecule* is a synonym for polymer.

1.1.2 Monomer

A monomer is a molecule that combines with other molecules of the same or different type to form a polymer. Acrylonitrile, $CH_2{=}CHCN$, is the monomer for polyacrylonitrile:



1-2

which is the basic constituent of "acrylic" fibers.

1.1.3 Oligomer

An oligomer is a low-molecular-weight polymer. It contains at least two monomer units. Hexatriacontane (n-$CH_3{-}(CH_2)_{29}{-}CH_3$) is an oligomer of polyethylene

$$\sim CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2 \sim:$$

1-3

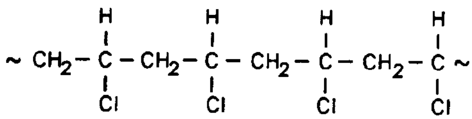
Generally speaking, a species will be called *polymeric* if articles made from it have significant mechanical strength and oligomeric if such articles are not strong enough to be practically useful. The distinction between the sizes of oligomers and the corresponding polymers is left vague, however, because there is no sharp transition in most properties of interest.

The terms used above stem from Greek roots: *meros* (part), *poly* (many), *oligo* (few), and *mono* (one).

1.1.4 Repeating Unit

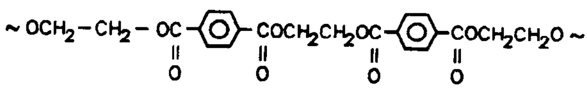
The repeating unit of a linear polymer (which is defined below) is a portion of the macromolecule such that the complete polymer (except for the ends) might be produced by linking a sufficiently large number of these units through bonds between specified atoms.

The repeating unit may comprise a single identifiable precursor as in polystyrene (**1-1**), polyacrylonitrile (**1-2**), polyethylene (**1-3**), or poly(vinyl chloride):



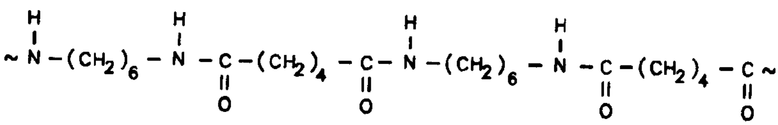
1-4

A repeating unit may also be composed of the residues of several smaller molecules, as in poly(ethylene terephthalate):



1-5

or poly(hexamethylene adipamide), nylon-6,6:



1-6

The polymers that have been mentioned to this point are actually synthesized from molecules whose structures are essentially those of the repeating units shown. It is not necessary for the definition of the term *repeating unit*, however, that such a