
The Elements of Polymer Science and Engineering

An Introductory Text for
Engineers and Chemists

ALFRED RUDIN

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of Polymer Science
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for Engineers and Chemists*

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and Chemical Engineering
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*To Pearl,
with thanks
for her wisdom and wit*

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Preface

This introductory text is intended as the basis for a two- or three-semester course in synthetic macromolecules. 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 polymers and micromolecules. If this text serves its 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 all the examples in this text are taken from industrial practice.

Chapter 1 is a general introduction aimed at giving the reader an appreciation for the language, applications, and versatility of synthetic polymers.

Polymer molecular weight distributions and averages seem to me to be little understood, even though there is nothing particularly difficult in the topic. This may be because many textbooks present the basic equations for \bar{M}_n , \bar{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 disposal. Chapter 2 focuses on the fundamentals of molecular weight statistics and the measurement of molecular weight averages. Chapter 3 is a description of the most important experimental techniques in this area. It will be of 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 5–7 and 9 are quite orthodox in their plans. I have, however, taken the opportunity in Chapter 5 to present alkyd calculations as an example of practice in the coatings industry.

Chapter 8 deals with free radical copolymerizations. This area has been considered “worked over” for some years. Recent research has shown, however, that many of our concepts in this area need reexamination, and I have tried to provide a critical picture of the current state of this field in this chapter.

No introductory text considers polymerization reaction engineering, at the time of this writing. Chapter 10 is a modest effort to fill this gap. Space does not permit consideration of the modeling of particular processes, and this chapter has more of a survey character than any other in this book because of this limitations.

Chapter 11 treats the basic elements of the mechanical properties of polymer solids and melts. Topics like impact strength are included here because of their great importance in the applications of polymers.

Polymer mixtures, which are now of great commercial importance, are treated in Chapter 12. There are two main groups of workers in this area: the scientists who study the statistical thermodynamics of polymer mixtures and the technologists who make blends. Neither pays much attention to the other. I have tried to introduce some elements of both viewpoints in this chapter and 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 text 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 attached to 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, so 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 sets can be graded relatively rapidly with the aid of the Solutions Manual.

My thanks go to all those students who endured this course before and during the writing of the book and to the scientists and engineers whose ideas and insights form the sum of our understanding of synthetic polymers.

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Chapter 1

Introductory Concepts and Definitions

1.1 SOME DEFINITIONS

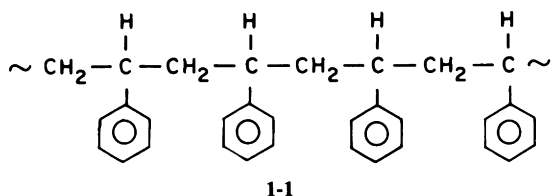
Some basic concepts and definitions of terms used in the polymer literature are reviewed in this chapter. Much of the terminology in current use in polymer science has technological origins, and some meanings may therefore be understood by convention as well as by definition. Some of these terms are 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

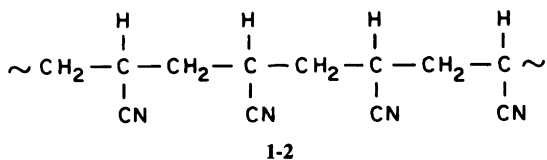
This word means “many parts” and designates a large molecule made up of smaller repeating units. Thus the structure of polystyrene can be written



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

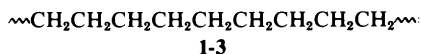
A monomer is a molecule which combines with other molecules of the same or different type to form a polymer. Acrylonitrile, $\text{CH}_2=\text{CHCN}$, is the monomer for polyacrylonitrile:



which is the basic constituent of “acrylic” fibers.

1.1.3 Oligomer

An oligomer is a low-molecular-weight polymer. It will contain at least two monomer units. Hexatriacontane ($n\text{-CH}_3\text{---}(\text{CH}_2)_{34}\text{---CH}_3$) is an oligomer of polyethylene



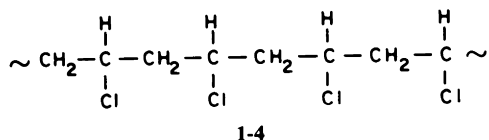
Generally speaking, a species will be called polymeric if articles made from it have significant mechanical strength and oligomeric if such articles are not strong enough to be practically useful. The distinction between the sizes of oligomers and the corresponding polymers is left vague, however, because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

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

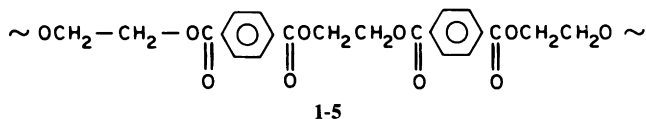
1.1.4 Repeating Unit

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 together a sufficiently large number of these units through bonds between specified atoms.

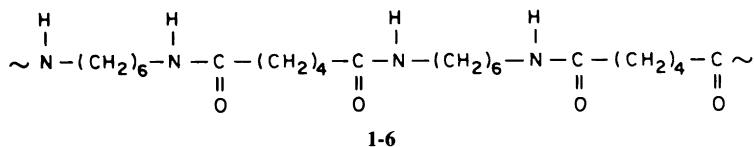
The repeating unit may comprise a single identifiable precursor as in polystyrene (1-1), polyacrylonitrile (1-2), polyethylene (1-3), or poly(vinyl chloride):



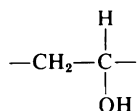
A repeating unit may also be composed of the residues of several smaller molecules, as in poly(ethylene terephthalate):



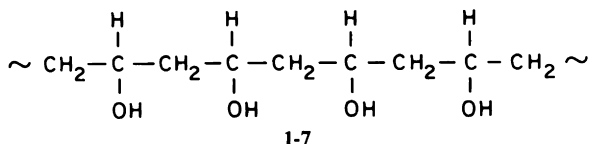
or poly(hexamethylene adipamide), nylon-66:



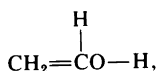
The polymers which have been mentioned to this point are actually synthesized from molecules whose structures are essentially those of the repeating units shown. It is not necessary for the definition of the term "repeating unit," however, that such a synthesis be possible. For example,



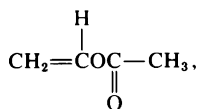
is evidently the repeating unit of poly(vinyl alcohol):



The ostensible precursor for this polymer is vinyl alcohol,



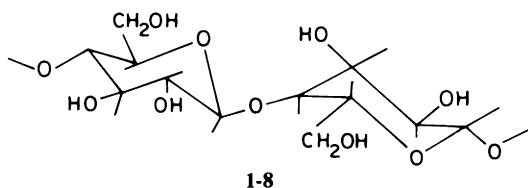
which does not exist (it is the unstable tautomer of acetaldehyde). Poly(vinyl alcohol), which is widely used as a water-soluble packaging film and suspension agent and as an insolubilized fiber, is instead made by linking together units of vinyl acetate,



and subsequently subjecting the poly(vinyl acetate) polymer to alcoholysis with ethanol or methanol.

Similarly, protein fibers like silk are degradable to mixtures of amino acids, but a direct synthesis of silk has not been accomplished yet. Another polymer for which there is no current synthetic method is cellulose,

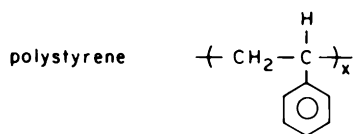
which is composed of β -1,4-linked D-glucopyranose units:



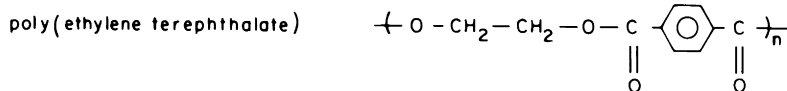
The concept of an identifiable simple repeating unit loses some of its utility with polymers which are highly branched, with species which consist of interconnected branches, or with those macromolecules which are synthesized from more than a few different smaller precursor monomers. Similar difficulties arise when the final polymeric structure is built up by linking different lower molecular polymers. This limitation to the definition will be clearer in context when some of these polymer types, like alkyds (Section 1.6) are discussed later in the text. Any deficiency in the general application of the term is not serious, since the concept of a repeating unit is in fact only employed where such groupings of atoms are readily apparent.

1.1.5 Representations of Polymer Structures

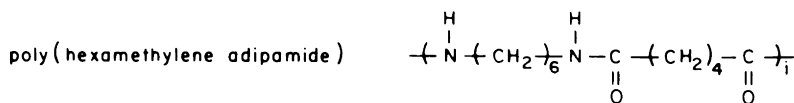
Polymer structures are normally drawn as follows by showing only one repeating unit. Each representation below is equivalent to the corresponding structure that has been depicted above.



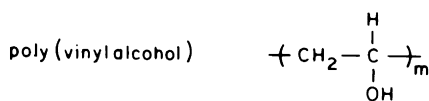
1-1a



1-5a



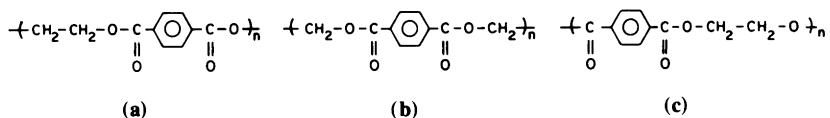
1-6a



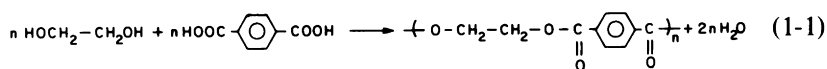
1-7a

The subscripts x , n , i , m , and so on represent the number of repeating units in the polymer molecule. This number is often not known definitely in commercial synthetic polymer samples, for reasons which are explained later in the text.

This representation of polymer structures implies that the whole molecule is made up of a sequence of such repeating units by linking the left-hand atom shown to the right-hand atom, and so on. Thus, the following structures are all equivalent to 1-5. Formula (b) would not normally be

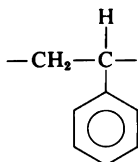


written because the nominal break is in the middle of a $\text{-OCH}_2\text{CH}_2\text{O-}$ unit, which is the residue of one of the precursors ($\text{HOCH}_2\text{CH}_2\text{OH}$) actually used in syntheses of this polymer by the reaction:



1.1.6 End Groups

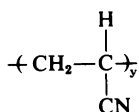
The exact nature of the end groups is frequently not known and the polymer structure is therefore written only in terms of the repeating unit, as in the foregoing structural representations. End groups usually have negligible effect on polymer properties of major interest. For example, most commercial polystyrenes used to make cups, containers, housings for electrical equipment, and so on have molecular weights of at least 150,000. An average polymer molecule will contain 1500



units compared to two end units.

1.2 DEGREE OF POLYMERIZATION

This term refers to the number of repeating units in the polymer molecule. The degree of polymerization of polyacrylonitrile



1-2a

is y . The definition given here is evidently useful only for polymers which have regular identifiable repeating units.

The term "degree of polymerization" is also used in some contexts in the polymer literature to mean the number of monomer residues in an average polymer molecule. This number will be equal to the one in the definition stated above if the repeating unit is the residue of a single monomer. The difference between the two terms is explained in more detail in Section 5.4.2 where it will be more readily understood. To that point in this book the definition given at the beginning of this section applies without qualification. We shall use the abbreviation DP for the degree of polymerization defined here and X for the term explained later on p. 170. (The coining of a new word for one of these concepts could make this book clearer, but it might confuse the reader's understanding of the general literature where the single term "degree of polymerization" is unfortunately used in both connections.)

The relation between degree of polymerization and molecular weight M , of the same macromolecule is given by

$$M = (DP)M_0 \quad (1-2)$$

where M_0 is the formula weight of the repeating unit.

1.3 POLYMERIZATION AND FUNCTIONALITY

1.3.1 Polymerization

Polymerization is a chemical reaction in which the product molecules are able to grow indefinitely in size so long as reactants are supplied.