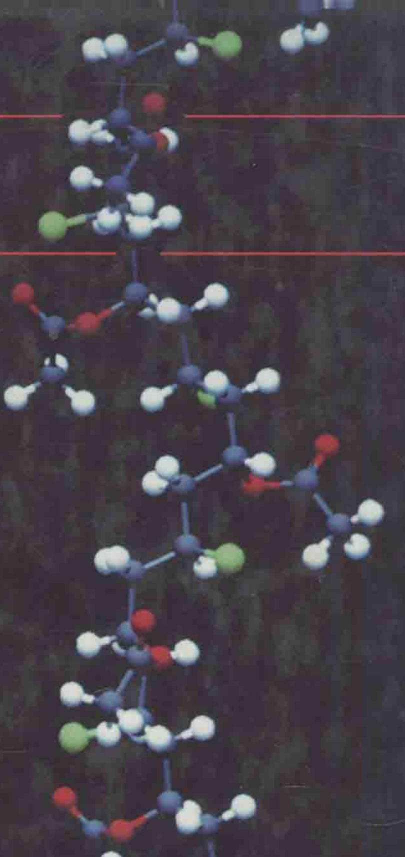
Eric A. Grulke



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POLYMER PROCESS ENGINEERING

Preface

The goal of this text is to provide an introduction to polymer processes for engineers. Polymer processes include the conversion of monomers to polymers, as well as the processing of polymeric liquids and solids into products. The conversion of monomer to polymer, its recovery from the reaction medium, and the processing of the polymer into a finished product are illustrated by the following example.

Some polymer processes might be used to make a polymer and to fabricate a product. One example of this type of application would be a coated wire rack used in dishwashers. Small particles are needed to form a uniform, glossy coating over the wire blanks, so an emulsion polymer with particles less than 1 micron in size would be used. The polymer emulsion is made by feeding monomer, water, initiators, and suspending agents into a series of continuously stirred tank reactors. Residual monomer would be stripped from the latex slurry and recycled. Dry polymer powder is produced by spray drying and screening operations. The dried powder is purchased by the part fabricator. The polymer is combined with additives such as color, stabilizers, lubricants, and plasticizers. The modified polymer is fluidized in an air bed, and heated wire blanks are dipped through the mixed powder. Particles hitting the wire surfaces will sinter and melt. A final baking step might be used to make a high-gloss finish.

The performance and quality of the finished racks depend on all steps in this sequence. Therefore, engineers working at any step in this sequence need to understand the relationships between processes and product performance.

Engineering of polymer processes should be based on the underlying polymer chemistry and physics; the engineering science of polymerization; phase equilibria; flow and mechanical properties; and the integration of transport phenomena, thermodynamics, and kinetics into the design process. Such data and models are available for commodity thermoplastics, thermosets, and elastomers. Fundamental property data and models may not generally be known for specialty and advanced materials. This text is intended to be general and broad. More details on many of the topics treated here are available in graduate texts, research monographs, and referreed journals.

The text is divided into four parts: an introduction to polymer systems with qualitative descriptions of polymer chemistry and physics; a section covering the engineering and physical sciences applying to polymerizations, phase equilibria, property analysis, flow properties, and mechanical properties; a section describing some polymer processes and illustrating design calculations; and appendices containing polymer property data. This material is directed toward senior undergraduate or first-year graduate students. However, it has been taught to students in their junior year of chemical engineering.

The first chapter, a primer of polymer science and engineering, is intended to provide a general overview of polymers for engineers. Chapter 2 has an inventory of different types of polymers, showing their structures and containing brief comments about properties and uses. In later chapters, specific polymers will be discussed without lengthy reference to their structures. Chapter 3 describes the physical state of polymer systems, beginning with polymer solutions and continuing through composites and liquid crystals.

The next section of the text covers engineering science of polymer systems. Chapter 4 demonstrates how to develop a set of rate expressions that simulate a given polymerization and solve these for batch processes. Polymer-solvent phase equilibria (Chapter 5) are critical to polymer precipitation, crystallization, and recovery from the reaction mixture. The measurement of molecular weight is sufficiently important to deserve a separate chapter (Chapter 6). Methods for thermal and chemical analyses are discussed in Chapter 7. It includes a section on qualitative methods for polymer evaluation that can be very useful to the practicing polymer engineer. The flow and mechanical properties are discussed in Chapter 8.

Polymerization processes and polymer fabrication are described in Chapters 9 and 10. The discussion emphasizes aspects of polymerization processes that are different from gas and liquid phase reactions of simple organic and inorganic compounds. These include constraints imposed by the polymerization system, mixing effects, and solvent and monomer removal.

The appendices are an integral part of the text. These data should help the student compare different polymer systems. Instructors can use the data to develop additional homework and example problems. Appendix B has a general properties list for a number of commercial polymers and monomers. Appendix C includes special properties that are important for fiber and elastomer applications. Appendix D contains information needed to do kinetic analyses of polymerization systems. Appendix E contains physical and processing properties such as viscosity and thermal properties. Appendix F has other physical property data.

Trademarks

Acrilan—Monsanto Chemical Co.
Acrylite—The Gilman Co., Inc. (acrylic sheet)
Acrylite GP, FF, PMMA & Plus—Cyro Industries
Araldite—Ciba-Geigy Corp.
Bakelite—Union Carbide Corp.
Caprolan—Allied Chemical Corp.
Celcon—Hoechst Celanese Corp., Advanced Materials Group
Creslan—American Cyanamid Co. (Fibers Div.)
Dacron—E.I. DuPont De Nemours & Co., Inc.
Delrin—DuPont
Dynel—Union Carbide Corp.
Epon—Shell Oil Co.
Kapton—Allied Signal, Inc. (plastic); DuPont (polyimide film)
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Ryton—Phillips Fibers Corporation
Saran—The Dow Chemical Company
Saran Wrap—Dow Brands (Household Products Division)
Styron—The Dow Chemical Company
Styrofoam—Dow Chemical U.S.A.
Super Glue—Pro Seal Products; Loctite Corporation (Automotive Division)
Teflon—DuPont
Thiokol—Thiokol Corp. [Chemical Division]
Vazo—Dupont Co., Dupont Chemicals
Vectra—Ocli-Optical Coating Laboratories, Inc. (sunglasses); Veeco Manufacturing Co. (beauty aids)
Vulkollan—Miles Inc.
Xylan—The Lannett Co., Inc.

Contents

1

A Primer of Polymer Science and Engineering

This book is an introduction to polymers and polymer processes for engineers. The material is divided into three sections: an overview of polymer science, engineering analysis of polymer systems, and descriptions of polymer processes and processing. This chapter presents some of the fundamental concepts and language of polymer science, including nomenclature, molecular weight, chemical bonding and entanglements, and thermal transitions. It is intended to act as a primer for the rest of the text.

1.1 GENERAL TYPES OF POLYMERS

This section describes some of the scientific classifications of polymers. These are related to the reaction steps for converting the starting materials, usually liquids at reaction conditions, into very viscous liquids or solids. A *polymer* is a large macromolecule made up of many small, repetitive units. "Poly" is the Greek word for many and "mer" is the Greek word for unit, so polymer means "many units." The word was first used by Berzelius, the Swedish chemist, in 1833. Although styrene was polymerized in 1839, and poly(ethylene glycol) and poly(ethylene succinate) were made in the 1860s, the long chain nature of these materials was not understood until much later. Most of the first polymer products were derivatives of cellulose. Nitrated cellulose, which was called nitrocellulose, was used as gun cotton.

Macromolecule is a synonym for polymer and applies to synthetic and biological materials. Most commercial polymers are polymerized from simple molecules called *monomers*. Polymers with solid-like properties usually have thousands of repeating units in each *chain*. These individual chains associate with each other to make up the polymer product. The physical state of the polymer may vary from *amorphous*, no repeating structure, to *crystalline*, regular repeating structure throughout much of the material, to *cross-linked*, chemical links between chain segments so that the "chain" is endless and has infinite molecular weight.

Polymers and Polymerizations. Polymers can have strikingly different properties depending on their chemical structure and chain morphology. Low molecular weight chains, *oligomers,* usually have liquid-like properties. The *degree of polymerization* describes the number of *repeat units* in the average chain. The repeating unit may be a monomer, or it may be a combination of several reacted units.

With the notable exception of the polysilicones, most of the specialty and commodity polymers produced have carbon atoms in their *chain backbone*. The types of polymers we use have been greatly influenced by the available sources of carbon compounds and their costs. Table 1.1 shows elemental analyses of the major hydrocarbon resources.

The raw materials used for today's polymers—natural gas, crude oil, and coal—contain very little oxygen. Their carbon to hydrogen ratio increases from natural gas to crude oil to coal. Renewable materials such as wood, algae, and sea kelp may be the carbon source for future polymers. These all contain significant amounts of oxygen in their chemical structure. Commodity polymers based on these oxygenated materials would be much different from the commercial polymers used today.

About 5% of the crude oil used in the United States is converted to polymers. The rest is made into liquid and gaseous fuels. Reuse or recycling of the polymeric materials could reduce the amount of the hydrocarbon resources used for materials. If commodity polymers were burned to recover energy at the end of their useful life, the energy contained by these materials could be reused in part. This could contribute a significant amount to the energy resources of the country.

There are several methods for polymerization. The two major methods are *chain (addition)* and *step (condensation)*. Commodity polystyrene is manufactured using a chain polymerization process. Styrene monomer is made using benzene and ethylene, both of which are derived from petroleum. The long polymer chains are described as having *n* repeating units (*n* is equivalent to the degree of polymerization). Chain polymerizations have a few reacting sites in the polymer phase at any given time. Long

TABLE 1.1 Hydrocarbon Resources

Type		Weight Ratio, C : H : O
Gas	Natural gas	3 : 1 : 0
Liquid	Crude oil	6 : 1 : 0
Solid	Coal	14 : 1 : 0
	Cellulose	6 : 1 : 5.3
	Hemicellulose	6 : 1 : 8
	Lignin	6.8 : 1 : 3