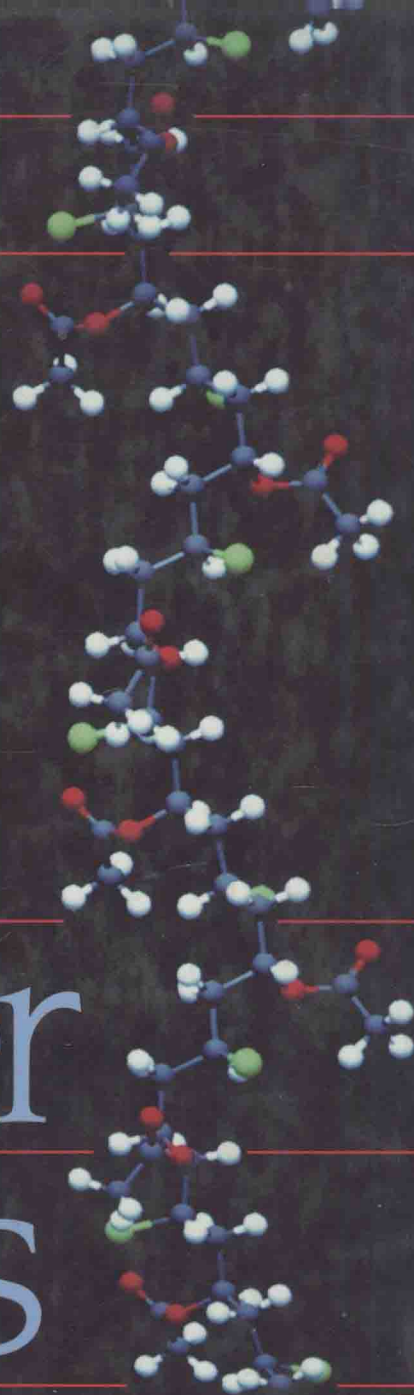


Eric A. Grulke



Polymer Process Engineering

POLYMER PROCESS ENGINEERING

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, ther-

modynamics, 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 refereed 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.

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Creslan—American Cyanamid Co. (Fibers Div.)
Dacron—E.I. DuPont De Nemours & Co., Inc.
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Melmec—American Cyanamid Corp.
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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

Preface xiii

Trademarks xv

Chapter 1	A Primer of Polymer Science and Engineering	1
1.1	GENERAL TYPES OF POLYMERS	1
1.2	POLYMER PRODUCTS AND INDUSTRIES	7
1.2.1	Plastics	8
1.2.2	Elastomers	11
1.2.3	Fibers	13
1.2.4	Coatings	16
1.2.5	Adhesives	16
1.2.6	Foams	17
1.2.7	Composites and Fiber-Reinforced Materials	17
1.3	POLYMER NOMENCLATURE	18
1.3.1	Rules	19
1.4	CONSEQUENCES OF LONG CHAIN LENGTH	20
1.5	CHEMICAL BONDING IN POLYMERS	22
1.5.1	Types of Primary Bonds	22
1.5.2	Secondary Bonding Forces	23
1.6	MOLECULAR WEIGHT AND MOLECULAR WEIGHT DISTRIBUTION	26

1.7 THERMAL TRANSITIONS	28
1.8 PHYSICAL PROPERTIES	29
1.8.1 Elasticity	29
1.8.2 Viscoelasticity	30
1.8.3 Yield and Fracture of Solids	30
NOMENCLATURE	31
PROBLEMS	31
REFERENCES	34

Chapter 2 Molecular Architecture 35

2.1 SYNTHETIC POLYMER CONSTITUTIONS AND CONFIGURATIONS	37
2.1.1 Carbon-Carbon Chains	38
2.1.2 Carbon-Nitrogen Chains	48
2.1.3 Carbon-Oxygen Chains	52
2.1.4 Carbon-Sulfur Chains	57
2.1.5 Inorganic Polymers	61
2.1.6 Copolymers	63
2.2 GENERAL TYPES OF POLYMER CONSTITUTIONS AND CONFIGURATIONS	64
2.3 CONFORMATIONS OF SINGLE MACROMOLECULES	68
2.4 RELATIONSHIPS BETWEEN POLYMER MORPHOLOGY AND USE PROPERTIES	75
NOMENCLATURE	79
PROBLEMS	79
REFERENCES	80

Chapter 3 Physical States of Polymers 81

3.1 POLYMER SOLUTIONS	81
3.2 THE GEL STATE	85
3.3 SUPERCRITICAL SOLUTIONS AND GELS	87
3.4 THE RUBBER-ELASTIC STATE	91
3.5 THE SOLID STATE	92
3.5.1 The Glassy State	92
3.5.2 The Crystalline State	93
3.6 NATURAL POLYMERS	99
3.6.1 Proteins	100
3.6.2 Polysaccharides	101
3.6.3 Other Natural Polymers	107
3.7 POLYMER BLENDS	110
3.8 POLYMER ADDITIVES	113
3.8.1 Thermoplastic Additives	115

3.8.2 Elastomer Additives	118
3.9 LIQUID CRYSTALS	119
3.10 STRUCTURED POLYMERS/COMPOSITES	122
NOMENCLATURE	124
PROBLEMS	124
REFERENCES	126

Chapter 4 Theory of Polymerization Reactions 127

4.1 FREE RADICAL CHAIN POLYMERIZATION	129
4.1.1 Reaction Mechanisms	130
4.1.2 Kinetic Rate Expressions	134
4.1.3 Chain Length and Chain Transfer Reactions	140
4.1.4 Inhibition and Retardation	146
4.1.5 Molecular Weight Distribution	149
4.1.6 Effects of Reactor Conditions of Polymer Properties	152
4.2 CHAIN COPOLYMERIZATION	157
4.2.1 Copolymer Composition Equation	157
4.2.2 Reactivity Ratios and the Alfrey-Price Relationship	161
4.2.3 Production of Uniform Composition Copolymers	162
4.2.4 Rate of Copolymerization	165
4.3 STEPWISE POLYMERIZATION	165
4.3.1 Examples of Stepwise Polymerization Mechanisms	166
4.3.2 Rate of Stepwise Polymerization: Diacid-Diol Example	168
4.3.3 Functional Groups and Degree of Polymerization	173
4.3.4 Polyfunctionality and Gelation	175
4.3.5 Molecular Weight Distribution	176
4.4 RING-OPENING POLYMERIZATION	177
4.5 STEREOSPECIFIC AND COORDINATION COMPLEX POLYMERIZATION	180
4.6 IONIC POLYMERIZATION	182
4.6.1 Cationic Polymerization	184
4.6.2 Anionic Polymerization	186
NOMENCLATURE	189
PROBLEMS	190
REFERENCES	198

Chapter 5 Polymer Solution Thermodynamics 199

5.1 REVIEW OF SOLUTION THERMODYNAMICS	199
5.1.1 Ideal Solutions	201
5.1.2 Regular Solutions	202
5.2 CONSEQUENCES OF LONG CHAINS FOR POLYMER SOLUTIONS PROPERTIES	203

5.3 STATISTICAL POLYMER MODELS: DILUTE POLYMER SOLUTIONS	208
5.3.1 Random Flight Chain Model	208
5.3.2 Real Polymer Molecules	210
5.4 POLYMER SOLUTION THERMODYNAMICS	213
5.4.1 Flory–Huggins Theory	
5.4.2 The Solvent Interaction Parameter	216
5.4.3 Solubility Parameter and Cohesive Energy Density	220
5.4.4 Flory–Krigbaum Theory: Theta Temperature	226
5.4.5 Extension to Polydisperse Systems	227
5.5 POLYMER PHASE EQUILIBRIA	228
5.5.1 Analysis of Phase Diagrams	228
5.5.2 Polymer Fractionation	234
5.5.3 Experimental Methods for Phase Diagrams	234
5.5.4 Models for Miscible Polymer Blend Properties	237
5.5.6 Typical Phase Equilibria for Ternary Systems	243
5.6 PHASE EQUILIBRIA PROBLEMS	247
NOMENCLATURE	257
PROBLEMS	258
REFERENCES	260

Chapter 6 Molecular Weight Analyses 262

6.1 MOLECULAR WEIGHT DISTRIBUTION	263
6.2 STATISTICAL ANALYSIS OF DISTRIBUTIONS	264
6.2.1 Discrete Distributions	264
6.2.2 Continuous Distributions	266
6.2.3 Statistical Tools	267
6.2.4 Mole Fraction and Weight Fraction Distributions	269
6.3 SELECTED DISTRIBUTION FUNCTIONS	274
6.4 MEASUREMENT OF MOLECULAR WEIGHT	282
6.4.1 End-Group Analysis	283
6.4.2 Colligative Methods	283
6.4.3 Sedimentation	289
6.4.4 Capillary Viscometry	289
6.4.5 Gel Permeation Chromatography	295
NOMENCLATURE	298
PROBLEMS	304
REFERENCES	309

Chapter 7 Polymer Analyses 310

7.1 Qualitative Evaluations	310
7.1.1 Thermal Properties	312

7.1.2 Solution Properties (Solvency Testing)	314
7.1.3 Environmental Stability	316
7.1.4 Mechanical Properties	317
7.1.5 Composition and Molecular Architecture	317
7.2 Thermal Analysis	318
7.2.1 Thermogravimetric Analysis	319
7.2.2 Differential Scanning Calorimetry	324
7.2.3 Thermal Mechanical Analysis	330
7.2.4 Dynamic Mechanical Analysis	332
7.3 Chain Microstructure Analysis	334
7.4 Polymer Macrostructure Analysis	339
7.5 Thermophysical Properties	339
7.5.1 Thermal Transitions	341
7.5.2 Volumetric Properties	350
7.5.3 Thermal Properties	353
NOMENCLATURE	358
PROBLEMS	359
REFERENCES	360

Chapter 8 Flow and Mechanical Properties of Polymers 363

8.1 FLOW PROPERTIES AND RHEOLOGY	366
8.1.1 Newtonian Fluids	366
8.1.2 Non-Newtonian Fluids	366
8.1.3 Time-Dependent Behavior	371
8.1.4 Generalized Newtonian Models	374
8.1.5 Free Volume Model of Polymer Melt Viscosity	379
8.1.6 Dependence of Viscosity on Molecular Weight, Temperature and Pressure	380
8.1.7 Linear Viscoelastic Models	386
8.1.8 Normal Stresses and Stress Relaxation	391
8.1.9 Nonlinear Viscoelastic (Dynamic) Models	392
8.1.10 Elongational Flows	392
8.2 THE ELASTIC STATE	394
8.2.1 Thermodynamic Analysis of Polymeric Solids	395
8.2.2 Deformation of Elastomer Chains	398
8.2.3 Deformation of Elastomer Networks	400
8.2.4 Other Models for Rubber Elasticity	403
8.3 FLUID-SOLID TRANSITIONS AND RELAXATIONS	406
8.3.1 Effects of Diluents on T_g	406
8.3.2 Effects of Pressure on T_g	408
8.3.3 Time-Temperature Superposition Principle	408
8.3.4 Polymer Properties and Polymer Performance: Engineering Use Temperatures	409

8.4 MECHANICAL PROPERTIES OF POLYMER SYSTEMS	410
8.4.1 Tensile Tests	411
8.4.2 Failure Mechanisms for Polymers	416
8.4.3 Tensile Properties of Structured Composites	420
8.4.4 Impact Resistance	422
Appendix: MECHANICAL ANALOGIES TO VISCOELASTICITY	428
NOMENCLATURE	434
PROBLEMS	436
REFERENCES	440

Chapter 9 Polymerization Processes 442

9.1 POLYMER PRODUCTION SYSTEMS	442
9.2 MONOMER SYNTHESIS	445
9.3 REACTANT STORAGE, TRANSPORT, AND FEED SYSTEMS	447
9.4 TYPES OF POLYMERIZATION SYSTEMS	448
9.4.1 Bulk Polymerization Systems	449
9.4.2 Solution Polymerization Systems	455
9.4.3 Suspension Polymerization Systems	459
9.4.4 Emulsion Polymerization Systems	467
9.5 MIXING AND POLYMERIZATION	474
9.5.1 Mixing Concepts	475
9.5.2 Rheology of Slurries	480
9.5.3 Reaction Injection Molding	487
9.6 POLYMER DEVOLATILIZATION: MONOMER AND SOLVENT RECOVERY	490
9.6.1 Devolatilization Theory	491
9.6.2 Devolatilization Equipment	497
9.6.3 Staged Systems	499
9.7 POLYMER RECOVERY	499
9.8 POST POLYMERIZATION REACTIONS	501
PROBLEMS	506
REFERENCES	510

Chapter 10 Polymer Processing 512

10.1 POLYMER DRYING BELOW T_g	515
10.1.1 Phase Equilibria Models for Glassy Polymer-Solvent Systems	519
10.1.2 Diffusion of Small Molecules in Glassy Polymers	521
10.1.3 Unsteady-state Diffusion in Particles and Pellets	523
10.2 STORAGE AND FLOW OF PARTICULATE SOLIDS	528

10.3 OVERVIEW OF POLYMER PROCESSING	536
10.3.2 Effects of Temperature and Concentration on Polymer Solution Flow	541
10.4 POLYMER EXTRUSION	545
10.5 DIE FLOWS	553
10.5.1 Capillary Die Flow	556
10.5.2 Sheet Die Flow	561
10.6 INJECTION MOLDING	565
10.6.1 Typical Design Problem: Injection-Molded Cup	567
10.6.2 Changes in Volume with Temperature and Pressure	574
10.7 CALENDERING	578
10.7.1 Process Description	579
10.7.2 Compounding of Solid Polymers	584
10.8 POLYMER RECYCLING, POLYMER DISPOSAL, AND BIODEGRADABLE POLYMERS	587
10.8.1 Industrial Plastic Waste	589
10.8.2 Consumer Waste	589
10.8.3 Recycling Plastic Packaging	592
PROBLEMS	596
REFERENCES	599

Appendix A Constants, Units, and Conversion Factors 602

Appendix B Properties of Commercial Products 606

Appendix C Special Properties of Fibers and Elastomers 620

Appendix D Polymerization Rate Constants and Coefficients 623

Appendix E Physical and Processing Properties 637

Appendix F Transport and Other Properties 644

Index 651

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