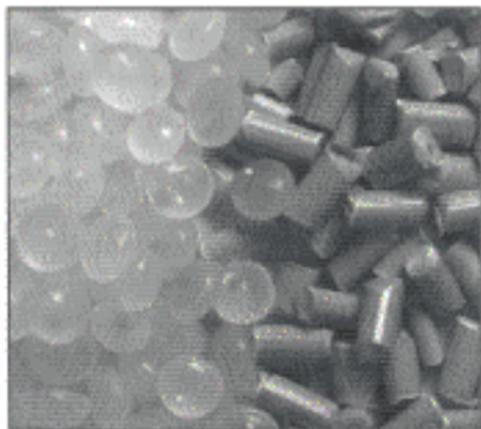


FUNDAMENTALS OF POLYMER ENGINEERING

**Second Edition
Revised and Expanded**



**Anil Kumar
Rakesh K. Gupta**

Contents

<i>Preface to the Second Edition</i>	v
<i>Preface to the First Edition</i>	vii
1. Introduction	1
1.1 Defining Polymers	1
1.2 Classification of Polymers and Some Fundamental Concepts	4
1.3 Chemical Classification of Polymers Based on Polymerization Mechanisms	16
1.4 Molecular-Weight Distributions	19
1.5 Configurations and Crystallinity of Polymeric Materials	22
1.6 Conformation of Polymer Molecules	27
1.7 Polymeric Supports in Organic Synthesis	29
1.8 Conclusion	38
	xi

References	39
Problems	39
2. Effect of Chemical Structure on Polymer Properties	45
2.1 Introduction	45
2.2 Effect of Temperature on Polymers	45
2.3 Additives for Plastics	50
2.4 Rubbers	61
2.5 Cellulose Plastics	66
2.6 Copolymers and Blends	68
2.7 Cross-Linking Reactions	72
2.8 Ion-Exchange Resins	80
2.9 Conclusion	89
References	90
Problems	91
3. Step-Growth Polymerization	103
3.1 Introduction	103
3.2 Esterification of Homologous Series and the Equal Reactivity Hypothesis	105
3.3 Kinetics of A-R-B Polymerization Using Equal Reactivity Hypothesis	107
3.4 Average Molecular Weight in Step-Growth Polymerization of ARB Monomers	111
3.5 Equilibrium Step-Growth Polymerization	116
3.6 Molecular-Weight Distribution in Step-Growth Polymerization	118
3.7 Experimental Results	125
3.8 Conclusion	140
Appendix 3.1: The Solution of MWD Through the Generating Function Technique in Step-Growth Polymerization	140
References	143
Problems	145
4. Reaction Engineering of Step-Growth Polymerization	153
4.1 Introduction	153

4.2	Analysis of Semibatch Reactors	156
4.3	MWD of ARB Polymerization in Homogeneous Continuous-Flow Stirred-Tank Reactors	166
4.4	Advanced Stage of Polymerization	169
4.5	Conclusion	174
Appendix 4.1: Similarity Solution of Step-Growth Polymerization in Films with Finite Mass Transfer		175
	References	181
	Problems	181
5.	Chain-Growth Polymerization	188
5.1	Introduction	188
5.2	Radical Polymerization	192
5.3	Kinetic Model of Radical Polymerization	197
5.4	Average Molecular Weight in Radical Polymerization	199
5.5	Verification of the Kinetic Model and the Gel Effect in Radical Polymerization	201
5.6	Equilibrium of Radical Polymerization	210
5.7	Temperature Effects in Radical Polymerization	215
5.8	Ionic Polymerization	216
5.9	Anionic Polymerization	222
5.10	Ziegler-Natta Catalysts in Stereoregular Polymerization	226
5.11	Kinetic Mechanism in Heterogeneous Stereoregular Polymerization	230
5.12	Stereoregulation by Ziegler-Natta Catalyst	232
5.13	Rates of Ziegler-Natta Polymerization	233
5.14	Average Chain Length of the Polymer in Stereoregular Polymerization	238
5.15	Diffusional Effect in Ziegler-Natta Polymerization	240
5.16	Newer Metallocene Catalysts for Olefin Polymerization	242
5.17	Conclusion	244
	References	244
	Problems	248
6.	Reaction Engineering of Chain-Growth Polymerization	255
6.1	Introduction	255
6.2	Design of Tubular Reactors	256
6.3	Copolymerization	273

6.4	Recycling and Degradation of Polymers	285
6.5	Conclusion	287
Appendix 6.1: Solution of Equations Describing Isothermal Radical Polymerization		287
	References	293
	Problems	294
7.	Emulsion Polymerization	299
7.1	Introduction	299
7.2	Aqueous Emulsifier Solutions	300
7.3	Smith and Ewart Theory for State II of Emulsion Polymerization	304
7.4	Estimation of the Total Number of Particles, N_t	313
7.5	Monomer Concentration in Polymer Particles, $[M]$	315
7.6	Determination of Molecular Weight in Emulsion Polymerization	319
7.7	Emulsion Polymerization in Homogeneous Continuous-Flow Stirred-Tank Reactors	324
7.8	Time-Dependent Emulsion Polymerization	326
7.9	Conclusions	334
	References	335
	Problems	336
8.	Measurement of Molecular Weight and Its Distribution	340
8.1	Introduction	340
8.2	End-Group Analysis	342
8.3	Colligative Properties	343
8.4	Light Scattering	350
8.5	Ultracentrifugation	354
8.6	Intrinsic Viscosity	358
8.7	Gel Permeation Chromatography	364
8.8	Conclusion	369
	References	369
	Problems	371
9.	Thermodynamics of Polymer Mixtures	374
9.1	Introduction	374

9.2	Criteria for Polymer Solubility	376
9.3	The Flory-Huggins Theory	379
9.4	Free-Volume Theories	396
9.5	The Solubility Parameter	398
9.6	Polymer Blends	401
9.7	Conclusion	403
	References	403
	Problems	405
10.	Theory of Rubber Elasticity	407
10.1	Introduction	407
10.2	Probability Distribution for the Freely Jointed Chain	408
10.3	Elastic Force Between Chain Ends	415
10.4	Stress-Strain Behavior	418
10.5	The Stress Tensor (Matrix)	420
10.6	Measures of Finite Strain	423
10.7	The Stress Constitutive Equation	427
10.8	Vulcanization of Rubber and Swelling Equilibrium	429
10.9	Conclusion	432
	References	433
	Problems	434
11.	Polymer Crystallization	437
11.1	Introduction	437
11.2	<i>Energetics of Phase Change</i>	443
11.3	Overall Crystallization Rate	447
11.4	Empirical Rate Expressions: The Avrami Equation	450
11.5	Polymer Crystallization in Blends and Composites	456
11.6	Melting of Crystals	459
11.7	Influence of Polymer Chain Extension and Orientation	462
11.8	Polymers with Liquid-Crystalline Order	464
11.9	Structure Determination	467
11.10	Working with Semicrystalline Polymers	479
11.11	<i>Conclusion</i>	480
	References	481
	Problems	484

12. Mechanical Properties	487
12.1 Introduction	487
12.2 Stress-Strain Behavior	488
12.3 The Glass Transition Temperature	497
12.4 Dynamic Mechanical Experiments	501
12.5 Time-Temperature Superposition	504
12.6 Polymer Fracture	508
12.7 Craze and Shear Yielding	511
12.8 Fatigue Failure	516
12.9 Improving Mechanical Properties	518
References	520
Problems	523
13. Polymer Diffusion	526
13.1 Introduction	526
13.2 Fundamentals of Mass Transfer	527
13.3 Diffusion Coefficient Measurement	531
13.4 Diffusivity of Spheres at Infinite Dilution	542
13.5 Diffusion Coefficient for Non-Theta Solutions	546
13.6 Free-Volume Theory of Diffusion in Rubbery Polymers	547
13.7 Gas Diffusion in Glassy Polymers	552
13.8 Organic Vapor Diffusion in Glassy Polymers: Case II Diffusion	557
13.9 Polymer-Polymer Diffusion	560
13.10 Conclusion	564
References	565
Problems	569
14. Flow Behavior of Polymeric Fluids	573
14.1 Introduction	573
14.2 Viscometric Flows	576
14.3 Cone-and-Plate Viscometer	578
14.4 The Capillary Viscometer	584
14.5 Extensional Viscometers	589
14.6 Boltzmann Superposition Principle	592
14.7 Dynamic Mechanical Properties	595
14.8 Theories of Shear Viscosity	598

Contents	xvii
14.9 Constitutive Behavior of Dilute Polymer Solutions	605
14.10 Constitutive Behavior of Concentrated Solutions and Melts	615
14.11 Conclusion	622
References	622
Problems	626
15. Polymer Processing	630
15.1 Introduction	630
15.2 Extrusion	631
15.3 Injection Molding	651
15.4 Fiber Spinning	667
15.5 Conclusion	680
References	680
Problems	684
<i>Index</i>	687