

Contents

Preface

xvii

Author

xxi

1 Introductory Concepts

1

1.1	Basic Definitions	1
1.1.1	Polymer	1
1.1.2	Monomer	2
1.1.3	Molecular Weight and Molar Mass	3
1.1.4	End Groups	3
1.1.5	Degree of Polymerization	4
1.1.6	Copolymers	4
1.2	Polymerization and Functionality	5
1.3	Polymerization Processes	7
1.3.1	Addition or Chain Polymerization	7
1.3.2	Step Polymerization	11
1.3.3	Supramolecular Polymerization	13
1.4	Molecular Architecture	18
1.5	Classification of Polymers	22
1.5.1	Thermoplastics and Thermosets	22
1.6	Plastics, Fibers, and Elastomers	26
1.7	Polymer Nomenclature	29
	References	31
	Exercises	31

2 Chain Dimensions, Structures, and Transitional Phenomena

35

2.1	Introduction	35
2.2	Polymer Chains: Structures and Dimensions	35
2.2.1	Conformational Changes	35
2.2.1.1	Polyethylene	38
2.2.1.2	Polyisobutylene	39
2.2.1.3	Polypropylene	40
2.2.2	Polymer Conformations in Crystals	40
2.2.3	Polymer Size in the Amorphous State	42
2.2.3.1	Freely Jointed Chains	43
2.2.3.2	Real Polymer Chains	44

2.3	Constitutional and Configurational Isomerism	47
2.3.1	Constitutional Isomerism	47
2.3.2	Configurational Isomerism	50
2.3.2.1	Geometrical Isomerism	50
2.3.2.2	Stereoisomerism	50
2.4	Crystallinity in Polymers	57
2.4.1	Structure of Bulk Polymers	59
2.4.1.1	Spherulites	59
2.5	Thermal Transitions in Polymers	61
2.5.1	T_g and T_m	61
2.5.2	First- and Second-Order Transitions	63
2.6	Regions of Viscoelastic Behavior	64
2.7	Factors Affecting T_g	66
2.8	Factors Affecting T_m	68
2.9	Relation Between T_m and T_g	68
2.10	Theoretical Treatment of Glass Transition	69
2.10.1	Quantitative Effects of Factors on T_g	74
2.11	Chain Movements in Amorphous State	80
2.11.1	The Reptation Model	81
2.12	Thermodynamics of Rubber Elasticity	83
2.12.1	Stress-Strain Behavior of Crosslinked Elastomers	85
2.12.2	Nonideal Networks	91
2.12.2.1	Network Defects	91
2.12.2.2	Elastically Active Chain Sections	91
	References	93
	Exercises	94
3	Polymers in Solution	101
3.1	Introduction	101
3.2	Thermodynamics of Liquid Mixtures	101
3.2.1	Low-Molecular-Weight Mixtures: van Laar Model	104
3.2.2	Polymer-Solvent Mixtures: Flory-Huggins Model	107
3.2.2.1	Flory-Huggins Expressions for Thermodynamic Functions	111
3.2.2.2	Colligative Properties and Interaction Parameter χ	113
3.2.2.3	Virial Coefficients	117
3.2.2.4	Modification of Flory-Huggins Theory	119
3.2.2.5	Flory-Krigbaum Theory	121
3.2.2.6	Excluded Volume Theory	122
3.3	Phase Equilibria in Poor Solvents	126
3.3.1	Upper and Lower Critical Solution Temperatures	129
3.4	Solubility Behavior of Polymers	131
3.5	Swelling of Crosslinked Polymers	138
3.5.1	Determination of χ from Swelling	142
3.6	Frictional Properties of Polymer Molecules in Dilute Solution	143
3.6.1	Viscosity of Dilute Polymer Solutions	145
3.6.1.1	Determination of Polymer Molecular Dimensions from Viscosity	148
	References	151

Exercises	152
4 Polymer Molecular Weights	159
4.1 Introduction	159
4.2 Molecular Weight Averages	159
4.2.1 Arithmetic Mean	159
4.2.2 Number-Average Molecular Weight	160
4.2.3 Weight-Average Molecular Weight	162
4.3 Molecular Weights in Terms of Moments	163
4.3.1 Ratio of First and Zeroth Moments	164
4.3.2 Ratios of Higher Moments	165
4.4 Molecular Weight Determination	166
4.4.1 End-Group Analysis	167
4.4.2 Colligative Property Measurement	168
4.4.2.1 Ebulliometry (Boiling Point Elevation)	168
4.4.2.2 Cryoscopy (Freezing Point Depression)	169
4.4.2.3 Membrane Osmometry	169
4.4.2.4 Vapor-Phase Osmometry	176
4.4.3 Light-Scattering Method	180
4.4.3.1 Rayleigh Ratio	181
4.4.3.2 Turbidity and Rayleigh Ratio	183
4.4.3.3 Turbidity and Molecular Weight of Polymer	184
4.4.3.4 Dissymmetry of Scattering	188
4.4.3.5 Zimm Plots	191
4.4.4 Dilute Solution Viscometry	194
4.4.4.1 Calibration of the Mark-Houwink-Sakurada Equation	196
4.4.4.2 Measurement of Intrinsic Viscosity	197
4.4.5 Gel Permeation Chromatography	200
4.4.5.1 Data Interpretation and Calibration	202
References	208
Exercises	208
5 Condensation (Step-Growth) Polymerization	213
5.1 Introduction	213
5.2 Rates of Polycondensation Reactions	214
5.2.1 Irreversible Polycondensation Kinetics	216
5.2.2 Reversible Polycondensation Kinetics	222
5.3 Number-Average Degree of Polymerization	224
5.4 Control of Molecular Weight	227
5.4.1 Quantitative Effect of Stoichiometric Imbalance	228
5.5 Molecular Weight Distribution (MWD)	232
5.5.1 Breadth of MWD	234
5.6 Nonlinear Step Polymerization	241
5.6.1 Branching	241
5.6.2 Crosslinking and Gelation	243
5.6.2.1 Statistical Approach	246
5.6.2.2 Model for Gelation Process	255
5.6.2.3 Molecular Size Distribution	255

5.6.2.4	Post-Gel Relations	258
5.7	Recursive Approach for Average Properties	260
5.7.1	Linear Step-Growth Polymerization	260
5.7.2	Nonlinear Step-Growth Polymerization	264
5.7.2.1	Polymerization of A_f ($f > 2$)	264
5.7.2.2	Polymerization of A_f ($f > 2$) + B_2	266
5.7.2.3	Polymerization of $\sum A_i + \sum B_j$	268
5.7.3	Post-Gel Properties	271
5.7.3.1	Polymerization of A_f	272
5.7.3.2	Polymerization of $A_f + B_2$	276
5.8	Polycondensation of A_xB Monomers	278
5.8.1	Dendritic and Hyperbranched Polymers	279
	References	281
	Exercises	283
6	Free Radical Polymerization	289
6.1	Introduction	289
6.2	Scheme of Radical Chain Polymerization	290
6.2.1	Overall Scheme	290
6.2.2	Chain Initiation	291
6.2.3	Chain Propagation	291
6.2.4	Chain Termination	292
6.2.5	Rate of Polymerization	293
6.2.6	Overall Extent of Polymerization	295
6.3	Experimental Determination of R_p : Dilatometry	298
6.4	Methods of Initiation	300
6.4.1	Thermal Decomposition of Initiators	300
6.4.1.1	Initiator Efficiency	301
6.4.2	Redox Initiation	305
6.4.3	Photochemical Initiation	308
6.4.3.1	Direct Photoinitiation	308
6.4.3.2	Photosensitization	309
6.4.3.3	Rate of Photoinitiated Polymerization	310
6.4.4	Initiation by High-Energy Radiations	311
6.4.5	Thermal Initiation in Absence of Initiator	312
6.5	Dead-End Polymerization	313
6.6	Determination of Absolute Rate Constants	316
6.6.1	Nonsteady-State Kinetics	316
6.7	Chain Length and Degree of Polymerization	321
6.7.1	Kinetic Chain Length	321
6.7.2	Mode of Chain Termination	323
6.7.3	Average Lifetime of Kinetic Chains	325
6.8	Chain Transfer	325
6.8.1	Degree of Polymerization	328
6.8.2	Chain Transfer to Polymer	334
6.8.3	Allylic Transfer	335
6.9	Deviations from Ideal Kinetics	337
6.9.1	Primary Radical Termination	337

6.9.2	Initiator-Monomer Complex Formation	338
6.9.3	Degradative Initiator Transfer	339
6.9.4	Autoacceleration	341
6.10	Inhibition/Retardation of Polymerization	343
6.10.1	Inhibition/Retardation Kinetics	345
6.11	Effects of Temperature	347
6.11.1	Rate of Polymerization	347
6.11.2	Degree of Polymerization	350
6.11.3	Polymerization-Depolymerization Equilibrium	351
6.12	Molecular Weight Distribution	355
6.12.1	Low-Conversion Polymerization	355
6.12.1.1	Termination by Disproportionation and/or Transfer	356
6.12.1.2	Termination by Coupling	357
6.12.1.3	Termination by Coupling, Disproportionation, and Chain Transfer	358
6.12.2	High-Conversion Polymerization	359
6.13	Polymerization Processes	359
6.13.1	Emulsion Polymerization	361
6.13.1.1	Qualitative Picture	361
6.13.1.2	Kinetics of Emulsion Polymerization	364
6.13.1.3	Other Theories	371
6.13.2	Photoemulsion Polymerization	372
6.13.3	“Grafting-From” Polymerization	373
6.14	Living Radical Polymerization	376
	References	376
	Exercises	377

7 Chain Copolymerization 383

7.1	Introduction	383
7.2	Binary Copolymer Composition – Terminal Model	384
7.2.1	Significance of Monomer Reactivity Ratios	386
7.2.2	Types of Copolymerization	387
7.2.2.1	Alternating Copolymerization	388
7.2.2.2	Ideal (random) Copolymerization	388
7.2.2.3	Random-Alternating Copolymerization	388
7.2.2.4	Block Copolymerization	389
7.2.3	Instantaneous Copolymer Composition	389
7.2.4	Integrated Binary Copolymer Equation	392
7.2.5	Evaluation of Monomer Reactivity Ratios	396
7.2.5.1	Plot of r_1 versus r_2	396
7.2.5.2	Plot of F_1 versus f_1	397
7.2.5.3	Direct Curve Fitting	399
7.2.6	The $Q-e$ Scheme	400
7.2.7	Sequence Length Distribution	402
7.2.8	Rate of Binary Free-Radical Copolymerization	405
7.3	Multicomponent Copolymerization: Terpolymerization	409
7.4	Deviations from Terminal Model	413
7.4.1	Penultimate Model	413
7.4.2	Complex-Participation Model	414

7.5	Copolymerization and Crosslinking	415
7.5.1	Vinyl and Divinyl Monomers of Equal Reactivity	415
7.5.2	Vinyl and Divinyl Monomers of Different Reactivities	418
7.5.3	One Group of Divinyl Monomer Having Lower Reactivity	419
7.6	Block and Graft Copolymerization	420
7.6.1	Block Copolymerization	421
7.6.1.1	Producing Internal Peroxide Linkages	421
7.6.1.2	Introducing Peroxide End Groups	421
7.6.1.3	Mechanical Cleaving of Polymer Chains	422
7.6.1.4	Controlled Radical Polymerization	423
7.6.2	Graft Copolymerization	423
7.6.2.1	Chain Transfer Methods	423
7.6.2.2	Irradiation with Ionizing Radiation	424
	References	425
	Exercises	426
8	Ionic Chain Polymerization	429
8.1	Introduction	429
8.2	Ionic Polymerizability of Monomers	430
8.3	Anionic Polymerization	433
8.3.1	Anionic Initiation	433
8.3.1.1	Nucleophilic Attack	433
8.3.1.2	Electron Transfer	434
8.3.2	Termination Reactions	436
8.3.2.1	Living Polymerization	436
8.3.2.2	Termination by Transfer Agents	436
8.3.2.3	Spontaneous Termination	438
8.3.3	Polymerization with Complete Dissociation of Initiator	438
8.3.3.1	Polymerization Kinetics	439
8.3.3.2	Experimental Methods	439
8.3.3.3	Average Kinetic Chain Length	441
8.3.3.4	Average Degree of Polymerization	441
8.3.3.5	Distribution of the Degree of Polymerization	443
8.3.3.6	Effects of Reaction Media	447
8.3.3.7	Effect of Excess Counterion	451
8.3.4	Polymerization with Incomplete Dissociation of Initiator	454
8.3.5	Polymerization with Simultaneous Propagation and Termination	455
8.4	Anionic Copolymerization	457
8.4.1	Reactivity Groups	458
8.4.2	Block Copolymers	459
8.4.2.1	Sequential Monomer Addition	460
8.4.2.2	Coupling Reactions	461
8.5	Cationic Polymerization	463
8.5.1	Cationic Initiation	463
8.5.1.1	Protonic Acids	464
8.5.1.2	Lewis Acids	464
8.5.2	Propagation of Cationic Chain	465
8.5.3	Chain Transfer and Termination	466

8.5.3.1	Chain Transfer to Monomer	466
8.5.3.2	Spontaneous Termination	467
8.5.3.3	Combination with Counterion	467
8.5.3.4	Transfer to Solvents/Reagents	469
8.5.3.5	Chain Transfer to Polymer	470
8.5.4	Kinetics	471
8.5.4.1	Ions and Ion Pairs	471
8.5.4.2	Simplified Kinetic Scheme	472
8.5.4.3	Degree of Polymerization	478
8.5.5	Molecular Weight Distribution	479
8.5.6	Cationic Copolymerization	482
	References	482
	Exercises	483

9 Coordination Addition Polymerization 487

9.1	Introduction	487
9.2	Ziegler-Natta Catalysts	488
9.2.1	Catalyst Composition	488
9.2.2	Nature of the Catalyst	488
9.2.3	Evolution of the Titanium-Aluminum System	489
9.3	Mechanism of Ziegler-Natta Polymerization	490
9.3.1	Mechanism of Stereospecific Placement	490
9.3.2	Bimetallic and Monometallic Mechanisms	491
9.3.2.1	Bimetallic Mechanism	492
9.3.2.2	Monometallic Mechanism	492
9.4	Kinetics of Ziegler-Natta Polymerization	495
9.4.1	Typical Shapes of Kinetic Curves	495
9.4.2	Effect of Catalyst Particle Size	497
9.4.3	Chain Termination	498
9.4.4	Kinetic Models	499
9.4.4.1	Early Models	499
9.4.4.2	Adsorption Models	502
9.4.4.3	Average Degree of Polymerization	514
9.5	Supported Metal Oxide Catalysts	515
9.5.1	Polymerization Mechanism	515
9.5.1.1	Bound-Ion-Radical Mechanism	516
9.5.1.2	Bound-Ion-Coordination Mechanism	520
9.6	Ziegler-Natta Copolymerization	521
9.7	Metallocene-Based Ziegler-Natta Catalysts	522
9.7.1	Catalyst Composition	523
9.7.2	The Active Center	525
9.7.3	Polymerization Mechanism	526
9.7.4	Kinetic Models	526
9.7.4.1	Ewen's Model	526
9.7.4.2	Chien's Model	527
9.7.4.3	Molecular Weight and Chain Transfer	530
9.8	Immobilized Metallocene Catalysts	531
9.9	Oscillating Metallocene Catalysts	534

References	536
Exercises	537
10 Ring-Opening Polymerization	541
10.1 Introduction	541
10.2 Polymerization Mechanism and Kinetics	543
10.2.1 Cyclic Ethers/Epoxides	544
10.2.1.1 Anionic Polymerization	544
10.2.1.2 Cationic Polymerization	548
10.2.2 Lactams	557
10.2.2.1 Hydrolytic Polymerization	557
10.2.2.2 Anionic Polymerization	560
10.2.3 Lactones	563
References	564
Exercises	565
11 Living/Controlled Radical Polymerization	567
11.1 Introduction	567
11.2 Stable Free Radical Polymerization	571
11.2.1 Monomers	573
11.2.2 Stable Nitroxide Radicals	573
11.2.3 Mechanism and Kinetics	573
11.2.4 Copolymerization	579
11.2.5 Aqueous Systems	589
11.3 Atom Transfer Radical Polymerization (ATRP)	593
11.3.1 ATRP Monomers	596
11.3.2 ATRP Initiators	599
11.3.3 ATRP Catalysts	600
11.3.4 ATRP Ligands	601
11.3.5 ATRP Solvents	601
11.3.6 ATRP Mechanism and Kinetics	602
11.3.7 Chain-End Functionality	607
11.3.8 Copolymerization	609
11.3.8.1 Block Copolymers	609
11.3.8.2 Graft Copolymers	618
11.3.8.3 Star and Hyperbranched Polymers	621
11.3.9 Aqueous Systems	624
11.4 Degenerative Chain Transfer	625
11.5 Reversible Addition-Fragmentation Chain Transfer	625
11.5.1 Mechanism and Kinetics	629
11.5.2 Theoretical Molecular Weight	635
11.5.3 Block Copolymers	636
11.5.3.1 Sequential Monomer Addition	636
11.5.3.2 Macro-CTA Method	641
11.5.4 Star (Co)polymers	641
11.5.5 Branched (Co)polymers	644
11.5.6 Surface Modification	644
11.5.7 Combination of RAFT and Other Polymerization Techniques	645

11.5.8 Transformation of RAFT Polymer End Groups	646
References	649
Exercises	653

12 Polymer Synthesis by Click Chemistry 661

12.1 Introduction	661
12.2 Copper-Catalyzed Azide-Alkyne Cycloaddition	665
12.2.1 Combination of ATRP and CuAAC Reactions	675
12.2.1.1 Macromonomer Synthesis	675
12.2.1.2 End-Functionalization of (Co)polymer Chains	680
12.2.1.3 Cyclization of Linear Polymers	681
12.2.1.4 Modular Synthesis of Block Copolymers	682
12.2.1.5 Nonlinear Polymer Synthesis	683
12.2.2 Combination of RAFT Polymerization and CuAAC	690
12.3 Strain-Promoted Azide-Alkyne Coupling	694
12.4 Diels-Alder Click Reactions	696
12.4.1 Copolymer Synthesis	697
12.4.2 Thermoresponsive Systems, Dendrons, and Dendrimers	702
12.4.3 Hetero-Diels-Alder (HDA) Cycloaddition	707
12.5 Thiol-Ene Reactions	710
12.5.1 Mechanisms of Thiol-Ene Reactions	714
12.5.2 Synthesis of Star Polymers and Dendrimers	716
References	719
Exercises	722

Appendix A Conversion of Units 727

Appendix B Fundamental Constants 729

Index 731