Preface xv

The Authors xvii

Chapter 1 Introduction 1

1.1 Birth of a Concept 1
1.2 Some Basic Definitions 2
1.3 Synthesis of Polymers 4
1.4 Nomenclature 4
1.5 Average Molar Masses and Distributions 8
1.6 Size and Shape 10
1.7 Configuration 12
1.8 The Glass Transition Temperature T_g and the Melting Temperature T_m 14
1.9 Elastomers, Fibers, and Plastics 16
1.10 Fiber-Forming Polymers 18
1.11 Plastics 18
1.12 Thermosetting Polymers 21
1.13 Elastomers 21
Problems 25
References 27
Bibliography 27

Chapter 2 Step-Growth Polymerization 29

2.1 General Reactions 29
2.2 Reactivity of Functional Groups 30
2.3 Carothers Equation 31
2.4 Control of the Molar Mass 32
2.5 Stoichiometric Control of M_n 34
2.6 Kinetics 36
2.7 Molar Mass Distribution in Linear Systems 38
2.8 Average Molar Masses 39
2.9 Characteristics of Step-Growth Polymerization 40
2.10 Typical Step-Growth Reactions 40
2.11 Ring Formation 41
2.12 Nonlinear Step-Growth Reactions 42
2.13 Statistical Derivation 43
2.14 Comparison with Experiment 44
2.15 Polyurethanes 46
2.16 Thermosetting Polymers 49
Problems 52
References 56
Bibliography 56

Chapter 3 Free-Radical Addition Polymerization 57

3.1 Addition Polymerization 57
3.2 Choice of Initiators 57
3.3 Free-Radical Polymerization 58
3.4 Initiators 59
3.4.1 Initiator Efficiency 60
3.5 Chain Growth 62
3.6 Termination 62
3.7 Steady-State Kinetics 63
3.8 High-Conversion Bulk Polymerizations 65
3.9 Chain Transfer 67
3.9.1 Consequences of Chain Transfer 70
3.10 Inhibitors and Retarders 70
3.11 Activation Energies and the Effect of Temperature 72
3.12 Thermodynamics of Radical Polymerization 73
3.13 Heats of Polymerization 76
3.14 Polymerization Processes 76
3.15 Features of Free-Radical Polymerization 79
3.16 Controlled Radical Polymerization 79
3.17 Nitroxide-Mediated Polymerizations 81
3.18 Atom Transfer Radical Polymerization (ATRP) 82
3.19 Reverse ATRP 83
3.20 Degenerative Chain Transfer Reaction (DT) 84
3.21 Reversible Addition Fragmentation Chain Transfer (RAFT) 84
3.22 CRP of Vinyl Chloride 87
3.23 The Kinetics of CRP Processes 87
3.24 Application to Experimental Data 90
Problems 92
References 96
Bibliography 96

Chapter 4 Ionic Polymerization 99

4.1 General Characteristics 99
4.2 Cationic Polymerization 100
4.3 Propagation by Cationic Chain Carriers 101
4.4 Termination 102
4.5 General Kinetic Scheme 103
4.6 Energetics of Cationic Polymerization 103
4.7 Telechelic Polymers via Cationic Polymerization 104
4.8 Cationic Ring Opening Polymerization 105
4.9 Stable Carbocations 107
4.10 Anionic Polymerization 108
4.11 Living Polymers 109
4.12 Kinetics and Molar Mass Distribution in Living Anionic Systems 110

4.13 Metal Alkyl Initiators 114
4.14 Solvent and Gegen Ion Effects 114
4.15 Anionic Ring-Opening Polymerization 114
Problems 116
References 118
Bibliography 119

Chapter 5 Linear Copolymers and Other Architectures 121

5.1 General Characteristics 121
5.2 Composition Drift 122
5.3 The Copolymer Equation 122
5.4 Monomer Reactivity Ratios 123
5.5 Reactivity Ratios and Copolymer Structure 124
5.6 Monomer Reactivities and Chain Initiation 127
5.7 Influence of Structural Effects on Monomer Reactivity Ratios 127
5.7.1 Resonance Effects 127
5.7.2 Polar Effects 129
5.8 The *Q–e* Scheme 129
5.9 Alternating Copolymers 131
5.10 Block Copolymer Synthesis 133
5.10.1 Transformation Reactions 135
5.10.1.1 Cationic to CRP 137
5.10.1.2 Anionic to CRP 138
5.10.1.3 ROMP to ATRP 139
5.10.1.4 Step-Growth ATRP 139
5.10.2 Coupling Reactions 140
5.10.3 Use of CRP Methods 142
5.11 Graft Copolymer Synthesis 145
5.12 Statistical and Gradient Copolymers 147
5.13 Complex Molecular Architectures 148
5.14 Dendrimers 149
5.14.1 Divergent Growth 150
5.14.2 Convergent Growth 151
5.14.3 Dendrimer Molecular Weight 152
5.14.4 Properties of Dendrimers 153
5.14.5 Applications of Dendrimers 154
Problems 155
References 156
Bibliography 156

Chapter 6 Polymer Stereochemistry 157

6.1 Architecture 157
6.2 Orientation 157
6.3 Configuration 158

6.3.1 Monotactic Polymers 159
6.3.2 Ditactic Polymers 160
6.3.3 Polyethers 160
6.4 Geometric Isomerism 162
6.5 Conformation of Stereoregular Polymers 163
6.6 Factors Influencing Stereoregulation 165
6.7 Homogeneous Stereospecific Cationic Polymerizations 167
6.8 Homogeneous Stereoselective Anionic Polymerizations 168
6.9 Homogeneous Diene Polymerization 170
6.10 Summary 172
Problems 172
References 173
Bibliography 173

Chapter 7 Polymerization Reactions Initiated by Metal Catalysts and Transfer Reactions 175

7.1 Polymerization Using Ziegler–Natta Catalysts 175
7.2 Nature of the Catalyst 176
7.3 Nature of Active Centers 177
7.4 Bimetallic Mechanism 177
7.5 Monometallic Mechanism 178
7.6 Stereoregulation 180
7.7 Ring-Opening Metathesis Polymerization (ROMP) 181
7.8 Monocyclic Monomers 182
7.9 Bicyclo- and Tricyclomonomers 183
7.10 Copolyalkenamers 184
7.11 Living Systems 184
7.12 Group Transfer Polymerization (GTP) 186
7.13 Aldol Group Transfer Polymerization 187
7.14 Metallocene Catalysts 188
7.14.1 Metallocene/Aluminoxane Catalysts 189
7.14.2 Stereoregulation 189
7.14.3 Cationic Metallocenes 192
7.14.4 Mechanism of Stereoregulation 192
7.15 Concluding Remarks 193
Problems 194
References 194
Bibliography 194

Chapter 8 Polymers in Solution 197

8.1 Thermodynamics of Polymer Solutions 197
8.2 Ideal Mixtures of Small Molecules 197
8.3 Nonideal Solutions 199
8.4 Flory–Huggins Theory: Entropy of Mixing 199

8.5 Enthalpy Change on Mixing 203
8.6 Free Energy of Mixing 204
8.7 Limitations of the Flory–Huggins Theory 205
8.8 Phase Equilibria 206
8.9 Flory–Krigbaum Theory 208
8.10 Location of the Theta Temperature 210
8.11 Lower Critical Solution Temperatures 213
8.12 Solubility and the Cohesive Energy Density 216
8.13 Polymer–Polymer Mixtures 219
8.14 Kinetics of Phase Separation 223
Problems 224
References 227
Bibliography 227

Chapter 9 Polymer Characterization — Molar Masses 229

9.1 Introduction 229
9.2 Molar Masses, Molecular Weights, and SI Units 229
9.3 Number-Average Molar Mass M_n 229
9.4 End-Group Assay 230
9.5 Colligative Properties of Solutions 230
9.6 Osmotic Pressure 231
9.7 Light Scattering 234
9.7.1 Scattering from Large Particles 236
9.8 Dynamic Light Scattering 239
9.9 Viscosity 240
9.9.1 Viscosity-Average Molecular Weight 242
9.10 Gel Permeation Chromatography 243
9.11 MALDI 247
Problems 248
References 251
Bibliography 252

Chapter 10 Polymer Characterization — Chain Dimensions, Structures, and Morphology 253

10.1 Average Chain Dimensions 253
10.2 Freely Jointed Chain Model 254
10.3 Short-Range Effects 255
10.4 Chain Stiffness 255
10.5 Treatment of Dilute Solution Data 256
10.5.1 The Second Virial Coefficient 256
10.5.2 Expansion Factor α 257
10.5.3 Flory–Fox Theory 258
10.5.4 Indirect Estimates of Unperturbed Chain Dimensions 259
10.5.5 Influence of Tacticity on Chain Dimensions 259

10.6 Nuclear Magnetic Resonance (NMR) 260
10.7 Infrared Spectroscopy 262
10.8 Thermal Analysis 264
10.9 Wide-Angle and Small-Angle Scattering 265
10.9.1 Wide-Angle X-Ray Scattering 266
10.9.2 Small-Angle X-Ray Scattering (SAXS) 267
10.9.3 Small-Angle Neutron Scattering (SANS) 268
10.10 Microscopy 271
10.10.1 Optical Microscopy 272
10.10.2 Scanning Electron Microscopy 273
10.10.3 Transmission Electron Microscopy 274
10.10.4 Atomic Force Microscopy and Scanning Tunneling Microscopy 274
Problems 276
References 277
Bibliography 277

Chapter 11 The Crystalline State and Partially Ordered Structures 279

11.1 Introduction 279
11.2 Mechanism of Crystallization 279
11.3 Temperature and Growth Rate 281
11.4 Melting 282
11.4.1 Effect of Crystallite Size on Melting 282
11.5 Thermodynamic Parameters 282
11.6 Crystalline Arrangement of Polymers 285
11.6.1 Factors Affecting Crystallinity and T_m 285
11.6.1.1 Symmetry 285
11.6.1.2 Intermolecular Bonding 286
11.6.1.3 Tacticity 287
11.6.1.4 Branching and Molar Mass 287
11.7 Morphology and Kinetics 287
11.8 Morphology 287
11.8.1 Crystallites 288
11.8.2 Single Crystals 288
11.8.3 Hedrites 289
11.8.4 Crystallization from the Melt 289
11.8.5 Spherulites 291
11.9 Kinetics of Crystallization 292
11.9.1 Isothermal Crystallization 293
11.9.2 The Avrami Equation 293
11.9.3 Deviations from Avrami Equation 294
11.10 Block Copolymers 294
11.11 Historical Development of Polymer Liquid Crystals 296
11.12 Liquid Crystalline Phases 297
11.13 Identification of the Mesophases 300

11.14 Lyotropic Main-Chain Liquid Crystal Polymers 302
11.15 Thermotropic Main-Chain Liquid Crystal Polymers 304
11.16 Side-Chain Liquid Crystal Polymers 309
11.17 Chiral Nematic Liquid Crystal Polymers 311
Problems 314
References 318
Bibliography 318

Chapter 12 The Glassy State and Glass Transition 321

12.1 The Amorphous State 321
12.2 The Glassy State 321
12.3 Relaxation Processes in the Glassy State 321
12.4 Glass Transition Region 323
12.4.1 The Glass Transition Temperature, T_g 323
12.4.2 Experimental Demonstration of T_g 324
12.4.2.1 Measurement of T_g from V–T Curves 325
12.4.2.2 Thermal Methods 326
12.4.3 Factors Affecting T_g 327
12.4.3.1 Chain Flexibility 328
12.4.3.2 Steric Effects 328
12.4.3.3 Configurational Effects 330
12.4.3.4 Effect of Cross-Links on T_g 330
12.5 Theoretical Treatments 330
12.5.1 The Free-Volume Theory 331
12.5.2 Gibbs–Di Marzio Thermodynamic Theory 335
12.5.3 Adam–Gibbs Theory 336
12.6 Dependence of T_g on Molar Mass 337
12.7 Structural Relaxation and Physical Aging 338
Problems 339
References 342
Bibliography 343

Chapter 13 Rheology and Mechanical Properties 345

13.1 Introduction to Rheology 345
13.2 The Five Regions of Viscoelastic Behavior 346
13.3 The Viscous Region 347
13.3.1 Shear Dependence of Viscosity 349
13.3.2 Kinetic Units in Polymer Chains 351
13.3.3 Effect of Chain Length 352
13.3.4 Temperature Dependence of η 353
13.3.5 Concentration Dependence of Viscosity 353
13.3.6 Time-Dependent Behavior 354
13.4 Mechanical Properties 355
13.4.1 Interrelation of Moduli 357

13.5 Mechanical Models Describing Viscoelasticity 357
13.6 Linear Viscoelastic Behavior of Amorphous Polymers 360
13.6.1 Creep 360
13.6.2 Stress–Strain Measurements 363
13.6.3 Effect of Temperature on Stress–Strain Response 363
13.6.4 Boltzmann Superposition Principle 364
13.6.5 Stress Relaxation 365
13.7 Dynamic Mechanical and Dielectric Thermal Analysis 366
13.7.1 Dynamic Mechanical Thermal Analysis (DMTA) 366
13.7.2 Dielectric Thermal Analysis (DETA) 369
13.7.3 Comparison Between DMTA and DETA 371
13.8 Time–Temperature Superposition Principle 373
13.9 Dynamic Viscosity 377
13.10 A Molecular Theory for Viscoelasticity 378
13.11 The Reptation Model 380
Problems 382
References 387
Bibliography 388

Chapter 14 The Elastomeric State 389

14.1 General Introduction 389
14.1.1 Natural Rubber 390
14.2 Experimental Vulcanization 391
14.3 Properties of Elastomers 391
14.4 Thermodynamic Aspects of Rubberlike Elasticity 392
14.5 Nonideal Elastomers 394
14.6 Distribution Function for Polymer Conformation 395
14.7 Statistical Approach 398
14.7.1 Experimental Stress–Strain Results 398
14.7.1.1 Simple Extension 398
14.7.1.2 Simple Compression 400
14.7.1.3 Pure Shear 400
14.7.1.4 Large Elastic Deformation 400
14.8 Swelling of Elastomeric Networks 400
14.9 Network Defects 401
14.10 Resilience of Elastomers 403
Problems 405
References 408
Bibliography 408

Chapter 15 Structure–Property Relations 409

15.1 General Considerations 409
15.2 Control of T_m and T_g 409
15.2.1 Chain Stiffness 410

15.2.2 Intermolecular Bonding 411
15.3 Relation Between T_m and T_g 413
15.4 Random Copolymers 413
15.5 Dependence of T_m and T_g on Copolymer Composition 414
15.6 Block Copolymers 417
15.7 Plasticizers 419
15.8 Crystallinity and Mechanical Response 420
15.9 Application to Fibers, Elastomers, and Plastics 422
15.10 Fibers 422
15.10.1 Chemical Requirements 423
15.10.1.1 Linear Polyesters 425
15.10.2 Mechanical Requirements for Fibers 426
15.10.2.1 Spinning Techniques 426
15.10.2.1.1 Melt Spinning 426
15.10.2.1.2 Wet and Dry Spinning 426
15.10.2.2 Drawing, Orientation, and Crystallinity 427
15.10.2.3 Modulus and Chain Stiffness 428
15.10.2.4 Other Factors 428
15.11 Aromatic Polyamides 429
15.12 Polyethylene 431
15.13 Elastomers and Cross-Linked Networks 434
15.13.1 Cross-Linking 435
15.13.2 Creep in Cross-Linked Polymers 435
15.13.3 Additives 435
15.14 Plastics 435
15.14.1 Plastic Selection for Bottle Crate Manufacture 437
15.14.2 Medical Applications 438
15.15 High-Temperature Speciality Polymers 439
15.16 Carbon Fibers 446
15.17 Concluding Remarks 446
Problems 448
References 453
Bibliography 454

Chapter 16 Polymers for the Electronics Industry 455

16.1 Introduction 455
16.2 Polymer Resists for IC Fabrication 455
16.3 The Lithographic Process 456
16.4 Polymer Resists 457
16.4.1 Sensitivity 458
16.4.2 Resolution 459
16.5 Photolithography 459
16.5.1 Positive Photoresists 459
16.5.2 Negative Photoresists 460
16.6 Electron Beam Sensitive Resists 463

16.6.1 Positive Resists 463
16.6.2 Negative Resists 464
16.7 X-ray and Ion Sensitive Resists 464
16.8 Electroactive Polymers 465
16.9 Conduction Mechanisms 466
16.10 Preparation of Conductive Polymers 467
16.11 Polyacetylene 469
16.12 Poly(*p*-phenylene) 472
16.13 Polyheterocyclic Systems 474
16.13.1 Polypyrrole 475
16.13.2 Sulfur Compounds 475
16.14 Polyaniline 476
16.15 Poly(Phenylene Sulfide) 476
16.16 Poly(1,6-heptadiyne) 476
16.17 Applications 476
16.18 Photonic Applications 477
16.19 Light-Emitting Polymers 477
16.19.1 Applications 478
16.20 Nonlinear Optics 478
16.21 Langmuir–Blodgett Films 481
16.22 Optical Information Storage 483
16.23 Thermorecording on Liquid Crystalline Polymers 486
References 487
Bibliography 487

Index 489