

CONTENTS

1 INTRODUCTION

- Types of Polymers and Polymerizations / 1
 - 1-1a Polymer Composition and Structure /
 - 1-1b Polymerization Mechanism / 6
- 1-2 Nomenclature of Polymers / 9
 - 1-2a Nomenclature Based on Source / 10
 - 1-2b Nomenclature Based on Structure (Non-IUPAC) /
 - 1-2c IUPAC Structure-Based Nomenclature System / 12
 - 1-2d Trade Names and Nonnames / 16
- 1-3 Linear, Branched, and Crosslinked Polymers / 17
- 4 Molecular Weight / 19
- 1-5 Physical State / 24
 - 1-5a Crystalline and Amorphous Behavior / 24
 - 1-5b Determinants of Polymer Crystallinity / 28
 - 1-5c Thermal Transitions / 29
- 6 Applications of Polymers / 33
 - 1-6a Mechanical Properties / 33
 - 1-6b Elastomers, Fibers, Plastics / 35
- References / 37

- 2- Reactivity of Functional Groups / 41
 - 2-1a Basis for Analysis of Polymerization Kinetics / 41
 - 2-1b Experimental Evidence / 43
 - 2-1c Theoretical Considerations / 44
 - 2-1d Equivalence of Groups in Bifunctional Reactants / 45
- 2-2 Kinetics of Step Polymerization / 45
 - 2-2a Self-Catalyzed Polymerization / 47
 - 2-2a-1 *Experimental Observations* / 48
 - 2-2a-2 *Reasons for Nonlinearity in Third-Order Plot* / 49
 - 2-2a-3 *Molecular Weight of Polymer* / 53
 - 2-2b External Catalysis of Polymerization / 54
 - 2-2c Step Polymerizations Other Than Polyesterification: Catalyzed versus Uncatalyzed / 56
 - 2-2d Nonequivalence of Functional Groups in Polyfunctional Reagents / 57
 - 2-2d-1 *Examples of Nonequivalence* / 57
 - 2-2d-2 *Kinetics* / 59
- 2-3 Accessibility of Functional Groups / 66
- 2-4 Equilibrium Considerations / 68
 - 2-4a Closed System / 68
 - 2-4b Open, Driven System / 70
 - 2-4c Kinetics of Reversible Polymerization / 71
- 2-5 Cyclization versus Linear Polymerization / 73
 - 2-5a Possible Cyclization Reactions / 73
 - 2-5b Thermodynamic and Kinetic Considerations / 74
 - 2-5c Other Considerations / 77
- 2-6 Molecular-Weight Control in Linear Polymerization / 78
 - 2-6a Need for Stoichiometric Control / 78
 - 2-6b Quantitative Aspects / 79
 - 2-6c Kinetics of Nonstoichiometric Polymerization / 82
- 2-7 Molecular-Weight Distribution in Linear Polymerization / 83
 - 2-7a Derivation of Size Distributions / 83
 - 2-7b Breadth of Molecular-Weight Distribution / 85
 - 2-7c Interchange Reactions / 87
 - 2-7d Alternate Approaches for Molecular-Weight Distribution / 87
 - 2-7e Effect of Reaction Variables on MWD / 90
 - 2-7e-1 *Unequal Reactivity of Functional Groups* / 90

- 2-8 Process Conditions / 91
 - 2-8a Physical Nature of Polymerization Systems / 91
 - 2-8b Different Reaction Systems / 93
 - 2-8c Interfacial Polymerization / 94
 - 2-8c-1 *Description of Process* / 94
 - 2-8c-2 *Utility* / 96
 - 2-8d Polyesters / 97
 - 2-8e Polycarbonates / 100
 - 2-8f Polyamides / 102
 - 2-8g Historical Aspects / 105
- 2-9 Multichain Polymerization / 106
 - 2-9a Branching / 106
 - 2-9b Molecular-Weight Distribution / 107
- 2-10 Crosslinking / 108
 - 2-10a Carothers Equations: $\bar{X}_n \rightarrow \infty$ / 110
 - 2-10a-1 *Stoichiometric Amounts of Reactants* / 110
 - 2-10a-2 *Extension to Nonstoichiometric Reactant Mixtures* / 111
 - 2-10b Statistical Approach to Gelation: $\bar{X}_w \rightarrow \infty$ / 112
 - 2-10c Experimental Gel Points / 115
 - 2-10d Extensions of Statistical Approach / 117
- 2-11 Molecular-Weight Distributions in Nonlinear Polymerizations / 119
- 2-12 Crosslinking Technology / 121
 - 2-12a Polyesters, Unsaturated Polyesters, and Alkyds / 123
 - 2-12b Phenolic Polymers / 125
 - 2-12b-1 *Resole Phenolics* / 125
 - 2-12b-2 *Novolac Phenolics* / 130
 - 2-12b-3 *Applications* / 131
 - 2-12c Amino Plastics / 132
 - 2-12d Epoxy Resins / 134
 - 2-12e Polyurethanes / 136
 - 2-12f Polysiloxanes / 138
 - 2-12g Polysulfides / 140
- 2-13 Step Copolymerization / 141
 - 2-13a Types of Copolymers / 142
 - 2-13b Methods of Synthesizing Copolymers / 144
 - 2-13b-1 *Statistical Copolymers* / 144

- 2-13b-2 *Alternating Copolymers* / 144
- 2-13b-3 *Block Copolymers* / 145
- 2-13c Utility of Copolymerization / 146
 - 2-13c-1 *Statistical Copolymers* / 147
 - 2-13c-2 *Block Copolymers* / 148
 - 2-13c-3 *Polymer Blends and Interpenetrating Polymer Networks* / 149
- 2-14 Newer Polymers and Polymerizations / 150
 - 2-14a Requirements for High-Temperature Polymers / 150
 - 2-14b Aromatic Polyethers by Oxidative Coupling / 152
 - 2-14c Aromatic Polyethers by Nucleophilic Substitution / 155
 - 2-14d Aromatic Polysulfides / 157
 - 2-14e Aromatic Polyimides / 158
 - 2-14f Reactive Telechelic Oligomer Approach / 162
 - 2-14g Liquid Crystal Polymers / 164
 - 2-14h 5-Membered Ring Heterocyclic Polymers / 167
 - 2-14i 6-Membered Ring Heterocyclic Polymers / 170
 - 2-14j Conducting Polymers / 172
 - 2-14j-1 *Electrochemical Polymerization* / 173
 - 2-14j-2 *Poly(p-phenylene) via Oxidative Polymerization* / 175
 - 2-14j-3 *Poly(p-phenylene Vinylene)* / 175
 - 2-14k Miscellaneous Polymerizations / 176
 - 2-14k-1 *Cycloaddition or Four-Center Polymerization* / 177
 - 2-14k-2 *Starburst Dendrimer Polymers* / 177
 - 2-14k-3 *Spiro Structures* / 178
- 2-15 Inorganic and Organometallic Polymers / 178
 - 2-15a Inorganic Polymers / 178
 - 2-15a-1 *Minerals* / 179
 - 2-15a-2 *Glasses* / 179
 - 2-15a-3 *Ceramics* / 180
 - 2-15b Organometallic Polymers / 182
 - 2-15b-1 *Polymerization via Reaction at Metal Bond* / 182
 - 2-15b-2 *Polymerization without Reaction at Metal Bond* / 182
 - 2-15b-3 *Polysilanes* / 185
- References / 186

3 RADICAL CHAIN POLYMERIZATION

- 3-1 Nature of Radical Chain Polymerization / 199
 - 3-1a Comparison of Chain and Step Polymerization / 199
 - 3-1b Radical versus Ionic Chain Polymerizations / 199
 - 3-1b-1 *General Considerations of Polymerizability* / 199

- 3-2 Structural Arrangement of Monomer Units / 203
 - 3-2a Possible Modes of Propagation / 203
 - 3-2b Experimental Evidence / 204
 - 3-2c Synthesis of Head-to-Head Polymers / 204
- 3-3 Rate of Radical Chain Polymerization / 205
 - 3-3a Sequence of Events / 205
 - 3-3b Rate Expression / 206
 - 3-3c Experimental Determination of R_p / 208
 - 3-3c-1 *Physical Separation and Isolation of Reaction Product* / 208
 - 3-3c-2 *Chemical and Spectroscopic Analysis* / 209
 - 3-3c-3 *Dilatometry* / 210
 - 3-3c-4 *Other Methods* / 210
- 3-4 Initiation / 211
 - 3-4a Thermal Decomposition of Initiators / 212
 - 3-4a-1 *Types of Initiators* / 212
 - 3-4a-2 *Kinetics of Initiation and Polymerization* / 214
 - 3-4a-3 *Dependence of Polymerization Rate on Initiator* / 216
 - 3-4a-4 *Dependence of Polymerization Rate on Monomer* / 218
 - 3-4b Redox Initiation / 219
 - 3-4b-1 *Types of Redox Initiators* / 219
 - 3-4b-2 *Rate of Redox Polymerization* / 221
 - 3-4c Photochemical Initiation / 222
 - 3-4c-1 *Bulk Monomer* / 223
 - 3-4c-2 *Irradiation of Thermal and Redox Initiators* / 224
 - 3-4c-3 *Rate of Photopolymerization* / 226
 - 3-4d Initiation by Ionizing Radiations / 229
 - 3-4e Pure Thermal Initiation / 230
 - 3-4f Other Methods of Initiation / 232
 - 3-4f-1 *Electroinitiation* / 232
 - 3-4f-2 *Plasma* / 232
 - 3-4g Initiator Efficiency / 232
 - 3-4g-1 *Definition of f* / 232
 - 3-4g-2 *Mechanism of $f < 1$: Cage Effect* / 233
 - 3-4g-3 *Experimental Determination of f* / 237
 - 3-4h Other Aspects of Initiation / 240
- 3-5 Molecular Weight / 241
 - 3-5a Kinetic Chain Length / 241
 - 3-5b Mode of Termination / 241

- 3-6 Chain Transfer / 243
 - 3-6a Effect of Chain Transfer / 243
 - 3-6b Transfer to Monomer and Initiator / 245
 - 3-6b-1 Determination of C_M and C_I / 245
 - 3-6b-2 Monomer Transfer Constants / 246
 - 3-6b-3 Initiator Transfer Constants / 249
 - 3-6c Transfer to Chain-Transfer Agent / 250
 - 3-6c-1 Determination of C_S / 250
 - 3-6c-2 Structure and Reactivity / 251
 - 3-6c-3 Applications of Chain-Transfer Agents / 254
 - 3-6d Chain Transfer to Polymer / 255
- 3-7 Inhibition and Retardation / 259
 - 3-7a Kinetics of Inhibition or Retardation / 260
 - 3-7b Types of Inhibitors and Retarders / 262
 - 3-7c Autoinhibition of Allylic Monomers / 266
- 3-8 Determination of Absolute Rate Constants / 267
 - 3-8a Non-Steady-State Kinetics / 267
 - 3-8b Rotating Sector Method / 270
 - 3-8c Typical Values of Reaction Parameters / 274
- 3-9 Energetic Characteristics / 275
 - 3-9a Activation Energy and Frequency Factor / 275
 - 3-9a-1 Rate of Polymerization / 276
 - 3-9a-2 Degree of Polymerization / 277
 - 3-9b Thermodynamics of Polymerization / 279
 - 3-9b-1 Significance of ΔG , ΔH , and ΔS / 279
 - 3-9b-2 Effect of Monomer Structure / 280
 - 3-9b-3 Polymerization of 1,2-Disubstituted Ethylenes / 281
 - 3-9c Polymerization-Depolymerization Equilibria / 283
 - 3-9c-1 Ceiling Temperature / 283
 - 3-9c-2 Floor Temperature / 286
- 3-10 Autoacceleration / 286
 - 3-10a Course of Polymerization / 286
 - 3-10b Diffusion-Controlled Termination / 287
 - 3-10c Effect of Reaction Conditions / 290
 - 3-10d Related Phenomena / 291
 - 3-10d-1 Occlusion (Heterogeneous) Polymerization / 291
 - 3-10d-2 Template Polymerization / 291
 - 3-10e Dependence of Polymerization Rate on Initiator and Monomer / 292

- 3-10f Other Accelerative Phenomena / 293
- 3-11 Molecular-Weight Distribution / 293
 - 3-11a Low-Conversion Polymerization / 293
 - 3-11b High-Conversion Polymerization / 296
- 3-12 Effect of Pressure / 297
 - 3-12a Effect on Rate Constants / 297
 - 3-12a-1 Volume of Activation / 297
 - 3-12a-2 Rate of Polymerization / 298
 - 3-12a-3 Degree of Polymerization / 299
 - 3-12b Thermodynamics of Polymerization / 300
 - 3-12c Other Effects of Pressure / 300
- 3-13 Process Conditions / 301
 - 3-13a General Considerations / 301
 - 3-13a-1 Bulk (Mass) Polymerization / 301
 - 3-13a-2 Solution Polymerization / 302
 - 3-13a-3 Heterogeneous Polymerization / 302
 - 3-13a-4 Other Processes / 303
 - 3-13b Specific Commercial Polymers / 303
 - 3-13b-1 Polyethylene / 303
 - 3-13b-2 Polystyrene / 306
 - 3-13b-3 Vinyl Family / 308
 - 3-13b-4 Acrylic Family / 311
 - 3-13b-5 Fluoropolymers / 313
 - 3-13b-6 Polymerization of Dienes / 314
 - 3-13b-7 Miscellaneous Commercial Polymers / 315
 - 3-13c Other Polymerizations / 317
 - 3-13c-1 Organometallic Polymers / 318
 - 3-13c-2 Functional Polymers / 318
 - 3-13c-3 Acetylenic Monomers / 320
- References / 320

4 EMULSION POLYMERIZATION

- 4-1 Description of Process / 335
 - 4-1a Utility / 335
 - 4-1b Qualitative Picture / 336
 - 4-1b-1 Components and Their Locations / 336
 - 4-1b-2 Site of Polymerization / 338
 - 4-1b-3 Progress of Polymerization / 339

- 4-2a Rate of Polymerization / 341
- 4-2b Degree of Polymerization / 345
- 4-2c Number of Polymer Particles / 347
- 4-3 Other Characteristics of Emulsion Polymerization / 348
 - 4-3a Initiators / 348
 - 4-3b Surfactants / 349
 - 4-3c Other Components / 349
 - 4-3d Propagation and Termination Rate Constants / 349
 - 4-3e Energetics / 350
 - 4-3f Molecular Weight and Particle Size Distributions / 350
 - 4-3g Surfactant-Free Emulsion Polymerization / 351
 - 4-3h Core-Shell Model / 352
 - 4-3i Inverse Emulsion Polymerization / 352
- References / 353

5 IONIC CHAIN POLYMERIZATION

- 5-1 Comparison of Radical and Ionic Polymerizations / 356
- 5-2 Cationic Polymerization of the Carbon-Carbon Double Bond / 3
 - 5-2a Initiation / 358
 - 5-2a-1 *Protonic Acids* / 358
 - 5-2a-2 *Lewis Acids* / 359
 - 5-2a-3 *Other Initiators* / 363
 - 5-2b Propagation / 366
 - 5-2c Chain Transfer and Termination / 369
 - 5-2c-1 *Chain Transfer to Monomer* / 369
 - 5-2c-2 *Spontaneous Termination* / 370
 - 5-2c-3 *Combination with Counterion* / 370
 - 5-2c-4 *Chain Transfer to Polymer* / 372
 - 5-2c-5 *Other Transfer and Termination Reactions* / 372
 - 5-2d Kinetics / 373
 - 5-2d-1 *Different Kinetic Situations* / 373
 - 5-2d-2 *Validity of the Steady-State Assumption* / 376
 - 5-2d-3 *Molecular-Weight Distribution* / 377
 - 5-2e Absolute Rate Constants / 377
 - 5-2e-1 *Experimental Methods* / 377
 - 5-2e-2 *Difficulty in Interpreting Rate Constants* / 379
 - 5-2e-3 *Comparison of Rate Constants* / 381
 - 5-2e-4 *C_M and C_S Values* / 382

- 5-2f-1 *Propagation by Covalent Species* / 385
- 5-2f-2 *Solvent Effects* / 387
- 5-2f-3 *Counterion Effects* / 389
- Living Polymerization / 389
- 5-2g-1 *Reaction Characteristics* / 390
- 5-2g-2 *Rate and Degree of Polymerization* / 393
- 5-2h *Energetics* / 394
- 5-2i *Commercial Applications of Cationic Polymerization* / 396
 - 5-2i-1 *Polyisobutylene Products* / 396
 - 5-2i-2 *Other Products* / 398
- 5-3 *Anionic Polymerization of the Carbon–Carbon Double Bond* / 398
 - 5-3a *Initiation* / 399
 - 5-3a-1 *Nucleophilic Initiators* / 399
 - 5-3a-2 *Electron Transfer* / 400
 - 5-3b *Termination* / 403
 - 5-3b-1 *Polymerizations without Termination* / 403
 - 5-3b-2 *Termination by Impurities and Deliberately Added Transfer Agents* / 403
 - 5-3b-3 *Spontaneous Termination* / 404
 - 5-3b-4 *Terminating Reactions of Polar Monomers* / 405
 - 5-3c *Group Transfer Polymerization* / 407
 - 5-3d *Kinetics of Polymerization with Termination* / 409
 - 5-3e *Kinetics of Living Polymerization* / 410
 - 5-3e-1 *Polymerization Rate* / 410
 - 5-3e-2 *Effects of Reaction Media* / 411
 - 5-3e-3 *Degree of Polymerization* / 416
 - 5-3e-4 *Energetics: Solvent-Separated and Contact Ion Pairs* / 417
 - 5-3e-5 *Association Phenomena in Alkylolithium* / 422
 - 5-3e-6 *Other Phenomena* / 424
- 5-4 *Block Copolymers* / 425
 - 5-4a *Sequential Monomer Addition* / 425
 - 5-4b *Telechelic Polymers* / 427
 - 5-4c *Coupling Reactions* / 429
 - 5-4d *Transformation Reactions* / 430
- 5-5 *Distinguishing between Radical, Cationic, and Anionic Polymerization* / 431

Carbonyl Polymerization / 431

- 5-6a Anionic Polymerization / 433
 - 5-6a-1 Formaldehyde / 433
 - 5-6a-2 Other Carbonyl Monomers / 433
- 5-6b Cationic Polymerization / 434
- 5-6c Radical Polymerization / 435
- 5-6d End-Capping / 436
- 5-7 Miscellaneous Polymerizations / 437
 - 5-7a Monomers with Two Different Polymerizable Groups
 - 5-7b Hydrogen-Transfer Polymerization / 438
 - 5-7c Polymerization and Cyclotrimerization of Isocyanates
 - 5-7d Monomers with Triple Bonds / 440
- References / 440

6 CHAIN COPOLYMERIZATION

- 6-1 General Considerations / 453
 - 6-1a Importance of Chain Copolymerization / 453
 - 6-1b Types of Copolymers / 453
- 6-2 Copolymer Composition / 454
 - 6-2a Copolymerization Equation; Monomer Reactivity Ratios / 457
 - 6-2b Statistical Derivation of Copolymerization Equation / 457
 - 6-2c Range of Applicability of Copolymerization Equation / 457
 - 6-2d Types of Copolymerization Behavior / 460
 - 6-2d-1 Ideal Copolymerization; $r_1 r_2 = 1$ / 460
 - 6-2d-2 Alternating Copolymerization: $r_1 = r_2 = 0$ / 461
 - 6-2d-3 Block Copolymerization: $r_1 > 1, r_2 > 1$ / 463
 - 6-2e Variation of Copolymer Composition with Conversion / 466
 - 6-2f Experimental Evaluation of Monomer Reactivity Ratios / 466
 - 6-2g Microstructure of Copolymers / 470
 - 6-2g-1 Sequence-Length Distribution / 470
 - 6-2g-2 Copolymer Compositions of Different Molecules / 470
 - 6-2h Multicomponent Copolymerization / 472
- 6-3 Radical Copolymerization / 476
 - 6-3a Effect of Reaction Conditions / 476
 - 6-3a-1 Reaction Medium / 476
 - 6-3a-2 Temperature / 477
 - 6-3a-3 Pressure / 478
 - 6-3b Reactivity / 478
 - 6-3b-1 Resonance Effects / 481

- 6-3b-2 *Steric Effects* / 484
- 6-3b-3 *Alternation; Polar Effects and Complex Participation* / 485
- 6-3b-4 *Q-e Scheme* / 489
- 6-3b-5 *Other Quantitative Approaches to Reactivity / Rate of Copolymerization* / 492
- 6-3c-1 *Chemical-Controlled Termination* / 492
- 6-3c-2 *Diffusion-Controlled Termination* / 495

- 6-4 **Ionic Copolymerization** / 496
 - 6-4a **Cationic Copolymerization** / 497
 - 6-4a-1 *Reactivity* / 497
 - 6-4a-2 *Effect of Solvent and Counterion* / 498
 - 6-4a-3 *Effect of Temperature* / 500
 - 6-4b **Anionic Copolymerization** / 500
 - 6-4b-1 *Reactivity* / 500
 - 6-4b-2 *Effects of Solvent and Counterion* / 501
 - 6-4b-3 *Temperature* / 502

- 6-5 **Deviations from Terminal Copolymerization Model** / 503
 - 6-5a **Kinetic Penultimate Behavior** / 503
 - 6-5b **Depropagation during Copolymerization** / 505
 - 6-5c **Copolymerization with Complex Participation** / 508
 - 6-5d **Discrimination between Models** / 509

- 6-6 **Copolymerizations Involving Dienes** / 510
 - 6-6a **Crosslinking** / 510
 - 6-6b **Alternating Intra-Intermolecular Polymerization: Cyclopolymerization** / 512
 - 6-6c **Interpenetrating Polymer Networks** / 516

- 6-7 **Other Copolymerizations** / 517
 - 6-7a **Miscellaneous Copolymerizations of Alkenes** / 517
 - 6-7b **Copolymerization of Carbonyl Monomers** / 518

- 6-8 **Applications of Copolymerization** 518
 - 6-8a **Styrene** / 518
 - 6-8b **Ethylene** / 519
 - 6-8c **Unsaturated Polyesters** / 521
 - 6-8d **Allyl Resins** / 521
 - 6-8e **Other Copolymers** / 522

- References** / 523

- 7-1a Scope; Polymerizability / 533
- 7-1b Polymerization Mechanism and Kinetics / 534
- 7-2 Cyclic Ethers / 535
 - 7-2a Anionic Polymerization of Epoxides / 536
 - 7-2a-1 Reaction Characteristics / 536
 - 7-2a-2 Exchange Reactions / 538
 - 7-2a-3 Chain Transfer to Monomer / 540
 - 7-2b Cationic Polymerization / 541
 - 7-2b-1 Propagation / 541
 - 7-2b-2 Initiation / 542
 - 7-2b-3 Termination and Transfer Processes / 544
 - 7-2b-4 Cyclic Acetals / 547
 - 7-2b-5 Kinetics / 549
 - 7-2b-6 Energetic Characteristics / 554
 - 7-2b-7 Commercial Applications / 557
- 7-3 Lactams / 558
 - 7-3a Cationic Polymerization / 558
 - 7-3b Hydrolytic Polymerization / 560
 - 7-3c Anionic Polymerization / 562
 - 7-3c-1 Use of Strong Base Alone / 562
 - 7-3c-2 Addition of *N*-Acylactam / 564
 - 7-3d Reactivity / 567
- 7-4 *N*-Carboxy- α -Amino Acid Anhydrides / 567
- 7-5 Lactones / 569
 - 7-5a Anionic Polymerization / 570
 - 7-5b Cationic Polymerization / 571
 - 7-5c Other Cyclic Esters / 572
- 7-6 Nitrogen Heterocyclics / 573
 - 7-6a Cyclic Amines / 573
 - 7-6b Other Nitrogen Heterocyclics / 574
- 7-7 Sulfur Heterocyclics / 575
- 7-8 Cycloalkenes / 577
- 7-9 Miscellaneous Oxygen Heterocyclics / 579
- 7-10 Other Ring-Opening Polymerizations / 581

- 7-11a Cyclosiloxanes / 582
- 7-11b Poly(organophosphazenes) / 584
- 7-11c Phosphorus-Containing Cyclic Esters / 586
- 7-11d Sulfur / 586
- 7-11e Polymeric Sulfur Nitride / 587
- 7-12 Copolymerization / 587
 - 7-12a Monomers with Same Functional Group / 588
 - 7-12b Monomers with Different Functional Groups / 590
 - 7-12c Block Copolymers / 591
 - 7-12d Zwitterion Polymerization / 592
- References / 593

8 STEREOCHEMISTRY OF POLYMERIZATION

- 8-1 Types of Stereoisomerism in Polymers / 605
 - 8-1a Monosubstituted Ethylenes / 606
 - 8-1a-1 Site of Steric Isomerism / 606
 - 8-1a-2 Tacticity / 607
 - 8-1b Disubstituted Ethylenes / 609
 - 8-1b-1 1,1-Disubstituted Ethylenes / 609
 - 8-1b-2 1,2-Disubstituted Ethylenes / 609
 - 8-1c Carbonyl and Ring-Opening Polymerizations / 611
 - 8-1d 1,3-Butadiene and 2-Substituted 1,3-Butadienes / 613
 - 8-1d-1 1,2- and 3,4-Polymerizations / 613
 - 8-1d-2 1,4-Polymerization / 614
 - 8-1e 4-Substituted and 1,4-Disubstituted 1,3-Butadienes / 615
 - 8-1e-1 1,2- and 3,4-Polymerizations / 615
 - 8-1e-2 1,4-Polymerization / 616
 - 8-1f Other Polymers / 618
- 8-2 Properties of Stereoregular Polymers / 619
 - 8-2a Significance of Stereoregularity / 619
 - 8-2a-1 *Isotactic, Syndiotactic, and Atactic Polypropylenes* 619
 - 8-2a-2 *cis- and trans-1,4-Poly-1,3-Dienes* / 619
 - 8-2a-3 *Cellulose and Amylose* / 620
 - 8-2b Analysis of Stereoregularity / 621
- 8-3 Forces of Stereoregulation in Alkene Polymerizations / 623
 - 8-3a Radical Polymerization / 623

- 8-3b-1 *Effect of Coordination* / 626
- 8-3b-2 *Mechanism of Stereospecific Placement* / 627
- 8-4 **Ziegler-Natta Polymerization of Nonpolar Alkene Monomers** / 630
 - 8-4a **Mechanism of Ziegler-Natta Polymerization** / 630
 - 8-4a-1 *Chemical Nature of Propagating Species* / 631
 - 8-4a-2 *Primary versus Secondary Insertion; Regiospecificity* / 632
 - 8-4a-3 *Propagation of Carbon-Transition-Metal Bond* / 633
 - 8-4a-4 *Bimetallic versus Monometallic Mechanisms* / 634
 - 8-4a-5 *Direction of Double-Bond Opening* / 636
 - 8-4a-6 *Mechanism of Isotactic Control* / 637
 - 8-4a-7 *Mechanism of Syndiotactic Polymerization* / 640
 - 8-4b **Effect of Components of Ziegler-Natta Initiator** / 642
 - 8-4b-1 *Transition-Metal Component* / 642
 - 8-4b-2 *Group I-III Metal Component* / 643
 - 8-4b-3 *Third Component; Lewis Base* / 644
 - 8-4c **Kinetics** / 645
 - 8-4c-1 *Observed Rate Behavior* / 645
 - 8-4c-2 *Termination* / 646
 - 8-4c-3 *Rate Expression* / 647
 - 8-4c-4 *Values of Kinetic Parameters* / 649
 - 8-4d **Scope of the Ziegler-Natta Initiator** / 650
 - 8-4d-1 *Cycloalkenes* / 651
 - 8-4d-2 *Alkynes* / 652
 - 8-4d-3 *Copolymerization* / 652
 - 8-4e **Transition-Metal Oxide Initiators** / 653
 - 8-4f **Homogeneous, Isospecific Polymerization by Rigid Chiral Metallocenes** / 653
 - 8-4g **Commercial Utilization** / 655
 - 8-4g-1 *Process Conditions* / 655
 - 8-4g-2 *High-Density (Linear) Polyethylene* / 656
 - 8-4g-3 *Linear Low-Density Polyethylene* / 657
 - 8-4g-4 *Polypropylene* / 657
 - 8-4g-5 *Ethylene-Propylene Elastomers* / 658
 - 8-4g-6 *Other Polymers* / 658
- 8-5 **Stereospecific Polymerization of Polar Vinyl Monomers** / 659
 - 8-5a **Methyl Methacrylate** / 659
 - 8-5b **Vinyl Ethers** / 661
 - 8-5c **Styrene** / 662

- 8-6a Radical Polymerization / 662
- 8-6b Anionic and Anionic Coordination Polymerizations / 664
- 8-6c Cationic Polymerization / 667
- 8-6d Other Polymerizations / 668
- 8-6e Commercial Polymers / 668
- 8-7 Aldehydes / 669
- 8-8 Optical Activity in Polymers / 669
 - 8-8a Optically Active Monomers / 669
 - 8-8b Chiral Conformation / 670
 - 8-8c Stereoselection and Stereoelection / 670
 - 8-8d Asymmetric Induction / 672
- 8-9 Ring-Opening Polymerization / 672
- 8-10 Statistical Models of Propagation / 675
 - 8-10a Polymer Chain End Control / 675
 - 8-10a-1 Bernoulli Model / 675
 - 8-10a-2 First-Order Markov Model / 676
 - 8-10b Initiator (Enantiomorphic Site) Control / 678
 - 8-10c Application of Propagation Statistics / 679
- References / 680

9 REACTIONS OF POLYMERS

- 9-1 Principles of Polymer Reactivity / 691
 - 9-1a Yield / 692
 - 9-1b Isolation of Functional Groups / 692
 - 9-1c Concentration / 692
 - 9-1d Crystallinity / 693
 - 9-1e Changes in Solubility / 693
 - 9-1f Crosslinking / 694
 - 9-1g Steric Effects / 695
 - 9-1h Electrostatic Effects / 695
 - 9-1i Neighboring-Group Effects / 697
 - 9-1j Hydrophobic Interactions / 698
 - 9-1k Other Considerations / 699
- 9-2 Crosslinking / 699
 - 9-2a Alkyds / 700
 - 9-2b Elastomers Based on 1,3-Dienes / 701
 - 9-2b-1 Sulfur Alone / 701

- 9-2b-2 *Accelerated Sulfur Vulcanization* / 702
- 9-2b-3 *Other Vulcanizations* / 704
- 9-2c Peroxide and Radiation Crosslinking / 705
- 9-2d Other Crosslinking Processes / 707
- 9-3 Reactions of Cellulose / 708
 - 9-3a Dissolution of Cellulose / 708
 - 9-3b Esterification of Cellulose / 709
 - 9-3c Etherification of Cellulose / 710
- 9-4 Reactions of Poly(vinyl acetate) / 711
- 9-5 Halogenation / 711
 - 9-5a Natural Rubber / 711
 - 9-5b Saturated Hydrocarbon Polymers / 712
- 9-6 Aromatic Substitution / 713
- 9-7 Cyclization / 713
- 9-8 Graft Copolymers / 715
 - 9-8a Radical Graft Polymerization / 715
 - 9-8a-1 *Chain Transfer and Copolymerization* / 715
 - 9-8a-2 *Ionizing Radiation* / 716
 - 9-8a-3 *Redox Initiation* / 718
 - 9-8b Anionic Graft Polymerization / 718
 - 9-8c Cationic Graft Polymerization / 719
 - 9-8d Other Approaches to Graft Copolymers / 719
- 9-9 Block Copolymers / 720
- 9-10 Polymers as Carriers or Supports / 721
 - 9-10a Synthesis / 721
 - 9-10a-1 *Attachment of Group to Polymer* / 721
 - 9-10a-2 *Polymerization of a Functional Monomer* / 723
 - 9-10a-3 *Comparison of the Two Approches* / 724
 - 9-10b Advantages of Polymer Reagents, Catalysts, and Substrates / 724
- 9-11 Polymer Reagents / 725
- 9-12 Polymer Catalysts / 728
- 9-13 Polymer Substrates / 731
 - 9-13a Solid-Phase Synthesis of Peptides / 731
 - 9-13b Other Applications / 737
- References / 738