

# Contents

<b>1 INTRODUCTION</b>	<b>1</b>
1-1 Types of Polymers and Polymerizations	1
1-1a Polymer Composition and Structure, 1	
1-1b Polymerization Mechanism, 7	
1-2 Nomenclature of Polymers	10
1-2a Nomenclature Based on Source, 10	
1-2b Nomenclature Based on Structure (Non-IUPAC), 11	
1-2c IUPAC Structure-Based Nomenclature System, 12	
1-2d Trade and Nonnames, 17	
1-3 Linear, Branched, and Crosslinked Polymers	18
1-4 Molecular Weight	20
1-5 Physical State	25
1-5a Crystalline and Amorphous Behavior, 25	
1-5b Determinants of Polymer Crystallinity, 28	
1-5c Thermal Transitions, 29	
1-6 Applications of Polymers	33
1-6a Mechanical Properties, 33	
1-6b Elastomers, Fibers, Plastics, 35	
<b>2 STEP POLYMERIZATION</b>	<b>40</b>
2-1 Reactivity of Functional Groups	41

2-1a	<i>Basis for Analysis of Polymerization Kinetics, 41</i>	
2-1b	<i>Experimental Evidence, 43</i>	
2-1c	<i>Theoretical Considerations, 44</i>	
2-1d	<i>Equivalence of Groups in Bifunctional Reactants, 45</i>	
2-2	<b>Kinetics of Step Polymerization</b>	<b>46</b>
2-2a	<i>Self-Catalyzed Polymerization, 48</i>	
2-2a-1	<i>Experimental Observations, 49</i>	
2-2a-2	<i>Reasons for Nonlinearity in Third-Order Plot, 51</i>	
2-2a-3	<i>Molecular Weight of Polymer, 54</i>	
2-2b	<i>External Catalysis of Polymerization, 55</i>	
2-2c	<i>Step Polymerizations Other Than Polyesterification: Catalyzed versus Uncatalyzed, 57</i>	
2-2d	<i>Nonequivalence of Functional Groups in Polyfunctional Reagents, 59</i>	
2-2d-1	<i>Examples of Nonequivalence, 59</i>	
2-2d-2	<i>Kinetics, 61</i>	
2-3	<b>Accessibility of Functional Groups</b>	<b>68</b>
2-4	<b>Equilibrium Considerations</b>	<b>70</b>
2-4a	<i>Closed System, 70</i>	
2-4b	<i>Open, Driven System, 73</i>	
2-4c	<i>Kinetics of Reversible Polymerization, 75</i>	
2-5	<b>Cyclization Versus Linear Polymerization</b>	<b>77</b>
2-5a	<i>Possible Cyclization Reactions, 77</i>	
2-5b	<i>Thermodynamic and Kinetic Considerations, 78</i>	
2-5c	<i>Other Considerations, 81</i>	
2-6	<b>Molecular Weight Control in Linear Polymerization</b>	<b>82</b>
2-6a	<i>Need for Stoichiometric Control, 82</i>	
2-6b	<i>Quantitative Aspects, 83</i>	
2-6c	<i>Kinetics of Nonstoichiometric Polymerization, 87</i>	
2-7	<b>Molecular Weight Distribution in Linear Polymerization</b>	<b>88</b>

2-7a	<i>Derivation of Size Distributions, 88</i>	
2-7b	<i>Breadth of Molecular Weight Distribution, 91</i>	
2-7c	<i>Interchange Reactions, 92</i>	
2-7d	<i>Experimental Verification, 92</i>	
2-7e	<i>Alternate Approaches for Molecular Weight Distribution, 93</i>	
2-7f	<i>MWD for Functional Groups of Unequal Reactivity, 95</i>	
2-8	<b>Process Conditions</b>	96
2-8a	<i>Physical Nature of Polymerization Systems, 96</i>	
2-8b	<i>Different Reactant Systems, 98</i>	
2-8c	<i>Interfacial Polymerization, 99</i>	
	2-8c-1 <i>Description of Process, 99</i>	
	2-8c-2 <i>Utility, 102</i>	
2-8d	<i>Polyesters, 102</i>	
2-8e	<i>Polyamides, 105</i>	
2-8f	<i>Polyurethanes, 108</i>	
2-8g	<i>Polysiloxanes, 109</i>	
2-9	<b>Multichain Polymerization</b>	109
2-9a	<i>Branching, 109</i>	
2-9b	<i>Molecular Weight Distribution, 110</i>	
2-10	<b>Crosslinking</b>	112
2-10a	<i>Carothers Equation: <math>\bar{X} \rightarrow \infty</math>, 113</i>	
	2-10a-1 <i>Equivalent Amounts of Reactants, 113</i>	
	2-10a-2 <i>Extension to Nonequivalent Reactant Mixtures, 115</i>	
2-10b	<i>Statistical Approach to Gelation: <math>\bar{X}_w \rightarrow \infty</math>, 116</i>	
2-10c	<i>Experimental Gel Points, 120</i>	
2-10d	<i>Extensions of Statistical Approach, 121</i>	
2-11	<b>Molecular Weight Distributions in Nonlinear Polymerizations</b>	124

<b>2-12</b>	<b>Crosslinking Technology</b>	<b>126</b>
2-12a	<i>Random Prepolymers, 127</i>	
2-12a-1	<i>Polyesters, 127</i>	
2-12a-2	<i>Formaldehyde Polymers, 128</i>	
2-12b	<i>Structoset Prepolymers, 135</i>	
2-12b-1	<i>Diol Prepolymers, 135</i>	
2-12b-2	<i>Epoxy Prepolymers, 136</i>	
2-12b-3	<i>Unsaturated Polyesters, 138</i>	
2-12b-4	<i>Phenol-Formaldehyde Polymers, 139</i>	
<b>2-13</b>	<b>Step Copolymerization</b>	<b>140</b>
2-13a	<i>Types of Copolymers, 140</i>	
2-13b	<i>Methods of Synthesizing Copolymers, 141</i>	
2-13c	<i>Utility of Copolymerization, 144</i>	
<b>2-14</b>	<b>Newer Types of Step Polymerizations</b>	<b>145</b>
2-14a	<i>Presently Available Polymers, 146</i>	
2-14a-1	<i>Polycarbonate, 146</i>	
2-14a-2	<i>Aromatic Polysulfone, 148</i>	
2-14a-3	<i>Aromatic Polyether, 149</i>	
2-14a-4	<i>Aromatic Polysulfide, 151</i>	
2-14a-5	<i>Aromatic Polyamides, 152</i>	
2-14a-6	<i>Aromatic Polyimides, 153</i>	
2-14b	<i>Research Polymers, 155</i>	
2-14b-1	<i>Polybenzimidazoles, 156</i>	
2-14b-2	<i>Polybenzoxazoles, Polybenzothiazoles, Polyoxadiazoles, and Polytriazoles, 157</i>	
2-14b-3	<i>Polyquinoxalines, 159</i>	
2-14b-4	<i>Polyimidazopyrrolones, 161</i>	
2-14b-5	<i>Oxidative Coupling Polymerization, 162</i>	
2-14b-6	<i>Friedel-Crafts Polymerization, 163</i>	
2-14b-7	<i>Cycloaddition or Four-Center Polymerization, 163</i>	
2-14b-8	<i>Polymerization by 1,3-Dipolar Addition, 164</i>	
2-14b-9	<i>Spiro Structures, 165</i>	
2-14b-10	<i>Inorganic and Semi-Inorganic Polymers, 165</i>	

<b>Contents</b>	<b>xiii</b>
<b>3 RADICAL CHAIN POLYMERIZATION</b>	<b>179</b>
<b>3-1 Nature of Radical Chain Polymerization</b>	<b>179</b>
<i>3-1a Comparison of Chain and Step Polymerization, 179</i>	
<i>3-1b Radical versus Ionic Chain Polymerizations, 180</i>	
<i>3-1b-1 General Considerations of Polymerizability, 180</i>	
<i>3-1b-2 Effects of Substituents, 181</i>	
<b>3-2 Structural Arrangement of Monomer Units</b>	<b>184</b>
<i>3-2a Possible Modes of Propagation, 184</i>	
<i>3-2b Experimental Evidence, 185</i>	
<i>3-2c Synthesis of Head-to-Head Polymers, 186</i>	
<b>3-3 Rate of Radical Chain Polymerization</b>	<b>186</b>
<i>3-3a Sequence of Events, 186</i>	
<i>3-3b Rate Expression, 188</i>	
<i>3-3c Experimental Determination of <math>R_p</math>, 190</i>	
<i>3-3c-1 Physical Separation and Isolation of Reaction Product, 190</i>	
<i>3-3c-2 Chemical and Spectroscopic Analysis, 191</i>	
<i>3-3c-3 Dilatometry, 192</i>	
<i>3-3c-4 Other Methods, 193</i>	
<b>3-4 Initiation</b>	<b>194</b>
<i>3-4a Thermal Decomposition of Initiators, 194</i>	
<i>3-4a-1 Types of Initiators, 194</i>	
<i>3-4a-2 Kinetics of Initiation and Polymerization, 197</i>	
<i>3-4a-3 Dependence of Polymerization Rate on Initiator, 198</i>	
<i>3-4a-4 Dependence of Polymerization Rate on Monomer, 200</i>	
<i>3-4b Redox Initiation, 201</i>	
<i>3-4b-1 Types of Redox Initiators, 201</i>	
<i>3-4b-2 Rate of Redox Polymerization, 204</i>	
<i>3-4c Photochemical Initiation, 205</i>	
<i>3-4c-1 Bulk Monomer, 206</i>	

3-4c-2	<i>Irradiation of Thermal and Redox Initiators</i> , 206	
3-4c-3	<i>Rate of Photopolymerization</i> , 209	
3-4d	<i>Initiation by Ionizing Radiations</i> , 212	
3-4e	<i>Pure Thermal Initiation</i> , 214	
3-4f	<i>Other Methods of Initiation</i> , 215	
3-4f-1	<i>Electroinitiation</i> , 215	
3-4f-2	<i>Plasma</i> , 215	
3-4g	<i>Initiator Efficiency</i> , 215	
3-4g-1	<i>Definition of <math>f</math></i> , 215	
3-4g-2	<i>Mechanism of <math>f &lt; 1</math>: Cage Effect</i> , 216	
3-4g-3	<i>Experimental Determination of <math>f</math></i> , 219	
3-5	<b>Molecular Weight</b>	223
3-5a	<i>Kinetic Chain Length</i> , 223	
3-5b	<i>Mode of Termination</i> , 224	
3-6	<b>Chain Transfer</b>	226
3-6a	<i>Effect of Chain Transfer</i> , 226	
3-6b	<i>Transfer to Monomer and Initiator</i> , 228	
3-6b-1	<i>Determination of <math>C_M</math> and <math>C_I</math></i> , 228	
3-6b-2	<i>Monomer Transfer Constants</i> , 230	
3-6b-3	<i>Initiator Transfer Constants</i> , 232	
3-6c	<i>Transfer to Chain Transfer Agent</i> , 233	
3-6c-1	<i>Determination of <math>C_S</math></i> , 233	
3-6c-2	<i>Structure and Reactivity</i> , 234	
3-6c-3	<i>Applications of Chain Transfer Agents</i> , 238	
3-6d	<i>Chain Transfer to Polymer</i> , 238	
3-7	<b>Inhibition and Retardation</b>	242
3-7a	<i>Kinetics of Inhibition or Retardation</i> , 243	
3-7b	<i>Types of Inhibitors and Retarders</i> , 246	
3-7c	<i>Autoinhibition of Allylic Monomers</i> , 250	
3-8	<b>Determination of Absolute Rate Constants</b>	251
3-8a	<i>Non-Steady-State Kinetics</i> , 251	
3-8b	<i>Rotating Sector Method</i> , 254	

3-8c	<i>Typical Values of Reaction Parameters</i> , 257	
3-9	<b>Energetic Characteristics</b>	259
3-9a	<i>Activation Energy and Frequency Factor</i> , 259	
3-9a-1	<i>Rate of Polymerization</i> , 260	
3-9a-2	<i>Degree of Polymerization</i> , 262	
3-9b	<i>Thermodynamics of Polymerization</i> , 263	
3-9b-1	<i>Significance of <math>\Delta G</math>, <math>\Delta H</math>, and <math>\Delta S</math></i> , 263	
3-9b-2	<i>Effect of Monomer Structure</i> , 265	
3-9b-3	<i>Polymerization of 1,2-Disubstituted Ethylenes</i> , 266	
3-9c	<i>Polymerization-Depolymerization Equilibria</i> , 268	
3-9c-1	<i>Ceiling Temperature</i> , 268	
3-9c-2	<i>Floor Temperature</i> , 271	
3-10	<b>Autoacceleration</b>	271
3-10a	<i>Course of Polymerization</i> , 271	
3-10b	<i>Diffusion-Controlled Termination</i> , 273	
3-10c	<i>Effect of Reaction Conditions</i> , 275	
3-10d	<i>Related Phenomena</i> , 276	
3-10d-1	<i>Occlusion (Heterogeneous) Polymerization</i> , 276	
3-10d-2	<i>Template or Matrix Polymerization</i> , 277	
3-10e	<i>Dependence of Polymerization Rate on Initiator and Monomer</i> , 277	
3-10f	<i>Other Accelerative Phenomena</i> , 278	
3-11	<b>Molecular Weight Distribution</b>	279
3-11a	<i>Low-Conversion Polymerization</i> , 279	
3-11b	<i>High-Conversion Polymerization</i> , 281	
3-12	<b>Effect of Pressure</b>	281
3-12a	<i>Effect on Rate Constants</i> , 282	
3-12a-1	<i>Volume of Activation</i> , 282	
3-12a-2	<i>Rate of Polymerization</i> , 283	
3-12a-3	<i>Degree of Polymerization</i> , 284	
3-12b	<i>Thermodynamics of Polymerization</i> , 285	

3-12c	<i>Other Effects of Pressure, 286</i>	
3-13	<b>Process Conditions</b>	<b>286</b>
3-13a	<i>General Considerations, 286</i>	
3-13a-1	<i>Bulk (Mass) Polymerization, 286</i>	
3-13a-2	<i>Solution Polymerization, 287</i>	
3-13a-3	<i>Heterogeneous Polymerization, 287</i>	
3-13a-4	<i>Other Processes, 288</i>	
3-13b	<i>Specific Commercial Polymers, 288</i>	
3-13b-1	<i>Polyethylene, 288</i>	
3-13b-2	<i>Polystyrene, 290</i>	
3-13b-3	<i>Vinyl Family, 292</i>	
3-13b-4	<i>Acrylic Family, 294</i>	
3-13b-5	<i>Fluoropolymers, 296</i>	
3-13b-6	<i>Polymerization of Dienes, 297</i>	
3-13b-7	<i>Miscellaneous Commercial Polymers, 298</i>	
3-13c	<i>Other Polymerizations, 301</i>	
3-13c-1	<i>Organometallic Polymers, 301</i>	
3-13c-2	<i>Functional Polymers, 302</i>	
3-13c-3	<i>Acetylene Monomers, 303</i>	
3-13c-4	<i>Poly(carbon suboxide), 304</i>	
4	<b>EMULSION POLYMERIZATION</b>	<b>319</b>
4-1	<b>Description of Process</b>	<b>319</b>
4-1a	<i>Utility, 319</i>	
4-1b	<i>Qualitative Picture, 320</i>	
4-1b-1	<i>Components and Their Locations, 320</i>	
4-1b-2	<i>Site of Polymerization, 321</i>	
4-1b-3	<i>Progress of Polymerization, 323</i>	
4-2	<b>Quantitative Aspects</b>	<b>325</b>
4-2a	<i>Rate of Polymerization, 325</i>	
4-2b	<i>Degree of Polymerization, 329</i>	
4-2c	<i>Number of Polymer Particles, 331</i>	
4-3	<b>Other Characteristics of Emulsion Polymerization</b>	<b>332</b>

- 4-3a *Initiators, 332*
- 4-3b *Surfactants, 333*
- 4-3c *Other Components, 333*
- 4-3d *Propagation and Termination Rate Constants, 334*
- 4-3e *Energetics, 334*
- 4-3f *Molecular Weight and Particle Size Distributions, 334*
- 4-3g *Surfactant-Free Emulsion Polymerization, 335*
- 4-3h *Other Theories, 336*
- 4-3i *Nonaqueous Emulsion Polymerization, 336*
- 4-3j *Semicontinuous and Continuous Processes, 337*

<b>5 IONIC CHAIN POLYMERIZATION</b>	<b>340</b>
5-1 Comparison of Radical and Ionic Polymerizations	340
5-2 Cationic Polymerization of the Carbon–Carbon Double Bond	342
5-2a <i>Initiation, 342</i>	
5-2a-1 <i>Protonic Acids, 342</i>	
5-2a-2 <i>Lewis Acids, 343</i>	
5-2a-3 <i>Other Initiators, 346</i>	
5-2b <i>Propagation, 349</i>	
5-2c <i>Termination, 350</i>	
5-2c-1 <i>Chain Transfer to Monomer, 350</i>	
5-2c-2 <i>Spontaneous Termination, 351</i>	
5-2c-3 <i>Combination with Counterion, 352</i>	
5-2c-4 <i>Backbiting, 353</i>	
5-2c-5 <i>Other Chain Transfer Reactions, 353</i>	
5-2c-6 <i>Retardation, 354</i>	
5-2d <i>Kinetics, 355</i>	
5-2d-1 <i>Different Kinetic Situations, 355</i>	
5-2d-2 <i>Validity of the Steady-State Assumption, 358</i>	
5-2d-3 <i>Molecular Weight Distribution, 358</i>	
5-2e <i>Absolute Rate Constants, 358</i>	
5-2e-1 <i>Experimental Methods, 358</i>	
5-2e-2 <i>Difficulty in Interpreting Rate Constants, 360</i>	

5-2e-3	<i>Comparison of Cationic and Radical Polymerization Rates, 362</i>	
5-2e-4	<i>C<sub>M</sub> and C<sub>S</sub> Values, 363</i>	
5-2f	<i>Effect of Reaction Medium, 365</i>	
5-2f-1	<i>Solvent Effects, 365</i>	
5-2f-2	<i>Effect of Gegenion, 367</i>	
5-2f-3	<i>Pseudocationic Polymerization, 367</i>	
5-2g	<i>Energetics, 369</i>	
5-2h	<i>Commercial Polymerization of Isobutene, 371</i>	
5-3	<b>Anionic Polymerization of the Carbon-Carbon Double Bond</b>	<b>372</b>
5-3a	<i>Initiation, 373</i>	
5-3a-1	<i>Nucleophilic Initiators, 373</i>	
5-3a-2	<i>Electron Transfer, 374</i>	
5-3b	<i>Termination, 377</i>	
5-3b-1	<i>Polymerizations Without Termination, 377</i>	
5-3b-2	<i>Termination by Impurities and Deliberately Added Transfer Agents, 378</i>	
5-3b-3	<i>Hydride Elimination, 378</i>	
5-3b-4	<i>Terminating Reactions of Polar Monomers, 379</i>	
5-3c	<i>Kinetics of Polymerization with Termination, 380</i>	
5-3d	<i>Kinetics of Living Polymerization, 382</i>	
5-3d-1	<i>Polymerization Rate, 382</i>	
5-3d-2	<i>Effects of Reaction Media, 383</i>	
5-3d-3	<i>Degree of Polymerization, 388</i>	
5-3d-4	<i>Energetics; Solvent-Separated and Contact Ion Pairs, 389</i>	
5-3d-5	<i>Association Phenomena in Alkylolithium, 394</i>	
5-3d-6	<i>Other Phenomena, 397</i>	
5-4	<b>Block Copolymers</b>	<b>398</b>
5-4a	<i>Sequential Monomer Addition, 398</i>	
5-4b	<i>Transformation Reactions, 400</i>	
5-4c	<i>Telechelic Polymers, 400</i>	
5-4d	<i>Coupling Reactions, 401</i>	
5-5	<b>Distinguishing Between Radical, Cationic, and Anionic Polymerizations</b>	<b>401</b>

<b>5-6 Carbonyl Polymerization</b>	<b>402</b>
5-6a <i>Anionic Polymerization, 403</i>	
5-6a-1 <i>Formaldehyde, 404</i>	
5-6a-2 <i>Other Carbonyl Monomers, 405</i>	
5-6b <i>Cationic Polymerization, 406</i>	
5-6c <i>Radical Polymerization, 407</i>	
5-6d <i>Step Polymerization, 407</i>	
5-6e <i>End-Capping, 408</i>	
<b>5-7 Miscellaneous Polymerizations</b>	<b>409</b>
5-7a <i>Monomers with Two Different Polymerizable Groups, 409</i>	
5-7b <i>Hydrogen-Transfer Polymerization, 410</i>	
5-7c <i>Polymerization and Cyclotrimerization of Isocyanates, 411</i>	
5-7d <i>Monomers with Triple Bonds, 412</i>	
<b>6 CHAIN COPOLYMERIZATION</b>	<b>423</b>
<b>6-1 General Considerations</b>	<b>423</b>
6-1a <i>Importance of Chain Copolymerization, 423</i>	
6-1b <i>Types of Copolymers, 424</i>	
<b>6-2 Copolymer Composition</b>	<b>425</b>
6-2a <i>Copolymerization Equation; Monomer Reactivity Ratios, 425</i>	
6-2b <i>Statistical Derivation of Copolymerization Equation, 428</i>	
6-2c <i>Range of Applicability of Copolymerization Equation, 430</i>	
6-2d <i>Types of Copolymerization Behavior, 431</i>	
6-2d-1 <i>Ideal Copolymerization, 431</i>	
6-2d-2 <i>Alternating Copolymerization, 433</i>	
6-2d-3 <i>Block Copolymerization, 435</i>	
6-2e <i>Variation of Copolymer Composition with Conversion, 435</i>	

6-2f	<i>Experimental Evaluation of Monomer Reactivity Ratios, 440</i>	
6-2g	<i>Microstructure of Copolymers, 441</i>	
6-2g-1	<i>Sequence-Length Distribution, 441</i>	
6-2g-2	<i>Copolymer Compositions of Different Molecules, 444</i>	
6-2h	<i>Multicomponent Copolymerization, 445</i>	
6-3	<b>Radical Copolymerization</b>	<b>448</b>
6-3a	<i>Effect of Reaction Conditions, 448</i>	
6-3a-1	<i>Reaction Medium, 448</i>	
6-3a-2	<i>Temperature, 449</i>	
6-3a-3	<i>Pressure, 450</i>	
6-3b	<i>Reactivity, 450</i>	
6-3b-1	<i>Resonance Effects, 455</i>	
6-3b-2	<i>Steric Effects, 458</i>	
6-3b-3	<i>Alternation; Polar Effects and Complex Participation, 460</i>	
6-3b-4	<i>Q-e Scheme, 463</i>	
6-3b-5	<i>Other Quantitative Approaches to Reactivity, 466</i>	
6-3c	<i>Rate of Copolymerization, 467</i>	
6-3c-1	<i>Chemical-Controlled Termination, 467</i>	
6-3c-2	<i>Diffusion-Controlled Termination, 470</i>	
6-4	<b>Ionic Copolymerization</b>	<b>472</b>
6-4a	<i>Cationic Copolymerization, 472</i>	
6-4a-1	<i>Monomer Reactivity, 472</i>	
6-4a-2	<i>Effect of Solvent and Gegenion, 474</i>	
6-4a-3	<i>Effect of Temperature, 476</i>	
6-4b	<i>Anionic Copolymerization, 476</i>	
6-4b-1	<i>Reactivity, 476</i>	
6-4b-2	<i>Effects of Solvent and Gegenion, 477</i>	
6-5	<b>Deviations from Copolymer Composition Equation</b>	<b>478</b>
6-5a	<i>Kinetic Penultimate Behavior, 478</i>	
6-5b	<i>Depropagation During Copolymerization, 481</i>	
6-5c	<i>Copolymerization with Complex Participation, 484</i>	

<b>Contents</b>	<b>xxi</b>
<b>6-6 Copolymerizations of Dienes</b>	<b>485</b>
6-6a <i>Crosslinking</i> , 485	
6-6b <i>Alternating Intra-Intermolecular Polymerization; Cyclopolymerization</i> , 488	
6-6c <i>Interpenetrating Polymer Networks</i> , 492	
<b>6-7 Other Copolymerizations</b>	<b>492</b>
6-7a <i>Miscellaneous Copolymerizations of Alkenes</i> , 492	
6-7b <i>Copolymerization of Carbonyl Monomers</i> , 494	
<b>6-8 Applications of Copolymerization</b>	<b>494</b>
6-8a <i>Styrene</i> , 494	
6-8b <i>Vinyl Chloride</i> , 495	
6-8c <i>Ethylene</i> , 496	
6-8d <i>Unsaturated Polyester</i> , 497	
<b>7 RING-OPENING POLYMERIZATION</b>	<b>508</b>
<b>7-1 General Characteristics</b>	<b>509</b>
7-1a <i>Scope; Polymerizability</i> , 509	
7-1b <i>Polymerization Mechanism and Kinetics</i> , 510	
<b>7-2 Cyclic Ethers</b>	<b>511</b>
7-2a <i>Anionic Polymerization of Epoxides</i> , 512	
7-2a-1 <i>Reaction Characteristics</i> , 512	
7-2a-2 <i>Exchange Reactions</i> , 514	
7-2a-3 <i>Chain Transfer to Monomer</i> , 515	
7-2b <i>Cationic Polymerization</i> , 517	
7-2b-1 <i>Initiation</i> , 518	
7-2b-2 <i>Termination</i> , 521	
7-2b-3 <i>Kinetics</i> , 524	
7-2b-4 <i>Cyclic Acetals</i> , 528	
7-2b-5 <i>Energetic Characteristics</i> , 530	
<b>7-3 Cyclic Amides</b>	<b>534</b>
7-3a <i>Hydrolytic Polymerization</i> , 534	

7-3b	<i>Anionic Polymerization, 536</i>	
7-3b-1	<i>Use of Strong Bases Alone, 536</i>	
7-3b-2	<i>Addition of N-Acylactam, 539</i>	
7-3c	<i>Cationic Polymerization, 541</i>	
7-3d	<i>Reactivity, 542</i>	
7-4	<i>N-Carboxy-<math>\alpha</math>-Amino Acid Anhydrides</i>	543
7-5	<i>Other Cyclic Monomers</i>	545
7-5a	<i>Lactones, 545</i>	
7-5b	<i>Cyclic Amines, 546</i>	
7-5c	<i>Cyclic Sulfides, 547</i>	
7-5d	<i>Miscellaneous Polymerizations, 547</i>	
7-6	<i>Polymerization of Inorganic or Partially Inorganic Cyclic Monomers</i>	548
7-6a	<i>Cyclosiloxanes, 548</i>	
7-6b	<i>Sulfur, 550</i>	
7-6c	<i>Poly(organophosphazenes), 550</i>	
7-6d	<i>Polymeric Sulfur Nitride, 552</i>	
7-7	<i>Copolymerization</i>	552
7-7a	<i>Monomers Containing the Same Polymerizing Group, 553</i>	
7-7b	<i>Monomers Containing Different Functional Groups, 555</i>	
7-7c	<i>Zwitterion Copolymerization, 556</i>	
8	<b>STEREOCHEMISTRY OF POLYMERIZATION</b>	566
8-1	<i>Types of Stereoisomerism in Polymers</i>	567
8-1a	<i>Monosubstituted Ethylenes, 568</i>	
8-1a-1	<i>Site of Steric Isomerism, 568</i>	
8-1a-2	<i>Tacticity, 568</i>	
8-1b	<i>Disubstituted Ethylenes, 570</i>	
8-1b-1	<i>1,1-Disubstituted Ethylenes, 570</i>	
8-1b-2	<i>1,2-Disubstituted Ethylenes, 570</i>	

8-1c	<i>Carbonyl and Ring-Opening Polymerizations</i> , 572	
8-1d	<i>1,3-Butadiene and 2-Substituted 1,3-Butadienes</i> , 574	
8-1d-1	<i>1,2- and 3,4-Polymerizations</i> , 574	
8-1d-2	<i>1,4-Polymerization</i> , 575	
8-1e	<i>4-Substituted and 1,4-Disubstituted 1,3-Butadienes</i> , 576	
8-1e-1	<i>1,2- and 3,4-Polymerizations</i> , 576	
8-1e-2	<i>1,4-Polymerization</i> , 577	
8-1f	<i>Other Polymers</i> , 578	
8-2	<b>Properties of Stereoregular Polymers</b>	580
8-2a	<i>Significance of Stereoregularity in Polymers</i> , 580	
8-2a-1	<i>Isotactic, Syndiotactic, and Atactic Polypropylenes</i> , 580	
8-2a-2	<i>cis- and trans- 1,4-Poly-1,3-Dienes</i> , 581	
8-2a-3	<i>Cellulose and Amylose</i> , 582	
8-2b	<i>Analysis of Stereoregularity</i> , 583	
8-3	<b>Forces of Stereoregulation in Alkene Polymerizations</b>	584
8-3a	<i>Radical Polymerization</i> , 585	
8-3b	<i>Ionic and Coordination Polymerization</i> , 587	
8-3b-1	<i>Effect of Coordination</i> , 587	
8-3b-2	<i>Mechanism of Stereospecific Placement</i> , 589	
8-4	<b>Ziegler-Natta Polymerization of Nonpolar Vinyl Monomers</b>	591
8-4a	<i>Mechanism of Ziegler-Natta Polymerization</i> , 592	
8-4a-1	<i>Chemical Nature of Propagating Species</i> , 593	
8-4a-2	<i>Primary versus Secondary Insertion</i> , 595	
8-4a-3	<i>Propagation of Carbon-Transition Metal Bond</i> , 595	
8-4a-4	<i>Bimetallic versus Monometallic Mechanisms</i> , 596	
8-4a-5	<i>Direction of Double Bond Opening</i> , 599	
8-4a-6	<i>Mechanism of Isotactic Control</i> , 601	
8-4a-7	<i>Mechanism of Syndiotactic Polymerization</i> , 605	
8-4b	<i>Effect of Components of Ziegler-Natta Initiator System</i> , 608	
8-4b-1	<i>Transition Metal Component</i> , 608	
8-4b-2	<i>Group I-III Metal Component</i> , 609	
8-4b-3	<i>Third Component</i> , 610	
8-4c	<i>Kinetics</i> , 611	

8-4c-1	<i>Observed Rate Behavior</i> , 611	
8-4c-2	<i>Termination</i> , 612	
8-4c-3	<i>Rate Expression</i> , 613	
8-4c-4	<i>Values of Kinetic Parameters</i> , 615	
8-4d	<i>Scope of the Ziegler-Natta Initiator</i> , 616	
8-4d-1	<i>Cycloalkenes</i> , 617	
8-4d-2	<i>Alkynes</i> , 618	
8-4d-3	<i>Copolymerization</i> , 618	
8-4e	<i>Commercial Polymerizations</i> , 619	
8-4e-1	<i>Supported Initiators</i> , 619	
8-4e-2	<i>Process Conditions</i> , 621	
8-5	<b>Stereospecific Polymerization of Polar Vinyl Monomers</b>	<b>623</b>
8-5a	<i>Methyl Methacrylate</i> , 623	
8-5b	<i>Vinyl Ethers</i> , 625	
8-5c	<i>Styrene</i> , 626	
8-6	<b>Stereospecific Polymerization of 1,3-Dienes</b>	<b>626</b>
8-6a	<i>Radical Polymerization</i> , 626	
8-6b	<i>Anionic and Coordination Polymerizations</i> , 628	
8-6c	<i>Cationic Polymerization</i> , 633	
8-6d	<i>Other Polymerizations</i> , 634	
8-7	<b>Carbonyl Monomers</b>	<b>634</b>
8-8	<b>Other Stereochemical Aspects of Polymerization</b>	<b>634</b>
8-8a	<i>Optical Activity in Polymers</i> , 634	
8-8b	<i>Stereoselection and Stereoelection</i> , 635	
8-8c	<i>Ring-Opening Polymerization</i> , 637	
8-8d	<i>Step Polymerization</i> , 638	
8-9	<b>Statistical Models of Propagation</b>	<b>639</b>
8-9a	<i>Bernoulli Model</i> , 639	
8-9b	<i>First-Order Markov Model</i> , 640	
8-9c	<i>Application of Propagation Statistics</i> , 641	

<b>9 REACTIONS OF POLYMERS</b>	<b>654</b>
<b>9-1 Principles of Polymer Reactivity</b>	<b>654</b>
9-1a <i>Yield</i> , 654	
9-1b <i>Isolation of Functional Groups</i> , 655	
9-1c <i>Concentration</i> , 655	
9-1d <i>Crystallinity</i> , 656	
9-1e <i>Change in Solubility</i> , 656	
9-1f <i>Crosslinking</i> , 657	
9-1g <i>Steric Effects</i> , 658	
9-1h <i>Electrostatic Effects</i> , 659	
9-1i <i>Neighboring Group Effects</i> , 660	
9-1j <i>Hydrophobic Interactions</i> , 661	
9-1k <i>Other Considerations</i> , 662	
<b>9-2 Crosslinking</b>	<b>663</b>
9-2a <i>Alkyds</i> , 663	
9-2b <i>Elastomers Based on 1,3-Dienes</i> , 665	
9-2b-1 <i>Sulfur Alone</i> , 665	
9-2b-2 <i>Accelerated Sulfur Vulcanization</i> , 666	
9-2b-3 <i>Other Vulcanizations</i> , 668	
9-2b-4 <i>Commercial Elastomers</i> , 669	
9-2c <i>Peroxide Crosslinking</i> , 669	
9-2d <i>Other Crosslinking Processes</i> , 671	
<b>9-3 Reactions of Cellulose</b>	<b>672</b>
9-3a <i>Dissolution of Cellulose</i> , 672	
9-3b <i>Esterification</i> , 674	
9-3c <i>Etherification</i> , 674	
<b>9-4 Reactions of Poly(vinyl acetate)</b>	<b>674</b>
<b>9-5 Halogenation</b>	<b>675</b>
9-5a <i>Natural Rubber</i> , 675	

9-5b	<i>Saturated Hydrocarbon Polymers</i> , 676	
9-6	Aromatic Substitution	677
9-7	Cyclization	678
9-8	Graft Copolymers	679
9-8a	<i>Radical Graft Polymerization</i> , 679	
9-8a-1	<i>Chain Transfer and Copolymerization</i> , 679	
9-8a-2	<i>Ionizing Radiation</i> , 680	
9-8a-3	<i>Ultraviolet Radiation</i> , 682	
9-8a-4	<i>Redox Initiation</i> , 682	
9-8a-5	<i>Other Grafting Systems</i> , 682	
9-8b	<i>Ionic Graft Polymerization</i> , 683	
9-8b-1	<i>Anionic Initiation</i> , 683	
9-8b-2	<i>Cationic Initiation</i> , 684	
9-9	Block Copolymers	684
9-9a	<i>Mechanochemical Bond Scission</i> , 684	
9-9b	<i>Special Initiators</i> , 685	
9-9c	<i>Other Methods</i> , 686	
9-10	Polymers as Carriers or Supports	687
9-10a	<i>Synthesis</i> , 687	
9-10a-1	<i>Attachment of Group to Polymer</i> , 687	
9-10a-2	<i>Polymerization of a Functional Monomer</i> , 689	
9-10a-3	<i>Comparison of the Two Synthetic Approaches</i> , 689	
9-10b	<i>Advantages of Polymer Reagents, Catalysts, and Substrates</i> , 690	
9-11	Polymer Reagents	691
9-12	Polymer Catalysts	694
9-13	Polymer Substrates	698
9-13a	<i>Solid-Phase Synthesis of Peptides</i> , 698	
9-13b	<i>Other Applications</i> , 702	