

Contents

1	Introduction	1
1.1	Types of Polymers	3
1.2	Types of Polymerization	3
1.3	Nomenclature of Polymers.	4
1.4	Polymer Recycling	7
1.5	Problems	7
	References	8
2	Polymer Size and Polymer Solutions	9
2.1	The Molecular Weight of Polymer	9
2.2	Polymer Solutions	12
2.3	Measurement of Molecular Weight.	16
2.4	Problems	24
	References	25
3	Structure Morphology Flow of Polymer	27
3.1	Chemical and Molecular Structure of Polymer	27
3.2	Crystal Structure of Homopolymer	31
3.3	Crystal Structure of Copolymer	33
3.4	Liquid Crystalline Polymer	37
3.5	Crosslinked Polymer	43
3.6	Polymer Blend	44
3.7	Polymer Flow Under Shear Force.	46
3.8	Polymer Flow Under Thermal Stress.	52
3.9	Problems	56
	References	58
4	Chemical and Physical Properties of Polymers	61
4.1	Chemical Property of Polymer	61
4.2	Mechanical Property of Polymer	66
4.3	Thermal Property of Polymer.	68
4.4	Electrical Property of Polymer	72

4.5	Optical Property of Polymer	76
4.6	Processability of Polymer	83
4.7	Problems	86
	References	87
5	Characterization of Polymer	89
5.1	Instruments and Testing Methods for Polymer	
	Characterization	89
5.2	Characterization of Chemical Structures of Polymers	90
5.2.1	Chemical Reaction Method	90
5.2.2	Infrared Spectroscopy	90
5.2.3	Raman Spectroscopy	92
5.2.4	UV-Visible Spectroscopy	93
5.2.5	Nuclear Magnetic Resonance Spectroscopy	95
5.2.6	Electron Spin Resonance	98
5.3	Characterization of Morphology and Physical Structure of Polymer	100
5.3.1	Transmission Electron Microscopy	100
5.3.2	X-Ray Scattering	102
5.3.3	Atomic Force Microscopy	103
5.4	Characterization of Thermal Properties of Polymers	104
5.4.1	Differential Thermal Analysis and Differential Scanning Calorimetry	104
5.4.2	Thermomechanical Analysis	106
5.4.3	Thermogravimetric Analysis	107
5.4.4	Flammability Test	108
5.5	Problems	109
	References	110
6	Step Polymerization	111
6.1	Chemical Reactions and Reaction Mechanisms of Step Polymerization	111
6.1.1	Carbonyl Addition: Elimination Reaction Mechanism	113
6.1.2	Carbonyl Addition: Substitution Reaction Mechanism	115
6.1.3	Nucleophilic Substitution Reaction Mechanism	116
6.1.4	Double-Bond Addition Reaction Mechanism	116
6.1.5	Free-Radical Coupling	117
6.1.6	Aromatic Electrophilic-Substitution Reaction Mechanism	117
6.2	Reaction Kinetics of Step Polymerization	117
6.3	Molecular Weight Control in Step Polymerization	119
6.4	Molecular Weight Distribution	122
6.5	Network Formation from Step Polymerization	124

6.6	Step Copolymerization	127
6.7	Techniques of Step Polymerization.	129
6.8	Synthesis of Dendritic Polymers.	130
6.8.1	Divergent Method.	130
6.8.2	Convergent System.	131
6.8.3	Molecular Weight of Dendrimer.	133
6.9	Hyperbranched Copolymer	133
6.10	Problems	134
	References	135
7	Radical Chain Polymerization.	137
7.1	Effect of Chemical Structure of Monomer on the Structural Arrangement of Polymer.	138
7.2	Initiators of Radical Chain Polymerization.	142
7.2.1	Thermal Initiators.	142
7.2.2	Decomposition Temperature and Half-Life of Thermal Initiators.	144
7.2.3	Initiation Promoters	147
7.2.4	Redox Initiators	147
7.2.5	Photoinitiators	148
7.2.6	Electrochemical Initiation	149
7.3	Techniques of Free Radical Chain Polymerization	150
7.3.1	Bulk Polymerization	150
7.3.2	Suspension Polymerization	150
7.3.3	Solution Polymerization	151
7.3.4	Emulsion Polymerization.	151
7.4	Reaction Mechanism of Free Radical Chain Polymerization	153
7.5	Kinetics of Free Radical Chain Polymerization	155
7.5.1	Rate of Polymerization	156
7.5.2	Average Kinetic Chain Length \bar{v}	157
7.5.3	Chain Transfer Reactions	158
7.6	Living Polymerization.	162
7.6.1	Living Radical Polymerization.	162
7.6.2	Atom Transfer Radical Polymerization	163
7.6.3	Nitroxide-Mediated Polymerization.	164
7.6.4	Radical Addition-Fragmentation Transfer	164
7.7	Polymerization of Dienes.	165
7.8	Temperature Effect of the Free Radical Polymerization.	168
7.8.1	Activation Energy and Frequency Factor	169
7.8.2	Rate of Polymerization	170
7.8.3	Degree of Polymerization	171

7.9	Thermodynamics of Free Radical Polymerization	172
7.9.1	Monomer Reactivity	173
7.9.2	Ceiling Temperature	175
7.9.3	Characteristics of ΔS Values of Free Radical Polymerization	176
7.10	Molecular Weight Distribution at Low Conversion	176
7.11	Synthesis of Commercial Polymers	178
7.11.1	Polyethylene	178
7.11.2	Polystyrene	179
7.11.3	Polyvinyl Chloride	180
7.11.4	Polyvinyl Acetate	180
7.11.5	Polyvinylidene Chloride	180
7.11.6	Acryl Polymer	180
7.11.7	Fluoropolymers	181
7.11.8	Cost of Common Polymers	182
7.12	Problems	182
	References	183
8	Ionic Chain Polymerization	185
8.1	Characteristics of Ionic Chain Polymerization	187
8.2	Cationic Polymerization	189
8.2.1	Initiators of Cationic Polymerization	189
8.2.2	Reaction Mechanisms of Cationic Polymerization	190
8.2.3	Kinetics of Cationic Polymerization	196
8.2.4	Commercial Cationic Polymerization	200
8.3	Anionic Polymerization	201
8.3.1	Reaction Mechanisms of Anionic Polymerization	201
8.3.2	Kinetics of Anionic Polymerization with Termination	204
8.4	Group Transfer Polymerization	209
8.5	Chain Polymerization of Carbonyl Monomer	213
8.5.1	Anionic Polymerization of Carbonyl Monomer	213
8.5.2	Cationic Polymerization of Carbonyl Monomer	215
8.5.3	Radical Polymerization of Carbonyl Monomer	215
8.5.4	End-Capping Polymerization	216
8.6	Problems	217
	References	218
9	Coordination Polymerization	219
9.1	Heterogeneous Ziegler–Natta Polymerization	219
9.1.1	Catalysts	219
9.1.2	Reaction Mechanisms	222
9.2	Homogeneous Ziegler–Natta Polymerization	225
9.3	Ziegler–Natta Copolymerization	229

9.4	Metathesis Polymerization	230
9.5	Problems	231
	References	232
10	Chain Copolymerization	233
10.1	Reaction Kinetics of Free Radical Copolymerization	234
10.1.1	Types of Copolymerization Behavior	237
10.1.2	Effect of Reaction Conditions on Radical Copolymerization	241
10.1.3	Reactivity and Composition of Free Radical Copolymerization	243
10.1.4	Rate of Polymerization of Free Radical Copolymerization	253
10.2	Cationic Copolymerization	256
10.3	Anionic Copolymerization	259
10.4	Copolymerization Involving Dienes	260
10.5	Block Copolymers	261
10.6	Commercial Copolymers	263
10.7	Problems	263
	References	265
11	Ring-Opening Polymerization	267
11.1	Reactivity of Cyclic Monomers	267
11.2	General Aspects of Mechanisms and Kinetics	270
11.3	Cyclic Ethers	271
11.3.1	Anionic Polymerization of Epoxides	272
11.3.2	Cationic Polymerization of Epoxides	277
11.3.3	Polymerization of Cyclic Acetals	282
11.3.4	Kinetic Characteristics	283
11.3.5	Thermodynamic Characteristics	285
11.3.6	Commercial Applications of Polymers of Cyclic Ether	287
11.4	Lactams	288
11.4.1	Cationic Polymerization	288
11.4.2	Hydrolytic Polymerization	290
11.4.3	Anionic Polymerization	291
11.4.4	Reactivity of Lactam	294
11.5	Cyclosiloxanes	294
11.6	Copolymerization	296
11.7	Problems	298
	References	299
Index	301