

A. Ravve

Principles of Polymer Chemistry

Third Edition

 Springer

Contents

1	Introduction and Nomenclature	1
1.1	Brief Historical Introduction	1
1.2	Definitions	2
1.3	Nomenclature of Polymers	7
1.3.1	Nomenclature of Chain-Growth Polymers	7
1.3.2	Nomenclature of Step-Growth Polymers	11
1.4	Steric Arrangement in Macromolecules	11
	Appendix	13
	Review Questions	13
	References	15
2	Physical Properties and Physical Chemistry of Polymers	17
2.1	Structure and Property Relationship in Organic Polymers	17
2.1.1	Effects of Dipole Interactions	17
2.1.2	Induction Forces in Polymers	18
2.2	The Amorphous State	21
2.2.1	The Glass Transition and the Glassy State	21
2.2.2	Elasticity	24
2.2.3	Rheology and Viscoelasticity of Polymeric Materials	27
2.3	The Crystalline State	34
2.3.1	Crystallization from the Melt	34
2.3.2	Crystallization from Solution	36
2.3.3	Spherulitic Growth	38
2.4	The Mesomorphic State, Liquid Crystal Polymers	43
2.5	Orientation of Polymers	47
2.6	Solutions of Polymers	48
2.6.1	Radius of Gyration	48
2.6.2	The Thermodynamics of Polymer Solutions	50
2.7	Molecular Weights and Molecular Weight Determinations	51
2.7.1	Molecular Weight Averages	51
2.7.2	Methods for Measuring Molecular Weights of Polymers	53
2.8	Optical Activity in Polymers	60
	Review Questions	61
	References	66

3	Free-Radical Chain-Growth Polymerization	69
3.1	Free-Radical Chain-Growth Polymerization Process	69
3.1.1	Kinetic Relationships in Free-Radical Polymerizations	69
3.2	Reactions Leading to Formation of Initiating Free Radicals	72
3.2.1	Thermal Decomposition of Azo Compound and Peroxides	72
3.2.2	Bimolecular Initiating Systems.....	76
3.2.3	Boron and Metal Alkyl Initiators of Free-Radical Polymerizations	79
3.2.4	Photochemical Initiators.....	79
3.2.5	Initiation of Polymerization with Radioactive Sources and Electron Beams	80
3.3	Capture of Free Radicals by Monomers.....	80
3.4	Propagation	84
3.4.1	Steric, Polar, and Resonance Effects in the Propagation Reaction	84
3.4.2	Effect of Reaction Medium.....	87
3.4.3	Ceiling Temperature.....	88
3.4.4	Autoacceleration.....	89
3.4.5	Polymerization of Monomers with Multiple Double Bonds.....	90
3.5	The Termination Reaction.....	92
3.6	Copolymerization	96
3.6.1	Reactivity Ratios.....	97
3.6.2	Q and e Scheme	99
3.6.3	Solvent Effect on Copolymerization	100
3.7	Terpolymerization	101
3.8	Allylic Polymerization.....	102
3.9	Inhibition and Retardation.....	103
3.10	Thermal Polymerization	106
3.11	Donor–Acceptor Complexes in Copolymerization.....	107
3.12	Polymerization of Complexes with Lewis Acids	111
3.13	Steric Control in Free-Radical Polymerization	113
3.14	Controlled/“Living” Free-Radical Polymerization.....	114
3.14.1	Cobalt Mediated Polymerizations	116
3.14.2	Atom Transfer Radical Polymerizations	117
3.14.3	Nitroxide-Mediated Radical Polymerizations.....	121
3.14.4	Reversible Addition-Fragmentation Chain Transfer Polymerization	126
3.14.5	Special Types of Controlled/“Living” Polymerizations	129
3.14.6	Kinetics of Controlled/Living Free-Radical Polymerizations	130
3.15	Thermodynamics of the Free-Radical Polymerization Reaction	131
3.15.1	Effects of Monomer Structure on the Thermodynamics of the Polymerization.....	131
3.15.2	Thermodynamics of the Constrains of the Free-Radical Polymerization Reaction.....	132
3.16	Polymer Preparation Techniques.....	132
	Review Questions	139
	References.....	143
4	Ionic Chain-Growth Polymerization	151
4.1	The Chemistry of Ionic Chain-Growth Polymerization.....	151
4.2	Kinetics of Ionic Chain-Growth Polymerization.....	152

4.3	Cationic Polymerization	154
4.3.1	Two Electron Transposition Initiation Reactions	155
4.3.2	One Electron Transposition Initiation Reactions	163
4.3.3	Propagation in Cationic Polymerization	167
4.3.4	Termination Reactions in Cationic Polymerizations	177
4.3.5	Living Cationic Polymerizations	178
4.3.6	Thermodynamics of Cationic Polymerization	181
4.4	Anionic Polymerization of Olefins	182
4.4.1	Initiation in Anionic Chain-Growth Polymerization	182
4.4.2	Propagation in Anionic Chain-Growth Polymerization	191
4.4.3	Termination in Anionic Polymerization	198
4.4.4	Thermodynamics of Anionic Polymerization	201
4.5	Coordination Polymerization of Olefins	201
4.5.1	Heterogeneous Ziegler–Natta Catalysts	202
4.5.2	Homogeneous Ziegler–Natta Catalysts	207
4.5.3	Steric Control in Polymerization of Conjugated Dienes	209
4.5.4	Post Ziegler and Natta Coordination Polymerization of Olefins	211
4.5.5	Effect of Lewis Bases	219
4.5.6	Terminations in Coordination Polymerizations	219
4.5.7	Reduced Transition Metal Catalysts on Support	219
4.5.8	Isomerization Polymerizations with Coordination Catalysts	220
4.6	Polymerization of Aldehydes	221
4.6.1	Cationic Polymerization of Aldehydes	221
4.6.2	Anionic Polymerization of Aldehydes	223
4.6.3	Polymerization of Unsaturated Aldehydes	226
4.6.4	Polymerizations of Di Aldehydes	227
4.7	Polymerization of Ketones and Isocyanates	228
4.8	Copolymerizations by Ionic Mechanism	228
4.9	Group Transfer Polymerization	231
4.10	Configurational Statistics and the Propagation Mechanism in Chain-Growth Polymerization	234
4.11	Thermodynamics of Equilibrium Polymerization	240
	Review Questions	241
	References	243
5	Ring-Opening Polymerizations	253
5.1	Chemistry of Ring-Opening Polymerizations	253
5.2	Kinetics of Ring-Opening Polymerization	253
5.3	Polymerization of Oxiranes	255
5.3.1	Cationic Polymerization	255
5.3.2	Anionic Polymerization	259
5.3.3	Polymerization by Coordination Mechanism	261
5.3.4	Steric Control in Polymerizations of Oxiranes	264
5.4	Polymerization of Oxetanes	266
5.4.1	The Initiation Reaction	267
5.4.2	The Propagation Reaction	268
5.5	Polymerization of Tetrahydrofurans	269
5.5.1	The Initiation Reaction	270
5.5.2	The Propagation Reaction	271
5.5.3	The Termination Reaction	272

5.6	Polymerization of Oxepanes.....	273
5.7	Ring-Opening Polymerizations of Cyclic Acetals	273
	5.7.1 Polymerization of Trioxane.....	274
	5.7.2 Polymerization of Dioxolane	276
	5.7.3 Polymerization of Dioxopane and Other Cyclic Acetals.....	277
5.8	Polymerization of Lactones	278
	5.8.1 Cationic Polymerization	278
	5.8.2 Anionic Polymerization of Lactones	280
	5.8.3 Polymerization of Lactones by Coordination Mechanism	281
	5.8.4 Special Catalysts for Polymerizations of Lactones.....	283
5.9	Polymerizations of Lactams	284
	5.9.1 Cationic Polymerization of Lactams.....	285
	5.9.2 Anionic Polymerization of Lactams	290
	5.9.3 Hydrolytic Polymerization of Lactams	296
5.10	Polymerization of <i>N</i> -Carboxy- α -Amino Acid Anhydrides	297
5.11	Metathesis Polymerization of Alicyclics.....	301
5.12	Polymerization of Cyclic Amines	307
5.13	Ring-Opening Polymerizations of Cyclic Sulfides.....	309
5.14	Copolymerization of Cyclic Monomers.....	311
5.15	Spontaneous Alternating Zwitterion Copolymerizations	312
5.16	Ring-Opening Polymerizations by a Free Radical Mechanism.....	316
5.17	Thermodynamics of Ring-Opening Polymerization	318
	Review Questions	319
	References.....	322
6	Common Chain-Growth Polymers	329
6.1	Polyethylene and Related Polymers.....	329
	6.1.1 Preparation of Polyethylene by a Free-Radical Mechanism	329
	6.1.2 Preparation of Polyethylene by Coordination Mechanism.....	332
	6.1.3 Commercial High-Density Polyethylene, Properties, and Manufacture	335
	6.1.4 Materials Similar to Polyethylene	338
6.2	Polypropylene	339
	6.2.1 Manufacturing Techniques.....	342
	6.2.2 Syndiotactic Polypropylene.....	342
6.3	Polyisobutylene.....	343
6.4	Poly(α -olefin)s.....	345
	6.4.1 Properties of Poly(α -olefin)s.....	345
	6.4.2 Poly(butene-1)	345
	6.4.3 Poly(4-methyl pentene-1).....	345
6.5	Copolymers of Ethylene and Propylene.....	347
	6.5.1 Ethylene and Propylene Elastomers	347
	6.5.2 Copolymers of Ethylene with α -Olefins and Ethylene with Carbon Monoxide	348
	6.5.3 Copolymers of Propylene with Dienes	351
	6.5.4 Copolymers of Ethylene with Vinyl Acetate.....	351
	6.5.5 Ionomers	351
6.6	Homopolymers of Conjugated Dienes	352
	6.6.1 Polybutadiene	352
	6.6.2 Polyisoprene.....	356

6.7	Methyl Rubber, Poly(2,3-dimethylbutadiene).....	358
6.8	Chloroprene Rubber, Poly(2-chloro-1,3-butadiene).....	358
6.9	Special Polymers from Dienes	360
6.10	Cyclopolymerization of Conjugated Dienes	360
6.11	Copolymers of Dienes	361
6.11.1	GR-S Rubber.....	361
6.11.2	GR-N Rubber	363
6.12	Polystyrene and Polystyrene-Like Polymers.....	364
6.12.1	Preparation of Polystyrene by Free-Radical Mechanism	364
6.12.2	Polystyrene Prepared by Ionic Chain-Growth Polymerization	365
6.12.3	Polymers from Substituted Styrenes	367
6.13	Copolymers of Styrene	370
6.13.1	High-Impact Polystyrene	370
6.13.2	ABS Resins	371
6.13.3	Copolymers of Styrene with Maleic Anhydride	372
6.14	Polymers of Acrylic and Methacrylic Esters.....	372
6.14.1	Polymerizations of Acrylic and Methacrylic Esters	373
6.14.2	Acrylic Elastomers.....	375
6.14.3	Thermoplastic and Thermoset Acrylic Resins	376
6.15	Acrylonitrile and Methacrylonitrile Polymers	379
6.16	Polyacrylamide, Poly(acrylic acid), and Poly(methacrylic acid)	381
6.17	Halogen-Bearing Polymers	382
6.17.1	Polytetrafluoroethylene	382
6.17.2	Polychlorotrifluoroethylene.....	383
6.17.3	Poly(vinylidene fluoride).....	383
6.17.4	Poly(vinyl fluoride)	383
6.17.5	Copolymers of Fluoroolefins	384
6.17.6	Miscellaneous Fluorine Containing Chain-Growth Polymers	385
6.17.7	Poly(vinyl chloride)	386
6.17.8	Poly(vinylidene chloride)	389
6.18	Poly(vinyl acetate).....	390
6.19	Poly(vinyl alcohol) and Poly(vinyl acetal)s.....	391
	Review Questions	393
	References.....	396
7	Step-Growth Polymerization and Step-Growth Polymers.....	403
7.1	Mechanism and Kinetics of Step-Growth Polymerization	403
7.1.1	Reactions of Functional Groups	403
7.1.2	Kinetic Considerations.....	405
7.1.3	Ring Formation in Step-Growth Polymerizations	410
7.1.4	Techniques of Polymer Preparation	412
7.2	Polyesters	412
7.2.1	Linear Saturated Polyesters	412
7.2.2	Linear Unsaturated Polyesters	424
7.2.3	Network Polyesters for Surface Coatings	425
7.2.4	Polycarbonates	427
7.2.5	Polyesters from Lactones	428
7.3	Polyamides.....	430
7.3.1	Nylons.....	430
7.3.2	Fatty Polyamides.....	441

7.3.3	Special Reactions for Formation of Polyamides	441
7.3.4	Aromatic Polyamides	443
7.4	Aromatic Polyamide-Imides and Aromatic Polyester-Imides	447
7.5	Polyimides	450
7.6	Polyethers	456
7.6.1	Poly(phenylene oxide)s	456
7.6.2	Phenoxy Polymers	459
7.7	Polyacetals and Polyketals	459
7.8	Poly(<i>p</i> -xylylene)s	461
7.9	Sulfur-Containing Polymers	463
7.9.1	Polysulfones	463
7.9.2	Polythiols and Polymercaptans	465
7.10	Polyurethanes	468
7.10.1	Preparations of Polyfunctional Isocyanates	469
7.10.2	Commercial Polyisocyanates	469
7.10.3	Chemical Reactions of the Isocyanates	470
7.10.4	The Effect of Catalysts	471
7.10.5	Polyurethane Fibers	472
7.10.6	Polyurethane Elastomers	473
7.10.7	Polyurethane Foams	474
7.11	Epoxy Resins	474
7.11.1	Preparation of Commercial Epoxy Resins	475
7.11.2	The Cross-linking Reactions	476
7.11.3	Cycloaliphatic Epoxides	482
7.12	Phenol-Formaldehyde Resins	483
7.12.1	Resols	483
7.12.2	Novolacs	487
7.12.3	Ammonia-Catalyzed Phenolic Resins	490
7.12.4	Typical Commercial Preparations	491
7.13	Amino Polymers	492
7.13.1	Urea-Formaldehyde Resins	492
7.13.2	Melamine-Formaldehyde Resins	493
7.14	Silicone Polymers	494
7.14.1	Polysiloxanes	494
7.14.2	Silicone Elastomers	496
7.14.3	Polysiloxane Coating Resins	498
7.14.4	Fluorosilicone Elastomers	498
7.14.5	Polyarylsiloxanes (Also See Sect. 7.17.4)	499
7.15	Polysilanes	499
7.16	Phosphonitrile Polymers	500
7.17	High-Performance Polymers	502
7.17.1	Fluorine Containing Aromatic Polymers	502
7.17.2	Polyphenylene	504
7.17.3	Diels-Alder Polymers	505
7.17.4	Silicon-Containing Aromatic Polymers	511
7.17.5	Direct Condensation Polymers	512
7.17.6	Oligomers with Terminal Functional Groups	514
7.17.7	Cardo Polymers	517
7.17.8	Double-Stranded Polymers	517
7.17.9	Poly(arylene ether)s and Poly(arylene ether ketone)s	520

7.18	Dendrimers and Polyrotaxanes	521
7.18.1	Dendrimers and Hyperbranched Polymers	522
7.18.2	Polyrotaxanes	523
7.19	Thermodynamics of Step-Growth Polymerization	524
	Review Questions	525
	References	529
8	Naturally Occurring Polymers	537
8.1	Naturally Occurring Polymers	537
8.2	Polysaccharides	537
8.2.1	Hemicelluloses	537
8.2.2	Starch	538
8.2.3	Cellulose	539
8.2.4	Miscellaneous Polysaccharides	545
8.3	Lignin	546
8.4	Polyisoprene	547
8.5	Proteins	547
8.5.1	α -Amino Acids	548
8.5.2	Structures and Chemistry of Proteins	548
8.5.3	Synthetic Methods for the Preparation of Polypeptides	554
8.5.4	Chemical Modification of Proteins	556
8.6	Nucleic Acids	557
8.6.1	DNA and RNA	559
8.6.2	Synthetic Methods for the Preparation of Nucleic Acids	560
8.7	Polyalkanoates	561
	Review Questions	562
	References	563
9	Organic Reactions of Polymers	567
9.1	Reactivity of Macromolecules	567
9.1.1	Diffusion-Controlled Reactions	569
9.1.2	Paired Group and Neighboring Group Effects	569
9.1.3	Effect of Molecular Size	570
9.1.4	Effects of Changes in Solubility	570
9.1.5	Effects of Crystallinity	571
9.1.6	Reactions That Favor Large Molecules	571
9.2	Addition Reactions	572
9.2.1	Halogenation	572
9.2.2	Hydrogenation	574
9.2.3	Addition of Carbenes	575
9.2.4	Electrophilic Additions of Aldehydes	576
9.2.5	Polar Additions	577
9.3	Rearrangement Reactions	584
9.3.1	Isomerization Reactions	584
9.3.2	Cyclizations and Intramolecular Rearrangements	586
9.4	Substitution Reactions	590
9.4.1	Substitution Reactions of Saturated Polymeric Hydrocarbons	590
9.4.2	Substitution Reactions of Halogen-Bearing Polymers	592
9.4.3	Substitution Reactions of Polymers with Aromatic Rings	597
9.4.4	Reactions of Acrylic, Methacrylic, and Related Polymers	606

9.4.5	Substitution Reactions of Poly(vinyl alcohol)	610
9.4.6	Miscellaneous Exchange Reactions	612
9.5	Cross-linking Reactions of Polymers	614
9.5.1	Vulcanization of Elastomers	614
9.5.2	Cross-linking of Polymers with the Aid of Peroxides	616
9.5.3	Miscellaneous Cross-linking Reactions of Polymers	617
9.6	Graft Copolymers	617
9.6.1	Free-Radical Grafting by Chain-Transferring Process	617
9.6.2	Free-Radical Grafting Reactions to Polymers with Double Bonds	619
9.6.3	Preparation of Graft Copolymers with the Aid of Macromonomers	620
9.6.4	Initiations of Polymerizations from the Backbone of Polymers	622
9.6.5	Photochemical Syntheses of Graft Copolymers	625
9.6.6	Graft Copolymer Formation with the Aid of High-Energy Radiation	626
9.6.7	Preparation of Graft Copolymers with Ionic Chain-Growth and Step-Growth Polymerization Reactions	627
9.6.8	Miscellaneous Graft Copolymerizations	630
9.7	Block Copolymers	631
9.7.1	Block Copolyesters	631
9.7.2	Block Copolyamides	632
9.7.3	Polyurethane-Polyamide Block Copolymers	633
9.7.4	Polyamide-Polyester Block Copolymers	633
9.7.5	Polyurethane Ionomers	633
9.7.6	Block Copolymers of Poly(α -Olefin)s	634
9.7.7	Simultaneous Use of Free Radical and Ionic Chain-Growth Polymerizations	635
9.7.8	Preparation of Block Copolymers by Homogeneous Ionic Copolymerization	637
9.7.9	Special Reactions for Preparation of Block Copolymers	639
9.7.10	Miscellaneous Block Copolymers	642
9.7.11	Mechanochemical Techniques for Formation of Block Copolymers	643
9.8	Processes in Polymer Degradation	643
9.8.1	Thermal Degradation of Common Chain-Growth Polymers	643
9.8.2	Thermal Degradation of Polyolefins and of Polymers from Conjugated Dienes	644
9.8.3	Thermal Degradation of Polystyrene and Polystyrene-Like Polymers	646
9.8.4	Thermal Degradation of Methacrylic and Acrylic Polymers	647
9.8.5	Thermal Degradation of Chlorocarbon and Fluorocarbon Polymers	649
9.8.6	Thermal Degradation of Poly(Vinyl Acetate)	652
9.9	Thermal Degradation of Common Step-Growth Polymers	652
9.9.1	Thermal Degradation of Polyoxides	652
9.9.2	Thermal Degradation of Polyesters	653
9.9.3	Thermal Degradation of Polyamides	656
9.9.4	Thermal Degradation of Epoxy Resins	658
9.9.5	Thermal Degradation of Polyimides, Polyoxidiazoles, and Polyquinoxalines	659
9.9.6	Thermal Degradation of Aromatic Polysulfones	661
9.9.7	Thermal Degradation of Polyethers	661
9.9.8	Thermal Degradation of Cellulosic Materials	661
9.9.9	Hydrolytic Degradation of Polymers at Elevated Temperatures	662
9.9.10	Oxidative Degradation of Polymers	663

9.9.11	Oxidation of Chain-Growth Polymers.....	663
9.9.12	Oxidation of Step-Growth Polymers	666
9.9.13	Photo-Degradation of Macromolecules	668
9.9.14	Photo-Oxidative Degradations of Polymers.....	674
9.9.15	Degradation of Polymeric Materials by Ionizing Radiation	677
	Review Questions.....	677
	References.....	682
10	Polymeric Materials for Special Applications	695
10.1	Polymer Supports for Reagents, Catalysts, and Drug Release.....	695
10.1.1	Support Materials.....	696
10.1.2	Special Gels for Drug Release	704
10.1.3	Utilization of Support Materials.....	705
10.2	Electricity-Conducting Polymers.....	710
10.3	Photonic Polymers.....	717
10.3.1	The Nature of Light	717
10.3.2	Quantum-Mechanical Description of Light	719
10.3.3	Interaction of Light with Organic Molecules	719
10.3.4	Energy Transfer Process.....	726
10.3.5	The Electron Transfer Process	729
10.3.6	The Charge Transfer Processes in Polymers	729
10.3.7	The Antenna Effect in Polymers	732
10.4	Photosensitizers.....	732
10.5	Photocross-Linkable Polymers	735
10.5.1	Polymers That Photocross-link by Formation of Cyclobutane Rings	736
10.5.2	Polymers with Functional Chalcone Groups	743
10.5.3	Polymers with Functional Groups Similar to Cinnamates	744
10.5.4	Polymers with Pendant Furan Groups.....	745
10.5.5	Polymers with Pendant Maleimide Groups	746
10.5.6	Polymers with Pendant Abietate and Dibenzazepine Groups.....	746
10.5.7	Polymers That Cross-link by Dimerization of Nitrenes and by Other Combinations of Free-Radicals to Form Covalent Bonds.....	748
10.5.8	Polymers with Pendant Azide Groups.....	748
10.5.9	Polymers Designed to Cross-link Upon Irradiation with Laser Beams.....	750
10.6	Photo-Responsive Polymers.....	750
10.6.1	Polymers for Harvesting the Sun's Energy	751
10.6.2	Photo-Isomerization of Polymeric Materials.....	755
10.6.3	Changes in Viscosity and Solubility of Polymeric Solutions	759
10.6.4	Application to Optical Data Storage	760
10.6.5	Liquid Crystalline Alignment	762
10.7	Photo-Conducting Polymers	767
10.7.1	Photoconductive Polymers Based on Carbazole	768
10.7.2	Photo-Conducting Polymers That Are Not Based on Carbazole	771
10.8	Polymer-Based Solar Cells.....	775
	Review Questions.....	782
	References	784
	Index	791