

C O N T E N T S

PREFACE	xiii
PREFACE TO FIRST EDITION	xv
ACKNOWLEDGMENTS	xvii
1 INTRODUCTION TO POLYMER SCIENCE	1
1.1 Classification of Polymers.....	4
1.1.1 Thermoplastics and Thermosets.....	4
1.1.2 Classification Based upon Polymerization Mechanism.....	4
1.1.3 Classification Based upon Polymer Structure.....	8
1.2 Polymer Structure.....	9
1.2.1 Copolymers.....	10
1.2.2 Tacticity.....	10
1.2.3 Geometric Isomerism.....	12
1.2.4 Nomenclature.....	13
1.3 Molecular Weight.....	15
1.3.1 Molecular-Weight Distribution.....	15
1.3.2 Molecular-Weight Averages.....	15
1.4 Chemical Structure and Thermal Transitions.....	19
2 POLYMER SYNTHESIS	23
2.1 Step-Growth Polymerization.....	24
2.1.1 Molecular Weight in a Step-Growth Polymerization.....	26
2.1.2 Step-Growth Polymerization Kinetics.....	28
2.2 Chain-Growth Polymerization.....	29
2.2.1 Free-Radical Polymerization and Copolymerization.....	29
2.2.2 Ionic Polymerization and Copolymerization.....	45
2.2.3 Coordination Polymerization.....	49
2.3 Polymerization Techniques.....	53
2.3.1 Bulk Polymerization.....	53
2.3.2 Solution Polymerization.....	54
2.3.3 Suspension Polymerization.....	55
2.3.4 Emulsion Polymerization.....	55
2.3.5 Solid-State, Gas-Phase, and Plasma Polymerization.....	57
2.3.6 Polymerization in Supercritical Fluids.....	60
2.4 Reactions of Synthetic Polymers.....	61
2.4.1 Chemical Modification.....	61
2.4.2 Preparation of Polymer Derivatives.....	62
2.5 Special Topics in Polymer Synthesis.....	65
2.5.1 Metathesis.....	66
2.5.2 Group-Transfer Polymerization.....	67

2.5.3	Macromers in Polymer Synthesis.....	69
2.5.4	Atom Transfer Radical Polymerization.....	69
2.5.5	Genetic Engineering.....	71
2.6	Chemical Structure Determination.....	72
2.6.1	Vibrational Spectroscopy.....	72
2.6.2	Nuclear Magnetic Resonance Spectroscopy.....	75
3	CONFORMATION, SOLUTIONS, AND MOLECULAR WEIGHT.....	87
3.1	Polymer Conformation and Chain Dimensions.....	88
3.2	Thermodynamics of Polymer Solutions.....	94
3.2.1	The Flory–Huggins Theory.....	96
3.2.2	Flory–Krigbaum and Modified Flory–Huggins Theory.....	102
3.2.3	Equation-of-State Theories.....	103
3.2.4	Phase Equilibria.....	108
3.2.5	Determination of the Interaction Parameter.....	112
3.2.6	Predictions of Solubilities.....	113
3.3	Measurement of Molecular Weight.....	128
3.3.1	Osmometry.....	129
3.3.2	Light-Scattering Methods.....	133
3.3.3	Intrinsic Viscosity Measurements.....	139
3.3.4	Gel-Permeation Chromatography.....	142
4	SOLID-STATE PROPERTIES.....	153
4.1	The Amorphous State.....	154
4.1.1	Chain Entanglements and Reptation.....	154
4.1.2	The Glass Transition.....	156
4.1.3	Secondary-Relaxation Processes.....	157
4.2	The Crystalline State.....	158
4.2.1	Ordering of Polymer Chains.....	158
4.2.2	Crystalline-Melting Temperature.....	162
4.2.3	Crystallization Kinetics.....	163
4.2.4	Techniques to Determine Crystallinity.....	165
4.3	Thermal Transitions and Properties.....	168
4.3.1	Fundamental Thermodynamic Relationships.....	168
4.3.2	Measurement Techniques.....	172
4.3.3	Structure–Property Relationships.....	177
4.3.4	Effect of Molecular Weight, Composition, and Pressure on T_g	180
4.4	Mechanical Properties.....	183
4.4.1	Mechanisms of Deformation.....	183
4.4.2	Methods of Testing.....	186
5	VISCOELASTICITY AND RUBBER ELASTICITY.....	207
5.1	Introduction to Viscoelasticity.....	208
5.1.1	Dynamic-Mechanical Analysis.....	208
5.1.2	Mechanical Models of Viscoelastic Behavior.....	221
5.1.3	Viscoelastic Properties of Polymer Solutions and Melts.....	230

5.1.4	Dielectric Analysis	232
5.1.5	Dynamic Calorimetry.....	240
5.1.6	Time-Temperature Superposition	242
5.1.7	Boltzmann Superposition Principle	245
5.1.8	Interrelationships between Transient and Dynamic Processes.....	247
5.2	Introduction to Rubber Elasticity.....	249
5.2.1	Thermodynamics.....	249
5.2.2	Statistical Theory	252
5.2.3	Phenomenological Model.....	254
5.2.4	Recent Developments.....	255
6	POLYMER DEGRADATION AND THE ENVIRONMENT	263
6.1	Polymer Degradation and Stability.....	264
6.1.1	Thermal Degradation	264
6.1.2	Oxidative and UV Stability	269
6.1.3	Chemical and Hydrolytic Stability	271
6.1.4	Effects of Radiation	273
6.1.5	Mechanodegradation.....	274
6.2	The Management of Plastics in the Environment	274
6.2.1	Recycling	274
6.2.2	Incineration.....	276
6.2.3	Biodegradation	277
7	ADDITIVES, BLENDS, AND COMPOSITES.....	283
7.1	Additives.....	284
7.1.1	Plasticizers.....	285
7.1.2	Fillers and Reinforcements.....	289
7.1.3	Other Important Additives.....	290
7.2	Polymer Blends and Interpenetrating Networks.....	295
7.2.1	Polymer Blends.....	295
7.2.2	Toughened Plastics and Phase-Separated Blends	304
7.2.3	Interpenetrating Network	306
7.3	Introduction to Polymer Composites	308
7.3.1	Mechanical Properties	310
7.3.2	Composite Fabrication.....	317
8	BIOPOLYMERS, NATURAL POLYMERS, AND FIBERS	325
8.1	Biopolymers and Other Naturally Occurring Polymers.....	326
8.1.1	Proteins	326
8.1.2	Polynucleotides.....	330
8.1.3	Polysaccharides.....	334
8.1.4	Naturally Occurring Elastomers	338
8.2	Fibers	339
8.2.1	Natural and Synthetic Fibers.....	339
8.2.2	Cellulosics	342
8.2.3	Noncellulosics	344

8.2.4	Fiber-Spinning Operations	347
9	THERMOPLASTICS, ELASTOMERS, AND THERMOSETS.....	353
9.1	Commodity Thermoplastics.....	354
9.1.1	Polyolefins.....	355
9.1.2	Vinyl Polymers.....	359
9.1.3	Thermoplastic Polyesters	364
9.2	Elastomers	366
9.2.1	Diene Elastomers	367
9.2.2	Nondiene Elastomers	371
9.2.3	Thermoplastic Elastomers	377
9.3	Thermosets	378
9.3.1	Epoxies	379
9.3.2	Unsaturated Polyesters	380
9.3.3	Formaldehyde Resins	382
10	ENGINEERING AND SPECIALTY POLYMERS	389
10.1	Engineering Thermoplastics	391
10.1.1	Polyamides	391
10.1.2	ABS.....	393
10.1.3	Polycarbonates.....	394
10.1.4	Modified Poly(phenylene oxide)	396
10.1.5	Acetal	397
10.1.6	Polysulfones.....	398
10.1.7	Poly(phenylene sulfide).....	400
10.1.8	Engineering Polyesters	401
10.1.9	Fluoropolymers.....	402
10.2	Specialty Polymers	404
10.2.1	Polyimides and Related Specialty Polymers.....	404
10.2.2	Ionic Polymers.....	411
10.2.3	Polyaryletherketones.....	412
10.2.4	Specialty Polyolefins.....	414
10.2.5	Inorganic Polymers.....	415
10.2.6	Liquid-Crystal Polymers	416
10.2.7	Conductive Polymers	419
10.2.8	High-Performance Fibers	421
10.2.9	Dendritic Polymers	422
11	POLYMER PROCESSING AND RHEOLOGY.....	427
11.1	Basic Processing Operations.....	428
11.1.1	Extrusion.....	428
11.1.2	Molding.....	429
11.1.3	Calendering.....	437
11.1.4	Coating	437
11.2	Introduction to Polymer Rheology	439
11.2.1	Non-Newtonian Flow.....	440

11.2.2	Viscosity of Polymer Solutions and Suspensions	445
11.2.3	Constitutive Equations.....	448
11.2.4	Elastic Properties of Polymeric Fluids	450
11.2.5	Melt Instabilities	452
11.2.6	Drag Reduction.....	453
11.3	Analysis of Simple Flows	454
11.3.1	Pressure (Poiseuille) Flow.....	457
11.3.2	Drag Flow.....	459
11.4	Rheometry	461
11.4.1	Capillary Rheometer	462
11.4.2	Couette Rheometer	465
11.4.3	Cone-and-Plate Rheometer.....	467
11.4.4	Rheometry of Polymer Solutions and Melts.....	467
11.5	Modeling of Polymer Processing Operations.....	468
11.5.1	Extrusion.....	468
11.5.2	Wire Coating.....	475
Appendices		
A.1	Relationships between WLF Parameters and Free Volume	477
A.2	Dynamic and Continuity Equations.....	479
12	POLYMERS FOR ADVANCED TECHNOLOGIES	485
12.1	Membrane Science and Technology.....	486
12.1.1	Barrier Polymers	486
12.1.2	Membrane Separations	488
12.1.3	Mechanisms of Transport.....	499
12.1.4	Membrane Preparation	510
12.2	Biomedical Engineering and Drug Delivery.....	518
12.3	Applications in Electronics.....	521
12.3.1	Electrically-Conductive Polymers.....	521
12.3.2	Electronic Shielding.....	525
12.3.3	Dielectrics.....	525
12.3.4	Encapsulation	525
12.4	Photonic Polymers	526
12.4.1	Nonlinear Optical Polymers.....	526
12.4.2	Light-Emitting Diodes.....	528
APPENDICES.....		535
A	Polymer Abbreviations.....	535
B	Representative Properties of Some Important Commercial Polymers.....	539
C	ASTM Standards for Plastics and Rubber.....	541
D	SI Units and Physical Constants	545
E	Mathematical Relationships.....	549
F	The Major Elements.....	555
INDEX		557