

Polymer Chemistry

Second Edition



Paul C. Hiemenz
Timothy P. Lodge



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Polymer Chemistry

Second Edition

Preface to the Second Edition

Polymer science is today a vibrant field. Its technological relevance is vast, yet fundamental scientific questions also abound. Polymeric materials exhibit a wealth of fascinating properties, many of which are observable just by manipulating a piece in your hands. Yet, these phenomena are all directly traceable to molecular behavior, and especially to the long chain nature of polymer molecules. The central goal of this book is to develop a molecular level understanding of the properties of polymers, beginning with the underlying chemical structures, and assuming no prior knowledge beyond undergraduate organic and physical chemistry. Although such an understanding should be firmly based in chemistry, polymer science is a highly interdisciplinary endeavor; concepts from physics, biology, materials science, chemical engineering, and statistics are all essential, and are introduced as needed.

The philosophy underlying the approach in this book is the same as that in the first edition, as laid out in the previous preface. Namely, we endeavor to develop the fundamental principles, rather than an encyclopedic knowledge of particular polymers and their applications; we seek to build a molecular understanding of polymer synthesis, characterization, and properties; we emphasize those phenomena (from the vast array of possibilities) that we judge to be the most interesting. The text has been extensively reorganized and expanded, largely to reflect the substantial advances that have occurred over the intervening years. For example, there is now an entire chapter (Chapter 4) dedicated to the topic of controlled polymerization, an area that has recently undergone a revolution. Another chapter (Chapter 11) delves into the viscoelastic properties of polymers, a topic where theoretical advances have brought deeper understanding. The book also serves as a bridge into the research literature. After working through the appropriate chapters, the student should be able to make sense of a large fraction of the articles published today in polymer science journals.

There is more than enough material in this book for a full-year graduate level course, but as with the first edition, the level is (almost) always accessible to senior level undergraduates. After an introductory chapter of broad scope, the bulk of the text may be grouped into three blocks of four chapters each. Chapter 2 through Chapter 5 describe the many ways in which polymers can be synthesized and how the synthetic route influences the resulting molecular structure. This material could serve as the basis for a single quarter or semester chemistry course that focuses on polymer synthesis. Chapter 6 through Chapter 9 emphasize the solution properties of polymers, including their conformations, thermodynamics, hydrodynamics, and light scattering properties. Much of this material is often found in a quarter or semester course introducing the physical chemistry of polymers. Chapter 10 through Chapter 13 address the solid state and bulk properties of polymers: rubber elasticity, viscoelasticity, the glass transition, and crystallization. These topics, while presented here from a physical chemical point of view, could equally well serve as the cornerstone of an introductory course in materials science or chemical engineering.

The style of the presentation, as with the previous edition, is chosen with the student in mind. To this end, we may point out the following features:

- There are over 60 worked example problems sprinkled throughout the book.
- There are 15 or more problems at the end of every chapter, to reinforce and develop further understanding; many of these are based on data from the literature.

- There are almost 200 figures, to illustrate concepts or to present experimental results from the literature.
- Studies chosen for the examples, problems, and figures range in vintage from very recent to over 50 years old; this feature serves to give the reader some sense of the historical progression of the field.
- Concise reviews of many topics (such as thermodynamics, kinetics, probability, and various experimental techniques) are given when the subject is first raised.
- A conscious effort has been made to cross-reference extensively between chapters and sections within chapters, in order to help tie the various topics together.
- Important equations and mathematical relations are almost always developed step by step. We have avoided, wherever possible, the temptation to pull equations out of a hat. Occasionally this leads to rather long stretches of algebra, which the reader is welcome to skip. However, at some point the curious student will want to know where the result comes from, and then this book should be a particularly valuable resource. Surprisingly, perhaps, the level of mathematical sophistication is only about the same as needed in undergraduate chemical thermodynamics. As a further help in this regard, an Appendix reviews many of the important mathematical tools and tricks.

An undertaking such as writing a textbook can never be completed without important contributions from many individuals. Large sections of manuscript were carefully typed by Becky Matsch and Lynne Johnsrud; Lynne also helped greatly with issues of copyright permissions and figure preparation. My colleagues past and present in the Polymer Group at Minnesota have been consistently encouraging and have provided both useful feedback and insightful examples: Frank Bates, Shura Grosberg, Marc Hillmyer, Chris Macosko, Wilmer Miller, David Morse, Steve Prager, and Matt Tirrell. In large measure the style adopted in this second edition has been inspired by the example set by my graduate instructors and mentors at the University of Wisconsin: R. Byron Bird, John Ferry, Arthur Lodge, John Schrag, and Hyuk Yu. In particular, it was in his graduate course Chemistry 664 that Hyuk Yu so ably demonstrated that no important equation need come out of thin air.

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Tim Lodge

Preface to the First Edition

Physical chemistry has been defined as that branch of science that is fundamental, molecular, and interesting. I have tried to write a polymer textbook that could be described this way also. To the extent that one subscribes to the former definition and that I have succeeded in the latter objective, then the approach of this book is physical chemical. As a textbook, it is intended for students who have completed courses in physical and organic chemistry. These are the prerequisites that define the level of the book; no special background in physics or mathematics beyond what is required for physical chemistry is assumed. Since chemistry majors generally study physical chemistry in the third year of the undergraduate curriculum, this book can serve as the text for a senior-level undergraduate or a beginning graduate-level course. Although I use chemistry courses and chemistry curricula to describe the level of this book, students majoring in engineering, materials science, physics, and various specialties in the biological sciences will also find numerous topics of interest contained herein.

Terms like “fundamental,” “molecular,” and “interesting” have different meanings for different people. Let me explain how they apply to the presentation of polymer chemistry in this text.

The words “basic concepts” in the title define what I mean by “fundamental.” This is the primary emphasis in this presentation. Practical applications of polymers are cited frequently—after all, it is these applications that make polymers such an important class of chemicals—but in overall content, the stress is on fundamental principles. “Foundational” might be another way to describe this. I have not attempted to cover all aspects of polymer science, but the topics that have been discussed lay the foundation—built on the bedrock of organic and physical chemistry—from which virtually all aspects of the subject are developed. There is an enormous literature in polymer science; this book is intended to bridge the gap between the typical undergraduate background in polymers—which frequently amounts to little more than occasional “relevant” examples in other courses—and the professional literature on the subject. Accordingly, the book assumes essentially no prior knowledge of polymers, and extends far enough to provide a usable level of understanding.

“Molecular” describes the perspective of the chemist, and it is this aspect of polymeric materials that I try to keep in view throughout the book. An engineering text might emphasize processing behavior; a physics text, continuum mechanics; a biochemistry text, physiological function. All of these are perfectly valid points of view, but they are not the approach of this book. It is polymer molecules—their structure, energetics, dynamics, and reactions—that are the primary emphasis throughout most of the book. Statistics is the type of mathematics that is natural to a discussion of molecules. Students are familiar with the statistical nature of, say, the kinetic molecular theory of gases. Similar methods are applied to other assemblies of molecules, or in the case of polymers, to the assembly of repeat units that comprise a single polymer molecule. Although we frequently use statistical arguments, these are developed quite thoroughly and do not assume any more background in this subject than is ordinarily found among students in a physical chemistry course.

The most subjective of the words which (I hope) describe this book is “interesting.” The fascinating behavior of polymers themselves, the clever experiments of laboratory researchers, and the elegant work of the theoreticians add up to an interesting total. I have tried to tell about these topics with clarity and enthusiasm, and in such a way as to make them intelligible to students. I can only hope that the reader agrees with my assessment of what is interesting.

This book was written with the student in mind. Even though “student” encompasses persons with a wide range of backgrounds, interests, and objectives; these are different than the corresponding experiences and needs of researchers. The following features have been included to assist the student:

1. Over 50 solved example problems are sprinkled throughout the book.
2. Exercises are included at the end of each chapter which are based on data from the original literature.
3. Concise reviews of pertinent aspects of thermodynamics, kinetics, spectrophotometry, etc. are presented prior to developing applications of these topics to polymers.
4. Theoretical models and mathematical derivations are developed in enough detail to be comprehensible to the student reader. Only rarely do I “pull results out of a hat,” and I scrupulously avoid saying “it is obvious that ...”
5. Generous cross-referencing and a judicious amount of repetition have been included to help unify a book which spans quite a wide range of topics.
6. SI units have been used fairly consistently throughout, and attention is paid to the matter of units whenever these become more than routine in complexity.

The book is divided into three parts of three chapters each, after an introductory chapter which contains information that is used throughout the book.

In principle, the three parts can be taken up in any order without too much interruption in continuity. Within each of the parts there is more carryover from chapter to chapter, so rearranging the sequence of topics within a given part is less convenient. The book contains more material than can be covered in an ordinary course. Chapter 1 plus two of the three parts contain about the right amount of material for one term. In classroom testing the material, I allowed the class to decide—while we worked on Chapter 1—which two of the other parts they wished to cover; this worked very well.

Material from Chapter 1 is cited throughout the book, particularly the discussion of statistics. In this connection, it might be noted that statistical arguments are developed in less detail further along in the book as written. This is one of the drawbacks of rearranging the order in which the topics are covered. Chapters 2 through 4 are concerned with the mechanical properties of bulk polymers, properties which are primarily responsible for the great practical importance of polymers. Engineering students are likely to have both a larger interest and a greater familiarity with these topics. Chapters 5 through 7 are concerned with the preparation and properties of several broad classes of polymers. These topics are closer to the interests of chemistry majors. Chapters 8 through 10 deal with the solution properties of polymers. Since many of the techniques described have been applied to biopolymers, these chapters will have more appeal to students of biochemistry and molecular biology.

Let me conclude by acknowledging the contributions of those who helped me with the preparation of this book. I wish to thank Marilyn Steinle for expertly typing the manuscript. My appreciation also goes to Carol Truett who skillfully transformed my (very) rough sketches into effective illustrations. Lastly, my thanks to Ron Manwill for preparing the index and helping me with the proofreading. Finally, let me acknowledge that some errors and/or obscurities will surely elude my efforts to eliminate them. I would appreciate reports about these from readers so that these mistakes can eventually be eliminated.

Contents

1	Introduction to Chain Molecules	1
1.1	Introduction	1
1.2	How Big Is Big?	3
1.2.1	Molecular Weight	3
1.2.2	Spatial Extent	5
1.3	Linear and Branched Polymers, Homopolymers, and Copolymers	7
1.3.1	Branched Structures	7
1.3.2	Copolymers	9
1.4	Addition, Condensation, and Natural Polymers	11
1.4.1	Addition and Condensation Polymers	11
1.4.2	Natural Polymers	13
1.5	Polymer Nomenclature	18
1.6	Structural Isomerism	20
1.6.1	Positional Isomerism	20
1.6.2	Stereo Isomerism	21
1.6.3	Geometrical Isomerism	22
1.7	Molecular Weights and Molecular Weight Averages	24
1.7.1	Number-, Weight-, and z-Average Molecular Weights	25
1.7.2	Polydispersity Index and Standard Deviation	26
1.7.3	Examples of Distributions	28
1.8	Measurement of Molecular Weight	31
1.8.1	General Considerations	31
1.8.2	End Group Analysis	32
1.8.3	MALDI Mass Spectrometry	35
1.9	Preview of Things to Come	37
1.10	Chapter Summary	38
	Problems	38
	References	41
	Further Readings	41
2	Step-Growth Polymerization	43
2.1	Introduction	43
2.2	Condensation Polymers: One Step at a Time	43
2.2.1	Classes of Step-Growth Polymers	43
2.2.2	First Look at the Distribution of Products	44
2.2.3	A First Look at Reactivity and Reaction Rates	46

2.3	Kinetics of Step-Growth Polymerization	49
2.3.1	Catalyzed Step-Growth Reactions.....	50
2.3.2	How Should Experimental Data Be Compared with Theoretical Rate Laws?	52
2.3.3	Uncatalyzed Step-Growth Reactions.....	53
2.4	Distribution of Molecular Sizes	55
2.4.1	Mole Fractions of Species	56
2.4.2	Weight Fractions of Species.....	58
2.5	Polyesters	60
2.6	Polyamides	64
2.7	Stoichiometric Imbalance	67
2.8	Chapter Summary	71
	Problems	71
	References.....	76
	Further Readings.....	76

3 Chain-Growth Polymerization.....77

3.1	Introduction.....	77
3.2	Chain-Growth and Step-Growth Polymerizations: Some Comparisons.....	77
3.3	Initiation.....	79
3.3.1	Initiation Reactions	80
3.3.2	Fate of Free Radicals	81
3.3.3	Kinetics of Initiation.....	82
3.3.4	Photochemical Initiation.....	84
3.3.5	Temperature Dependence of Initiation Rates.....	85
3.4	Termination.....	86
3.4.1	Combination and Disproportionation	86
3.4.2	Effect of Termination on Conversion to Polymer	88
3.4.3	Stationary-State Radical Concentration	89
3.5	Propagation	90
3.5.1	Rate Laws for Propagation	91
3.5.2	Temperature Dependence of Propagation Rates.....	92
3.5.3	Kinetic Chain Length.....	94
3.6	Radical Lifetime	96
3.7	Distribution of Molecular Weights.....	99
3.7.1	Distribution of <i>i</i> -mers: Termination by Disproportionation	99
3.7.2	Distribution of <i>i</i> -mers: Termination by Combination.....	102
3.8	Chain Transfer	104
3.8.1	Chain Transfer Reactions	105
3.8.2	Evaluation of Chain Transfer Constants	106
3.8.3	Chain Transfer to Polymer	108
3.8.4	Suppressing Polymerization	109
3.9	Chapter Summary	110
	Problems	110
	References.....	114
	Further Readings.....	115

4	Controlled Polymerization	117
4.1	Introduction	117
4.2	Poisson Distribution for an Ideal Living Polymerization	118
4.2.1	Kinetic Scheme	119
4.2.2	Breadth of the Poisson Distribution	122
4.3	Anionic Polymerization	126
4.4	Block Copolymers, End-Functional Polymers, and Branched Polymers by Anionic Polymerization.....	129
4.4.1	Block Copolymers	129
4.4.2	End-Functional Polymers	133
4.4.3	Regular Branched Architectures.....	135
4.5	Cationic Polymerization	137
4.5.1	Aspects of Cationic Polymerization	138
4.5.2	Living Cationic Polymerization	140
4.6	Controlled Radical Polymerization	142
4.6.1	General Principles of Controlled Radical Polymerization.....	142
4.6.2	Particular Realizations of Controlled Radical Polymerization	144
4.6.2.1	Atom Transfer Radical Polymerization (ATRP).....	144
4.6.2.2	Stable Free-Radical Polymerization (SFRP).....	145
4.6.2.3	Reversible Addition-Fragmentation Transfer (RAFT) Polymerization	146
4.7	Polymerization Equilibrium.....	147
4.8	Ring-Opening Polymerization (ROP)	150
4.8.1	General Aspects	150
4.8.2	Specific Examples of Living Ring-Opening Polymerizations.....	152
4.8.2.1	Poly(ethylene oxide).....	152
4.8.2.2	Polylactide.....	153
4.8.2.3	Poly(dimethylsiloxane).....	154
4.8.2.4	Ring-Opening Metathesis Polymerization (ROMP)	155
4.9	Dendrimers.....	156
4.10	Chapter Summary	160
	Problems	161
	References.....	163
	Further Readings.....	163
5	Copolymers, Microstructure, and Stereoregularity.....	165
5.1	Introduction	165
5.2	Copolymer Composition.....	166
5.2.1	Rate Laws	166
5.2.2	Composition versus Feedstock	168
5.3	Reactivity Ratios.....	170
5.3.1	Effects of r Values.....	171
5.3.2	Relation of Reactivity Ratios to Chemical Structure.....	173
5.4	Resonance and Reactivity.....	175
5.5	A Closer Look at Microstructure	179
5.5.1	Sequence Distributions	180
5.5.2	Terminal and Penultimate Models	183

5.6	Copolymer Composition and Microstructure: Experimental Aspects	185
5.6.1	Evaluating Reactivity Ratios from Composition Data	185
5.6.2	Spectroscopic Techniques.....	188
5.6.3	Sequence Distribution: Experimental Determination	190
5.7	Characterizing Stereoregularity	193
5.8	A Statistical Description of Stereoregularity	196
5.9	Assessing Stereoregularity by Nuclear Magnetic Resonance.....	200
5.10	Ziegler–Natta Catalysts	205
5.11	Single-Site Catalysts	208
5.12	Chapter Summary	211
	Problems	212
	References.....	216
	Further Readings.....	216
6	Polymer Conformations	217
6.1	Conformations, Bond Rotation, and Polymer Size	217
6.2	Average End-to-End Distance for Model Chains	219
Case 6.2.1	The Freely Jointed Chain	220
Case 6.2.2	The Freely Rotating Chain	221
Case 6.2.3	Hindered Rotation Chain	222
6.3	Characteristic Ratio and Statistical Segment Length.....	223
6.4	Semiflexible Chains and the Persistence Length.....	225
6.4.1	Persistence Length of Flexible Chains.....	227
6.4.2	Worm-Like Chains	228
6.5	Radius of Gyration.....	230
6.6	Spheres, Rods, and Coils	234
6.7	Distributions for End-to-End Distance and Segment Density	235
6.7.1	Distribution of the End-to-End Vector.....	236
6.7.2	Distribution of the End-to-End Distance.....	239
6.7.3	Distribution about the Center of Mass	240
6.8	Self-Avoiding Chains: A First Look	241
6.9	Chapter Summary	242
	Problems	242
	References.....	244
	Further Readings.....	245
7	Thermodynamics of Polymer Solutions	247
7.1	Review of Thermodynamic and Statistical Thermodynamic Concepts	247
7.2	Regular Solution Theory	249
7.2.1	Regular Solution Theory: Entropy of Mixing.....	249
7.2.2	Regular Solution Theory: Enthalpy of Mixing	251
7.3	Flory–Huggins Theory.....	254
7.3.1	Flory–Huggins Theory: Entropy of Mixing by a Quick Route	255
7.3.2	Flory–Huggins Theory: Entropy of Mixing by a Longer Route	255
7.3.3	Flory–Huggins Theory: Enthalpy of Mixing	257
7.3.4	Flory–Huggins Theory: Summary of Assumptions	258

7.4	Osmotic Pressure	258
7.4.1	Osmotic Pressure: General Case	259
7.4.1.1	Number-Average Molecular Weight	261
7.4.2	Osmotic Pressure: Flory–Huggins Theory	263
7.5	Phase Behavior of Polymer Solutions	264
7.5.1	Overview of the Phase Diagram	265
7.5.2	Finding the Binodal	268
7.5.3	Finding the Spinodal	269
7.5.4	Finding the Critical Point	270
7.5.5	Phase Diagram from Flory–Huggins Theory	271
7.6	What's in χ ?	275
7.6.1	χ from Regular Solution Theory	275
7.6.2	χ from Experiment	276
7.6.3	Further Approaches to χ	278
7.7	Excluded Volume and Chains in a Good Solvent	280
7.8	Chapter Summary	283
	Problems	284
	References	287
	Further Readings	288
8	Light Scattering by Polymer Solutions	289
8.1	Introduction: Light Waves	289
8.2	Basic Concepts of Scattering	291
8.2.1	Scattering from Randomly Placed Objects	292
8.2.2	Scattering from a Perfect Crystal	292
8.2.3	Origins of Incoherent and Coherent Scattering	293
8.2.4	Bragg's Law and the Scattering Vector	294
8.3	Scattering by an Isolated Small Molecule	296
8.4	Scattering from a Dilute Polymer Solution	298
8.5	The Form Factor and the Zimm Equation	304
8.5.1	Mathematical Expression for the Form Factor	305
8.5.2	Form Factor for Isotropic Solutions	306
8.5.3	Form Factor as $qR_g \rightarrow 0$	307
8.5.4	Zimm Equation	307
8.5.5	Zimm Plot	308
8.6	Scattering Regimes and Particular Form Factors	312
8.7	Experimental Aspects of Light Scattering	314
8.7.1	Instrumentation	316
8.7.2	Calibration	317
8.7.3	Samples and Solutions	319
8.7.4	Refractive Index Increment	319
8.8	Chapter Summary	320
	Problems	321
	References	325
	Further Readings	325
9	Dynamics of Dilute Polymer Solutions	327
9.1	Introduction: Friction and Viscosity	327
9.2	Stokes' Law and Einstein's Law	330

9.2.1	Viscous Forces on Rigid Spheres	331
9.2.2	Suspension of Spheres.....	332
9.3	Intrinsic Viscosity	334
9.3.1	General Considerations	334
9.3.2	Mark–Houwink Equation.....	336
9.4	Measurement of Viscosity	341
9.4.1	Poiseuille Equation and Capillary Viscometers	341
9.4.2	Concentric Cylinder Viscometers	345
9.5	Diffusion Coefficient and Friction Factor	346
9.5.1	Tracer Diffusion and Hydrodynamic Radius.....	347
9.5.2	Mutual Diffusion and Fick’s Laws	348
9.6	Dynamic Light Scattering	354
9.7	Hydrodynamic Interactions and Draining	357
9.8	Size Exclusion Chromatography (SEC)	360
9.8.1	Basic Separation Process	361
9.8.2	Separation Mechanism	365
9.8.3	Two Calibration Strategies	367
9.8.3.1	Limitations of Calibration by Standards.....	367
9.8.3.2	Universal Calibration	368
9.8.4	Size Exclusion Chromatography Detectors	369
9.8.4.1	RI Detector	369
9.8.4.2	UV–Vis Detector.....	370
9.8.4.3	Light Scattering Detector.....	371
9.8.4.4	Viscometer.....	372
9.9	Chapter Summary.....	372
	Problems.....	373
	References	378
	Further Readings	379
10	Networks, Gels, and Rubber Elasticity	381
10.1	Formation of Networks by Random Cross-Linking.....	381
10.1.1	Definitions	381
10.1.2	Gel Point.....	383
10.2	Polymerization with Multifunctional Monomers	386
10.2.1	Calculation of the Branching Coefficient.....	387
10.2.2	Gel Point.....	388
10.2.3	Molecular-Weight Averages	389
10.3	Elastic Deformation	392
10.4	Thermodynamics of Elasticity	394
10.4.1	Equation of State	394
10.4.2	Ideal Elastomers	396
10.4.3	Some Experiments on Real Rubbers	397
10.5	Statistical Mechanical Theory of Rubber Elasticity: Ideal Case	398
10.5.1	Force to Extend a Gaussian Chain	400
10.5.2	Network of Gaussian Strands.....	402
10.5.3	Modulus of the Gaussian Network	403
10.6	Further Developments in Rubber Elasticity	406
10.6.1	Non-Gaussian Force Law.....	406
10.6.2	Front Factor	407

10.6.3	Network Defects.....	408
10.6.4	Mooney–Rivlin Equation.....	409
10.7	Swelling of Gels.....	410
10.7.1	Modulus of a Swollen Rubber.....	411
10.7.2	Swelling Equilibrium.....	412
10.8	Chapter Summary.....	414
	Problems.....	416
	References.....	418
	Further Readings.....	418
11	Linear Viscoelasticity	419
11.1	Basic Concepts.....	419
11.1.1	Stress and Strain.....	421
11.1.2	Viscosity, Modulus, and Compliance.....	421
11.1.3	Viscous and Elastic Responses.....	422
11.2	Response of the Maxwell and Voigt Elements.....	423
11.2.1	Transient Response: Stress Relaxation.....	423
11.2.2	Transient Response: Creep.....	425
11.2.3	Dynamic Response: Loss and Storage Moduli.....	426
11.2.4	Dynamic Response: Complex Modulus and Complex Viscosity.....	429
11.3	Boltzmann Superposition Principle.....	430
11.4	Bead–Spring Model.....	432
11.4.1	Ingredients of the Bead–Spring Model.....	432
11.4.2	Predictions of the Bead–Spring Model.....	434
11.5	Zimm Model for Dilute Solutions, Rouse Model for Unentangled Melts.....	439
11.6	Phenomenology of Entanglement.....	444
11.6.1	Rubbery Plateau.....	444
11.6.2	Dependence of M_e on Molecular Structure.....	447
11.7	Reptation Model.....	450
11.7.1	Reptation Model: Longest Relaxation Time and Diffusivity.....	451
11.7.2	Reptation Model: Viscoelastic Properties.....	453
11.7.3	Reptation Model: Additional Relaxation Processes.....	456
11.8	Aspects of Experimental Rheometry.....	458
11.8.1	Shear Sandwich and Cone and Plate Rheometers.....	458
11.8.2	Further Comments about Rheometry.....	459
11.9	Chapter Summary.....	460
	Problems.....	461
	References.....	464
	Further Readings.....	464
12	Glass Transition.....	465
12.1	Introduction.....	465
12.1.1	Definition of a Glass.....	465
12.1.2	Glass and Melting Transitions.....	466
12.2	Thermodynamic Aspects of the Glass Transition.....	468
12.2.1	First-Order and Second-Order Phase Transitions.....	469

12.2.2	Kauzmann Temperature	471
12.2.3	Theory of Gibbs and DiMarzio	472
12.3	Locating the Glass Transition Temperature	474
12.3.1	Dilatometry	474
12.3.2	Calorimetry	476
12.3.3	Dynamic Mechanical Analysis	478
12.4	Free Volume Description of the Glass Transition.....	479
12.4.1	Temperature Dependence of the Free Volume	480
12.4.2	Free Volume Changes Inferred from the Viscosity	481
12.4.3	Williams–Landel–Ferry Equation	483
12.5	Time–Temperature Superposition.....	486
12.6	Factors that Affect the Glass Transition Temperature	491
12.6.1	Dependence on Chemical Structure.....	491
12.6.2	Dependence on Molecular Weight	492
12.6.3	Dependence on Composition	492
12.7	Mechanical Properties of Glassy Polymers	496
12.7.1	Basic Concepts	496
12.7.2	Crazing, Yielding, and the Brittle-to-Ductile Transition	498
12.7.3	Role of Chain Stiffness and Entanglements	501
12.8	Chapter Summary.....	504
	Problems.....	505
	References	508
	Further Readings	508
13	Crystalline Polymers.....	511
13.1	Introduction and Overview	511
13.2	Structure and Characterization of Unit Cells	513
13.2.1	Classes of Crystals	513
13.2.2	X-Ray Diffraction	515
13.2.3	Examples of Unit Cells	518
13.3	Thermodynamics of Crystallization: Relation of Melting Temperature to Molecular Structure	521
13.4	Structure and Melting of Lamellae.....	526
13.4.1	Surface Contributions to Phase Transitions.....	526
13.4.2	Dependence of T_m on Lamellar Thickness.....	527
13.4.3	Dependence of T_m on Molecular Weight	530
13.4.4	Experimental Characterization of Lamellar Structure	532
13.5	Kinetics of Nucleation and Growth	536
13.5.1	Primary Nucleation	537
13.5.2	Crystal Growth	539
13.6	Morphology of Semicrystalline Polymers	545
13.6.1	Spherulites	545
13.6.2	Nonspherulitic Morphologies.....	548
13.7	Kinetics of Bulk Crystallization	551
13.7.1	Avrami Equation	552

13.7.2 Kinetics of Crystallization: Experimental Aspects	556
13.8 Chapter Summary.....	561
Problems.....	562
References	565
Further Readings	565
Appendix	567
A.1 Series Expansions	567
A.2 Summation Formulae.....	568
A.3 Transformation to Spherical Coordinates.....	569
A.4 Some Integrals of Gaussian Functions	570
A.5 Complex Numbers	572
Index	575