
Contents

Preface	V
Topics that are Different for Polymers and Small Molecules	VII
General References	VIII
Acknowledgments	VIII
 1 Atoms, Small, and Large Molecules	
1.1 Microscopic Description of Matter and History of Polymer Science	
1.1.1 History	1
1.1.2 Molecular Structure and Bonding	3
1.1.3 Classification Scheme for Molecules	6
1.1.4 The History of Covalent Structures	9
1.1.5 The History of Natural Polymers	9
1.1.6 The History of Synthetic Polymers	11
1.2 Nomenclature	
1.2.1 Source- and Structure-based Names	13
1.2.2 Copolymers and Isomers	22
1.2.3 Branched, Ladder, and Network Polymers	24
1.2.4 Funny Polymers	25
1.3 Chain Statistics of Macromolecules	
1.3.1 Molecular Mass Distribution	27
1.3.2 Random Flight	31
1.3.3 Mean Square Distance from the Center of Gravity	32
1.3.4 Distribution Functions	33
1.3.5 Steric Hindrance and Rotational Isomers	37
1.3.6 Monte Carlo Simulations	40
1.3.7 Molecular Mechanics Calculations	41
1.3.8 Molecular Dynamics Simulations	43
1.3.9 Equivalent Freely Jointed Chain	47
1.3.10 Stiff Chain Macromolecules	47
1.4 Size and Shape Measurement	
1.4.1 Introduction	50
1.4.2 Light Scattering	50
1.4.3 Freezing Point Lowering and Boiling Point Elevation	58
1.4.4 Size-exclusion Chromatography	62
1.4.5 Solution Viscosity	63
1.4.6 Membrane Osmometry	65
1.4.7 Other Characterization Techniques	66
 References	68

2 Basics of Thermal Analysis

2.1	Heat, Temperature, and Thermal Analysis	
2.1.1	History	71
2.1.2	The Variables of State	75
2.1.3	The Techniques of Thermal Analysis	76
2.1.4	Temperature	79
2.1.5	Heat (The First Law of Thermodynamics)	81
2.1.6	The Future of Thermal Analysis	84
2.2	The Laws of Thermodynamics	
2.2.1	Description of Systems	88
2.2.2	The First Law of Thermodynamics	90
2.2.3	The Second Law of Thermodynamics	91
2.2.4	The Third Law of Thermodynamics	94
2.2.5	Multi-component Systems	96
2.2.6	Multi-phase Systems	98
2.3	Heat Capacity	
2.3.1	Measurement of Heat Capacity	101
2.3.2	Thermodynamic Theory	104
2.3.3	Quantum Mechanical Descriptions	106
2.3.4	The Heat Capacity of Solids	111
2.3.5	Complex Heat Capacity	117
2.3.6	The Crystallinity Dependence of Heat Capacities	118
2.3.7	ATHAS	121
2.3.8	Polyoxide Heat Capacities	128
2.3.9	Heat Capacities of Liquids	131
2.3.10	Examples of the Application of ATHAS	134
	Polytetrafluoroethylene	134
	Poly(oxybenzoate-co-oxy-naphthoate)	134
	Large-amplitude motions of polyethylene	136
	Polymethionine	136
	MBPE-9	137
	Liquid selenium	138
	Poly(styrene-co-1,4-butadiene)	139
	Hypothetical entropy of the liquid at absolute zero of temperature	140
	Starch and water	142
	Conclusions	144
2.4	Nonequilibrium Thermodynamics	
2.4.1	Flux and Production	147
2.4.2	Melting of Lamellar Crystals	148
2.4.3	Experimental Data	154
2.4.4	Internal Variables	155
2.4.5	Transport and Relaxation	158
2.4.6	Relaxation Times	159
2.5	Phases and Their Transitions	
2.5.1	Description of Phases	162

2.5.2	Phases of Different Sizes	167
2.5.3	Mesophases	169
2.5.4	Mesophase Glasses	175
2.5.5	Thermodynamics and Motion	176
2.5.6	Glass Transitions	178
2.5.7	First-order Transitions	181
	References	184
3	Dynamics of Chemical and Phase Changes	
3.1	Stepwise and Step Reactions	
3.1.1	Stepwise Reactions	189
3.1.2	Mechanism of Step Reactions	193
3.1.3	Examples	196
3.1.4	Conditions	198
3.1.5	Reaction Rates	200
3.1.6	Lithium Phosphate Polymerization	201
3.2	Chain and Matrix Reactions	
3.2.1	Mechanism of Chain Reactions	206
3.2.2	Kinetics	212
3.2.3	Equilibrium	214
3.2.4	Chain Reactions without Termination	215
3.2.5	Emulsion Polymerization	217
3.2.6	Matrix Reaction	218
3.3	Molecular Mass Distributions	
3.3.1	Number and Mass Fractions, Step Reactions	219
3.3.2	Number and Mass Fractions, Chain Reactions	221
3.3.3	Step Reaction Averages	224
3.3.4	Chain Reaction Averages	225
3.4	Copolymerization and Reactions of Polymers	
3.4.1	Chain Reaction Copolymers	227
3.4.2	Step Reaction Copolymers	229
3.4.3	Gelation	230
3.4.4	Decomposition	231
3.4.5	Polymer Reactions	233
3.5	Crystal and Molecular Nucleation Kinetics	
3.5.1	Observation of Nucleation and Crystal Growth	238
3.5.2	Evaluation of Nucleation Rates	240
3.5.3	Mathematical Description of Primary Nucleation	242
3.5.4	Heterogeneous Nucleation	246
3.5.5	Secondary Nucleation	249
3.5.6	Molecular Nucleation	253
3.6	Crystallization and Melting Kinetics	
3.6.1	Linear Melting and Crystallization Rates	255
3.6.2	Directional Dependence of Crystallization	256
3.6.3	Diffusion Control of Crystallization	257

3.6.4	Growth of Spherulites	259
3.6.5	Avrami Equation	260
3.6.6	Nonisothermal Kinetics	263
3.6.7	Experimental Data	264
	References	276
4	Thermal Analysis Tools	
4.1	Thermometry and Dilatometry	
4.1.1	Principle and History of Thermometry	279
4.1.2	Liquid-in-glass Thermometers	283
4.1.3	Resistance Thermometers and Thermocouples	285
4.1.4	Applications of Thermometry	290
4.1.5	Principle and History of Dilatometry	291
4.1.6	Length, Volume, and Density Measurement	293
4.1.7	Applications of Dilatometry	298
4.2	Calorimetry	
4.2.1	Principle and History	304
4.2.2	Isothermal and Isoperibol Calorimeters	307
4.2.3	Loss Calculation	310
4.2.4	Adiabatic Calorimetry	312
4.2.5	Compensating Calorimeters	314
4.2.6	Modern Calorimeters	317
4.2.7	Applications of Calorimetry	319
	Purity analysis	319
	Thermochemistry	320
	Thermodynamic functions of three allotropes of carbon	325
	Thermodynamic functions of paraffins	327
4.3	Differential Scanning Calorimetry	
4.3.1	Principle and History	329
4.3.2	Heat-flux Calorimetry	331
4.3.3	Power Compensation DSC	335
4.3.4	Calibration	338
4.3.5	Mathematical Treatment	340
4.3.6	DSC Without Temperature Gradient	344
4.3.7	Applications	349
	Heat capacity	349
	Finger printing of materials	350
	Quantitative analysis of the glass transition	354
	Quantitative analysis of the heat of fusion	355
4.4	Temperature-modulated Calorimetry	
4.4.1	Principles of Temperature-modulated DSC	359
4.4.2	Mathematical Treatment	362
4.4.3	Data Treatment and Modeling	369
4.4.4	Instrumental Problems	373
4.4.5	Heat Capacity Measurement	385
4.4.6	Glass Transition Measurement	388

4.4.7	First-order Transition Analysis	396
4.4.8	Chemical Reactions	402
4.5	Thermomechanical Analysis, DMA and DETA	
4.5.1	Principle of TMA	404
4.5.2	Instrumentation of TMA	406
4.5.3	Applications of TMA	408
4.5.4	Principles and Instrumentation of DMA	412
4.5.5	Applications of DMA	419
4.5.6	DETA	424
4.6	Thermogravimetry	
4.6.1	Principle and History	428
4.6.2	Instrumentation	430
4.6.3	Standardization and Technique	437
4.6.4	Decomposition	438
4.6.5	Coupled Thermogravimetry and Differential Thermal Analysis	439
4.6.6	Applications of Thermogravimetry	443
	Calcium oxalate/carbonate decomposition	444
	Lifetime prediction	446
	Summary of Chapter 4	448
	References	450

5 Structure and Properties of Materials

5.1	Crystal Structure	
5.1.1	Introduction	455
5.1.2	Lattice Description	457
5.1.3	Unit Cells	457
5.1.4	Miller Indices	458
5.1.5	Symmetry Operations	460
5.1.6	Helices	463
5.1.7	Packing in Crystals	468
5.1.8	Packing of Helices	471
5.1.9	Selected Unit Cells	474
5.1.10	Isomorphism	481
5.1.11	Crystals with Irregular Motifs	483
5.2	Crystal Morphology	
5.2.1	Crystal Habit	486
5.2.2	Molecular Macroconformation	486
5.2.3	Fold Length	488
5.2.4	Lamellar Crystals	493
5.2.5	Dendrites and Spherulites	497
5.2.6	Fibers	503
5.2.7	Isometric Crystals	508
5.3	Defects in Polymer Crystals	
5.3.1	Materials Properties	512
5.3.2	Crystallinity Analysis	512
5.3.3	Summary of Defect Types	516

5.3.4	Supercomputer Simulation of Crystal Defects	524
5.3.5	Deformation of Polymers	530
5.3.6	Ultimate Strength of Polymers	533
5.4	Transitions and Prediction of Melting	
5.4.1	Transitions of Macromolecules	536
5.4.2	Crystals of Spherical Motifs	538
5.4.3	Crystals of Non-spherical Motifs	541
5.4.4	Crystals of Linear Hydrocarbons	542
5.4.5	Crystals of Macromolecules	544
5.5	Mesophases and Their Transitions	
5.5.1	Multiple Transitions	547
5.5.2	Classes of Mesophases	551
5.5.3	Jump-motion in Crystals	555
5.5.4	Conformational Disorder	558
5.5.5	Examples	561
	Summary of the section on morphology	571
5.6	Melts and Glasses	
5.6.1	Structure of the Amorphous Phase	572
5.6.2	Properties of the Amorphous Phase	574
5.6.3	Viscosity	575
5.6.4	Energy Elasticity	578
5.6.5	Entropy Elasticity	579
5.6.6	Viscoelasticity	583
	References	586
6	Single Component Materials	
6.1	The Order of Transitions	
6.1.1	Review of Thermodynamics, Motion, and Reversibility	591
6.1.2	First Order Phase Transition	593
6.1.3	Glass Transitions	597
	The hole model of the glass transition	598
	Enthalpy relaxation	599
	The kinetics of the number of holes	600
	Effect of the size of the phase on the glass transition	605
	Rigid-amorphous fraction, RAF, in semicrystalline polymers	607
	Differences in T_g by DSC and DMA	609
6.2	Size, Extension, and Time Effects During Fusion	
6.2.1	Melting of Polyethylene	611
6.2.2	Reversible Melting and Poor Crystals	624
	Poly(oxyethylene)	624
	Polyterephthalates	628
	Polynaphthoate	634
	Polycarbonate	637
	Poly(phenylene oxide)	639
	Poly(ϵ -caprolactone)	641
	Polypropylenes	644

Decoupling of segments of polymer chains	649
Poor crystals	652
6.2.3 Annealing and Recrystallization Effects	655
6.2.4 Melting of Poly(oxymethylene)	666
6.2.5 Melting of PEEK	668
6.2.6 Melting of Fibers	672
6.3 Analysis of the Sample History Through Study of the Glass Transition	
6.3.1 Time and Temperature Effects	682
6.3.2 Modeling of the Glass Transition	686
6.3.3 Pressure and Strain Effects	689
6.3.4 Crystallinity Effects	693
6.3.5 Network Effects	698
References	701

7 Multiple Component Materials

7.1 Macromolecular Phase Diagrams	
7.1.1 Phase Diagrams	706
7.1.2 Flory-Huggins Equation	709
7.1.3 Upper and Lower Critical Temperatures	712
7.1.4 Phase Diagrams with Low-mass Compounds	714
7.1.5 Phase Diagrams with Low-mass Homologs	717
7.1.6 Block Copolymers	723
7.2 Melting Transitions of Copolymers	
7.2.1 Theory of Copolymer Melting and Crystallization	725
7.2.2 Applications	733
LLDPE	733
POBcoON	743
7.2.3 Melting Transitions of Block Copolymers	747
7.2.4 Melting Transitions of Regular Copolymers	756
7.3 Glass Transitions of Copolymers, Solutions, and Blends	
7.3.1 Theory of Glass Transitions	759
7.3.2 Glass Transitions of Solutions	763
7.3.3 Glass Transitions of Copolymers	766
7.3.4 Glass Transitions of Block Copolymers	768
7.3.5 Glass Transitions of Multi-phase Systems	772
References	774

Appendices

A.1 Table of Thermal Properties of Linear Macromolecules and Related Small Molecules—The ATHAS Data Bank	777
A.2 Radiation Scattering (Essay by W. Heller)	801
A.3 Derivation of the Rayleigh Ratio	806
A.4 Neural Network Predictions	811

A.5	Legendre Transformations, Maxwell Relations, Linking of Entropy and Probability, and Derivation of (dS/dT)	813
A.6	Boltzmann Distribution, Harmonic Vibration, Complex Numbers, and Normal Modes	815
A.7	Summary of the Basic Kinetics of Chemical Reactions	817
A.8	The ITS 1990 and the Krypton-86 Length Standard	818
A.9	Development of Classical DTA to DSC	820
A.10	Examples of DTA and DSC under Extreme Conditions	824
A.11	Description of an Online Correction of the Heat-flow Rate	831
A.12	Derivation of the Heat-flow Equations	835
A.13	Description of Sawtooth-modulation Response	837
A.14	An Introduction to Group Theory, Definitions of Configurations and Conformations, and a Summary of Rational and Irrational Numbers ...	848
A.15	Summary of Birefringence and Polarizing Microscopy	850
A.16	Summary of X-ray Diffraction and Interference Effects	851
A.17	Optical Analog of Electron Double Diffraction to Produce Moiré Patterns	852
Substance Index		855
Subject Index		875