

CONTENTS

Preface	V
Acknowledgements	IX
Chapter 1. Introduction	1
A. Properties of polymers	1
B. Group contribution techniques	4
1. Basic technique	4
2. An extension	6
C. Topological technique	7
1. Topology and geometry	7
2. Graph theory and connectivity indices	8
3. Nature and scope of the new approach	9
D. Interconversion between mole, weight and volume fractions	15
E. Outline of the remaining chapters of this book	16
References and notes for Chapter 1	19
Chapter 2. Topological Method for Structure-Property Correlations	22
A. Review of connectivity index calculations for simple molecules	22
B. Extension of connectivity index calculations to polymers	27
C. General forms of the correlations in terms of connectivity indices	46
D. Backbone and side group portions of the connectivity indices	51
E. Shortest path across the backbone of a polymeric repeat unit	54
F. Extensions for the calculation of some conformation-related properties	55
References and notes for Chapter 2	56
Chapter 3. Volumetric Properties	57
A. Background information	57
1. Definitions and phenomenology	57
2. Simple empirical relationships	61
3. Synopsis of further treatment of volumetric properties	65
B. Correlation for the van der Waals volume	66
1. Development of the correlation	66
2. Nature of the correction terms used in the correlations	74
3. Examples of the predictive use of the correlation	77

C. Correlation for the molar volume at room temperature	78
D. Final equations for temperature dependences of volumetric properties	86
1. Introductory remarks	86
2. Polymers with $T_g \geq 298\text{K}$	87
3. Polymers with $T_g < 298\text{K}$	88
E. Pressure-volume-temperature relationships	88
F. Effects of crystallinity	95
References and notes for Chapter 3	99

Chapter 4. Thermodynamic Properties**102**

A. Background information	102
1. Thermophysical properties	102
2. Thermodynamic properties	103
3. Heat capacity	106
B. Improvements in the ability to predict the heat capacities of polymers	110
C. Rotational degrees of freedom of the backbone and the side groups	112
D. Correlation for the heat capacity of "solid" polymers at room temperature	115
E. Correlation for the heat capacity of "liquid" polymers at room temperature	120
F. Correlation for the change in the heat capacity at the glass transition	126
G. Equations for thermodynamic properties as functions of temperature	132
References and notes for Chapter 4	133

Chapter 5. Cohesive Energy and Solubility Parameter**135**

A. Background information	135
1. Cohesive energy	135
2. Components of the cohesive energy	136
3. Solubility parameter	137
4. Components of the solubility parameter	142
5. Improvements in the ability to predict the cohesive energies and solubility parameters of polymers	144
B. Correlation for the Fedors-type cohesive energy	146
C. Correlation for the van Krevelen-type cohesive energy	151
D. Solubility parameter calculations	158
E. Correlation for dispersion component of the molar attraction constant	162
References and notes for Chapter 5	167

Contents

Chapter 6. Transition and Relaxation Temperatures	169
A. Background information	169
1. Operational definition of the glass transition	169
2. Practical importance and common methods for measurement of T_g	170
3. Key physical aspects of the glass transition	173
4. Fundamental theoretical considerations concerning the glass transition	174
5. Quantitative structure-property relationships for T_g	175
6. Detailed simulations of the glass transition	177
7. Comprehensive list of factors determining T_g	179
8. Outline of remainder of this chapter	182
B. Correlation for the glass transition temperature	182
1. Outline	182
2. The structural parameters	187
3. The correlation	198
C. Effects of number-average molecular weight	211
D. Effects of plasticization	217
E. Effects of crosslinking	219
1. A correlation	219
2. Other developments	226
F. Effects of tacticity	228
G. Secondary relaxations	231
H. Crystalline melting temperature	234
1. Homopolymers	234
2. Copolymers and crosslinked polymers	239
I. T_m/T_g as indicator of intrinsic crystallizability	241
J. Roles of T_g and T_m in determining the crystallization kinetics	245
1. Introductory remarks	245
2. Overall rate for isothermal crystallization	245
3. Overall rate for non-isothermal crystallization	248
4. Nucleation	249
5. Isothermal crystal growth rate from existing nuclei	252
References and notes for Chapter 6	252
Chapter 7. Surface Tension and Interfacial Tension	261
A. Surface tension	261
1. Total surface tension	261
2. Components of surface tension	266

B. Interfacial tension	269
C. Adhesion	272
D. Improvements in the ability to predict surface tension and interfacial tension	273
E. Approximate "master curve" as a function of reduced temperature	274
F. Correlation for the molar parachor	276
G. Frontiers of interfacial modeling	283
References and notes for Chapter 7	290
Chapter 8. Optical Properties	292
A. Background information	292
1. Types of optical properties	292
2. Refractive index and molar refraction	293
3. Optical losses	296
4. Stress-optic coefficient	298
B. Improvements in the ability to predict the refractive indices of polymers	301
C. Correlation for the refractive index at room temperature	302
D. Example of application: specific refractive index increments of solutions	310
E. Calculation of the molar refraction	317
References and notes for Chapter 8	321
Chapter 9. Electrical Properties	324
A. Background information	324
B. Correlation for the dielectric constant at room temperature	330
C. Calculation of the molar polarization	336
D. Calculation of the effective dipole moment	339
E. Dissipation factor	343
F. Dielectric strength	353
References and notes for Chapter 9	355
Chapter 10. Magnetic Properties	358
A. Background information	358
B. Correlation for the molar diamagnetic susceptibility	360
References and notes for Chapter 10	367
Chapter 11. Mechanical Properties	368
A. Stress-strain behavior of polymers	368

B. Small-strain behavior: moduli, compliances, and Poisson's ratio	371
1. Definitions and phenomenology	371
2. Structure-property relationships for glassy polymers	375
a. Introductory remarks	375
b. Correlations by Seitz for the elastic moduli	375
c. Bulk modulus via molar Rao function	379
d. Shear modulus via molar Hartmann function	386
e. Thermosets	393
3. Structure-property relationships for rubbery polymers	394
a. Shear modulus	394
b. Bulk modulus and Young's modulus	398
4. Effects of anisotropy (orientation)	400
C. Large-strain behavior: failure mechanisms	401
1. Phenomenology	401
a. General mechanisms	401
b. Toughening by incorporating another phase	411
2. Structure-property relationships for the brittle fracture stress	414
3. Structure-property relationships for the yield stress of thermoplastics	416
4. Attempts to model rate dependence of yield stress of thermoplastics	419
5. Structure-property relationships for the crazing stress	421
6. Stress-strain curves of elastomers	424
7. Ductile thermoplastics at large extension ratios	431
8. Thermoset resins	433
a. General observations	433
b. Yield stress	436
c. Fracture toughness	437
d. Residual stresses	441
9. Effects of anisotropy (orientation)	444
D. Creep, stress relaxation, fatigue and durability	445
E. Improvements in the ability to predict the mechanical properties	453
References and notes for Chapter 11	454

Chapter 12. Properties of Polymers in Dilute Solutions

A. Background information	464
1. General considerations	464
2. Steric hindrance parameter	466
3. Characteristic ratio	467
4. Persistence length	468

5. Radius of gyration	469
6. Statistical chain (Kuhn) segment length	470
7. Intrinsic viscosity under theta conditions	471
8. Intrinsic viscosity away from theta conditions	473
9. Solution viscosity at small but finite concentrations	478
B. Correlation for the steric hindrance parameter	482
1. Definitions of the fitting variables	482
2. Development of the correlation	483
C. Calculation of the characteristic ratio	488
D. Correlation for the molar stiffness function	491
References and notes for Chapter 12	497

Chapter 13. Shear Viscosity

499

A. Definitions and general considerations	499
B. Dependence of melt zero-shear viscosity on average molecular weight	502
1. Dependence on critical molecular weight	502
2. A correlation for the critical molecular weight	503
3. Alternative correlation for critical molecular weight	504
C. Dependence of melt zero-shear viscosity on temperature	505
1. General relationships	505
2. Estimation of $E_{\eta\infty}$ without using group contributions	508
D. Dependence of melt zero-shear viscosity on hydrostatic pressure	519
E. Melt zero-shear viscosity: summary, examples and possible refinements	520
F. Combined effects of shear rate and polydispersity on melt viscosity	525
G. Zero-shear viscosity of concentrated polymer solutions	528
H. Shear viscosity of dispersions of solid particles in fluids	532
References and notes for Chapter 13	541

Chapter 14. Thermal Conductivity and Thermal Diffusivity

543

A. Background information	543
1. Definition and general considerations	543
2. Temperature dependence of the thermal conductivities of amorphous polymers	546
3. Thermal conductivities of amorphous polymers at room temperature	548
4. Improvements in the ability to predict the thermal conductivities of polymers	549
B. Direct correlation for the thermal conductivity at room temperature	550
References and notes for Chapter 14	554

Contents**XVII**

Chapter 15. Transport of Small Penetrant Molecules	555
A. Background information	555
1. Definitions and major industrial applications	555
2. The solution-diffusion mechanism	556
3. Theories, simulations and empirical correlations	561
B. Correlations for the permeability at room temperature	564
References and notes for Chapter 15	572
Chapter 16. Thermal Stability	576
A. Background information	576
1. Definitions	576
2. Measurement of thermal and thermooxidative stability	576
3. Mechanisms of weight loss during degradation	578
4. Effects of structure on thermal and thermooxidative stability	580
a. Qualitative summary of trends	580
b. Reactive molecular dynamics simulations	581
c. Quantitative structure-property relationships	583
B. Correlation for the molar thermal decomposition function	585
References and notes for Chapter 16	596
Chapter 17. Extensions, Generalizations, Shortcuts, and Possible Directions for Future Work	598
A. Introduction	598
B. Examples of designer correlations	600
1. Glass transition temperatures of a family of polyimides	600
2. Glass transition temperatures of polyesters	601
3. Fedors-type cohesive energies of hydrocarbon polymers	603
4. Glass transition temperatures of hydrogenated styrenic polymers	607
C. Combination of new correlations and group contributions	608
1. Calculation of group contributions from the new correlations	608
2. Combined use of new correlations and group contributions	611
D. Calculation of the properties of alternating copolymers	612
E. Calculation of the properties of random copolymers	614
F. A software package implementing the key correlations	617
G. Utilization to provide input parameters for other types of methods	621
H. Possible directions for future work	622
References and notes for Chapter 17	625

Chapter 18. Detailed Examples	627
A. Introductory remarks	627
B. Polystyrene	627
C. Random copolymers of styrene and oxytrimethylene	641
Chapter 19. Morphologies of Multiphase Materials	649
A. Materials and morphologies	649
B. Interplay between thermodynamic and kinetic factors	655
C. Prediction of morphologies	657
1. Introductory remarks	657
2. Methods and examples of their use	657
3. Common themes	668
References and notes for Chapter 19	670
Chapter 20. Properties of Multiphase Materials	675
A. General considerations	675
B. Analytical expressions	676
1. Thermoelastic properties	676
2. Transport properties	689
C. Numerical simulations	691
1. Thermoelastic and transport properties	691
2. Mechanical properties under large deformation	694
a. Overview of various methods	694
b. Understanding the influence of interfaces via simulations	696
References and notes for Chapter 20	701
Glossary: Symbols and Abbreviations	706
A. Terms starting with a lower-case letter of the Latin alphabet	706
B. Terms starting with a capital letter of the Latin alphabet	710
C. Terms starting with a lower-case letter of the Greek alphabet	718
D. Terms starting with a capital letter of the Greek alphabet	722
Appendix: Repeat Unit Molecular Weights	724
Index	728