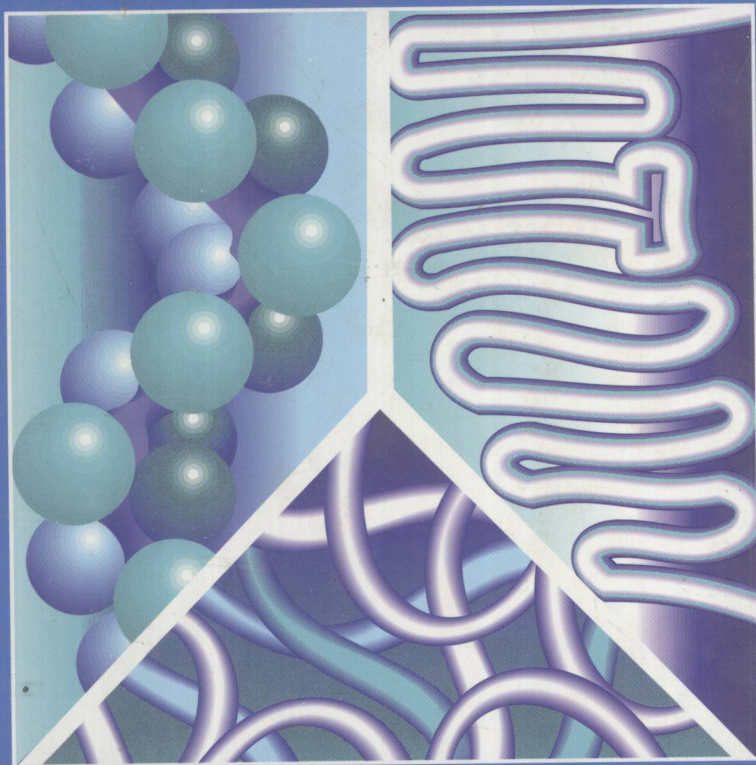


Hans-Georg Elias

An Introduction to Polymer Science



063
E42

E960562
1997

Hans-Georg Elias

An Introduction to Polymer Science



E9960562



Weinheim · New York · Basel · Cambridge · Tokyo

Prof. Dr. Hans-Georg Elias
Michigan Molecular Institute
1910 West St. Andrews Road
Midland, MI 48640
USA

This book was carefully produced. Nevertheless, author and publishers do not warrant the information contained therein to be free of errors. Readers are advised to keep in mind that statements, data, illustrations, procedural details or other items may inadvertently be inaccurate.

1st edition 1997

Published jointly by
VCH Verlagsgesellschaft mbH, Weinheim (Federal Republic of Germany)
VCH Publishers, Inc., New York, NY (USA)

Editorial Director: Dr. Barbara Böck
Production Manager: Dipl.-Wirt.-Ing. (FH) Bernd Riedel

Library of Congress Card No. applied for.
A CIP catalogue record for this book is available from the British Library

Die Deutsche Bibliothek — CIP Einheitsaufnahme

Elias, Hans-Georg:

An introduction to polymer science / Hans-Georg Elias. —
1. ed. — Weinheim ; New York ; Basel ; Cambridge ; Tokyo :
VCH, 1997
ISBN 3-527-28790-6

© VCH Verlagsgesellschaft mbH, D-69469 Weinheim (Federal Republic of Germany), 1997

Printed on acid-free and low chlorine paper.

All rights reserved (including those of translation into other languages). No part of this book may be reproduced in any form — by photoprinting, microfilm, or any other means — nor transmitted or translated into a machine language without written permission from the publishers. Registered names, trademarks, etc. used in this book, even when not specifically marked as such, are not to be considered unprotected by law.

Printing: Strauss Offsetdruck GmbH, D-69509 Mörlenbach
Bookbinding: J. Schäffer & Co. KG., D-67261 Grünstadt

Printed in the Federal Republic of Germany

Hans-Georg Elias

**An Introduction to
Polymer Science**



Preface

Polymer science began with the discovery and synthesis of macromolecules. Physical methods were then employed to characterize these molecules and their applications as plastics, fibers, elastomers, coatings, adhesives, etc. Most introductory textbooks reflect this historical approach: they emphasize the chemistry of polymers and the characterization of polymers by physical methods.

My colleagues and I have long felt that this traditional approach does not do justice to the interdisciplinary nature of polymer science which is firmly rooted not only in the chemistry of macromolecules but also in their physical chemistry and physics. A modern book should furthermore provide the student with some information on the three most important uses of synthetic polymers as elastomers, fibers, and plastics but should not neglect biopolymers either.

This book is therefore divided into three approximately equal sized parts covering the chemistry, physical chemistry and physics of polymers, followed by a part on technology. The parts are preceded by an Introduction (Chapter 1) which defines the most important terms and reflects on the discovery of macromolecules.

The **chemistry** sections first introduce the constitution, configuration and micro-conformation of macromolecules (Chapter 2). Syntheses are then presented in Chapter 3 covering chain-growth polymerizations and Chapter 4 dealing with step-growth polymerizations and polymer reactions. This division seems natural since chain polymerizations are most expediently discussed via kinetics whereas non-chain polymerizations such as polycondensation and polyaddition are better treated according to their individual chemistry. Chapter 4 also contains information on biological macromolecules with special emphasis on industrially important ones.

The next three chapters are concerned with the **physical chemistry** of single macromolecules: size and shape (Chapter 5), thermodynamics of polymer solutions (Chapter 6), and polymer hydrodynamics (Chapter 7). Experimental methods are mentioned in the context of the corresponding physical phenomena; they are not listed in the usual handbook style according to the information they deliver. Prior knowledge is assumed for instrumental methods used in organic chemistry (NMR, IR, UV, etc.). Methods specific to polymer science are described but not in detail due to the prescribed size of the book. The reader should also bear in mind that experimental methods cannot be learned from books but need hands-on experience.

The chapters on single molecules are followed by three chapters on **polymer physics**. Chapter 8 discusses the structure of polymer assemblies, i.e., melts, amorphous solids, crystalline solids, liquid-crystalline polymers, domain formation, etc. Chapter 9 describes not only thermal transitions and relaxations but also diffusion and permeation phenomena. Mechanical, electrical and optical properties of solid polymers are treated in Chapter 10.

Chapters 1-10 are rounded off by four chapters on selected aspects of **polymer technology**. These chapters on the three most important applications of polymers intend to show that elastomers (Chapter 12), fibers (Chapter 13) and plastics (Chapter 14) are not simply polymers but polymer systems comprising additives (Chapter 11).

Chapter 14 also discusses reinforced and rubber-modified plastics. Chapters 11-14 have many cross-references to Chapters 1-10 which show the complexity of such polymer systems and the effect of processing on properties.

The book employs recommended IUPAC nomenclature and symbols and SI units. Since American industry continues to use Anglo-Saxon units, Chapter 15 therefore lists SI units and conversions of Anglo-Saxon units, as well as abbreviations and acronyms of polymer names and some important trade names.

Whenever possible, physical equations are not just presented but derived step by step from theories. Exceptions are those few equations that result from sophisticated theories requiring an elaborate mathematical apparatus. In many cases, numerical examples are given so that the student gets some feel for numerical values.

The book was envisioned for students with a basic knowledge of chemistry, physical chemistry and physics. Since it intends not only to acquaint the student with the basic terms, facts, methods, and theories but also to provide a bridge to an understanding of the primary literature, it uses a more formal, compact style than that commonly adopted by other introductory textbooks. Important terms are emphasized by bold type. Since the language of science is part of our heritage, explanations of the Greek, Latin, French, German, etc., linguistic roots of scientific terms are explained throughout the book.

The book is based on a short German-language text published in 1996 but it is not a cover-to-cover translation: sections have been rearranged and new paragraphs, tables and graphs have been added. The German language edition has been thoroughly worked over, keeping in mind the differences in background, knowledge, and cultural heritage of students in the United States and in German-speaking countries based on my experience with graduate students and postdoctoral fellows from 15 countries.

I am indebted to my former colleagues at Michigan Molecular Institute who read and checked the "final" drafts of several chapters: Professors Petar R. Dvornic (all Chapters), Steven A. Keinath (Chapters 1-7), Dale J. Meier (parts of Chapter 10), Robert L. Miller (Chapters 1, 2, 8, 9), and Karel Solc (Chapters 1, 2, 5, and 6 plus all chapters of the German version),

Midland, Michigan, Summer 1996

Hans-Georg Elias

List of Symbols for Physical Quantities

Abbreviations for languages:

E: English (American spelling)

F: French

G: Greek

L: Latin

Conventions for symbols of chemical entities (IUPAC) unless noted otherwise:

R: monovalent ligand, e.g. CH_3^- , C_6H_5^-

Z: bifunctional atom or group, e.g., $-\text{CH}_2-$, $-(p\text{-C}_6\text{H}_4)-$

Y: trifunctional atom or group, e.g., $-\text{N}<$

X: tetrafunctional atom or group

Other conventions in this book:

A, B: monomers leading to monomeric units -a- and -b- respectively, *or* leaving parts of functional groups (e.g., -OH from -COOH)

L = AB: symbol for a leaving molecule, e.g., H_2O from $-\text{OH} + \text{HOOC}-$;

$p\text{-C}_6\text{H}_4$, $p\text{Ph}$: in para position (1,4-position) substituted benzene ring (= *para*-phenylene)

Exponents

α exponent of the relationship between intrinsic viscosity and molar mass

ν exponent of the relationship between radius of gyration and molar mass (Flory exponent)

Indices:

1 solvent

2 solute (usually polymer)

a atom

c chain

crit critical (occasionally as c)

cryst crystalline

end end group

f free or functionality

G glass transformation

i i th component

i initiation

M melting

m molar quantity

mix mixing, mixture

mol molecule

mon monomer

n number-related quantity

p polymer, polymerization, or propagation

p quantity at constant pressure

r	related to end-to-end distance
rel	relative
s	related to radius of gyration
T	quantity at constant temperature
tr	transfer
u	monomeric unit
V	quantity at constant volume
w	mass-related quantity
η	viscosity-related quantity

Physical quantities and units: Usually following IUPAC and ISO recommendations, see I.Mills, T.Cvitas, K.Homann, N.Kallay, K.Kuchitsu, eds., (International Union of Pure and Applied Chemistry, Division of Physical Chemistry), "Quantities, Units and Symbols in Physical Chemistry", Blackwell Scientific Publications, Oxford 1988.

A	area; A_c = cross-sectional area of a chain
A_2	second virial coefficient; A_3 = third virial coefficient
$[A]$	molar concentration of chemical compound A
a	persistence length
a_T	shift factor in the WLF equation
B	bulk compliance
b	bond length; b_{eff} = effective bond length
C	electric capacitance
C	heat capacity; C_p (isobaric); C_V (isochoric)
C	number concentration (number of entities per total volume)
$[C]$	amount-of-substance concentration = amount of substance per total volume = molar concentration
C_j	chain transfer constant (always with index, e.g., $j = s$ (regulator))
C_N	characteristic ratio; C_∞ = characteristic ratio at infinite molar mass
c	concentration = mass concentration (= mass of substance per total volume)
c_p	specific heat capacity at constant pressure
D	diffusion coefficient
D	tensile compliance
d	diameter; d_{blob} = diameter of a blob, d_{sph} = diameter of a sphere
E	energy, $E^\ddagger$ = activation energy
E	tensile modulus (Young's modulus)
F	force
f	fraction (unless specified)

f	functionality of a group or molecule
G	Gibbs energy; e.g., $\Delta G_{\text{mix,m}}$ = molar Gibbs energy of mixing
G	statistical weight fraction ($G_i \equiv g_i/\Sigma_i g_i$)
G	shear modulus
G	electrical conductance
g	statistical weight
g	branching parameter
H	enthalpy; ΔH_{mix} = enthalpy of mixing, $\Delta H_{\text{mix,m}}$ = molar enthalpy of mixing
h	Planck constant ($h \approx 6.626 \cdot 10^{-34}$ J s)
I	intensity
I	electric current
J	shear compliance
K	constant; K_n = equilibrium constant; K_ϑ = optical constant (scattering)
K	bulk modulus
k	rate constant (always with index); k_p = propagation rate constant, k_t = rate constant of termination, k_{tr} = rate constant of transfer
k_B	Boltzmann constant ($k_B \approx 1.3805 \cdot 10^{-23}$ J K ⁻¹)
L	length (always geometric); L_K = Kuhn length
M	molar mass (mass per amount of substance); $\overline{M}_n$ = number-average molar mass, $\overline{M}_w$ = mass-average molar mass, M_{end} = molar mass of end group
M_r	relative molecular mass (molecular weight; dimensionless); $\overline{M}_{r,n}$ = number-average molecular weight, $\overline{M}_{r,w}$ = weight-average molecular weight
m	mass; m_{mol} = mass of a molecule
N	number of entities (molecules, segments, groups, atoms, etc.); N_{end} = number of end groups; N_g = number of lattice sites
N_A	Avogadro constant ($N_A \approx 6.023 \cdot 10^{23}$ mol ⁻¹)
n	amount of substance (in mol)
n	refractive index
P	permeability coefficient
P	power
$P(\vartheta)$	scattering function
p	extent of reaction; p_A = extent of reaction of group A
p	conditional probability
p	pressure

Q	intermediate variable or constant, usually a ratio
Q	electric charge (quantity of electricity)
$Q(\vartheta)$	parameter in the scattering function
q	order of a moment
q	intermediate variable or constant
R	molar gas constant ($R \approx 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)
R	radius; R_d = Stokes radius, R_v = Einstein radius
R	rate of reaction
R	electrical surface resistance
R_0	Rayleigh constant at angle zero; R_ϑ = Rayleigh constant at angle ϑ
r	spatial end-to-end distance of a chain, usually as $\langle r^2 \rangle^{1/2}$ with various indices; r_{cont} = physical contour length of a chain
r_o	initial ratio of amounts of substances
r_A	copolymerization parameter of chemical compound A
S	entropy; ΔS_{mix} = entropy of mixing, $\Delta S_{\text{mix},m}$ = molar entropy of mixing
S	solubility coefficient
s	radius of gyration (IUPAC)
s	sedimentation coefficient
s	Staverman coefficient
T	thermodynamic temperature (in K); T_c = ceiling temperature, T_G = glass temperature, T_M = melting temperature
t	time
U	electric potential
u	excluded volume
V	volume; V_m = molar volume, *V_m = partial molar volume
v	specific volume; *v = partial specific volume
w	mass fraction (weight fraction)
X	degree of polymerization; X_u = degree of polymerization of a unit (e.g., monomeric unit, repeating unit, etc.); $\bar{X}_n$ = number-average degree of polymerization; $\bar{X}_w$ = mass-average degree of polymerization
x	mole fraction (amount-of-substance fraction); x_u = mole fractions of units, x_i = mole fraction of isotactic diads, x_{ii} = mole fraction of isotactic triads, etc.
y	yield of substance
z	number of immediate neighbors
z	dissymmetry (light scattering)

α	polarizability
α	linear expansion coefficient of materials or coils (α_s if radius of gyration, α_r if end-to-end distance, α_h if hydrodynamic dimensions)
β	cubic expansion coefficient
γ	shear deformation; $\dot{\gamma}$ = shear rate
γ	surface tension
Γ_s	degree of solvation
δ	solubility parameter
ε	elongation
ε	cohesion energy
ε_r	relative permittivity (formerly: dielectric constant)
η	viscosity; η_o = Newtonian viscosity, η_e = extensional viscosity, η_r = relative viscosity, η_{sp} = specific viscosity, $[\eta]$ = intrinsic viscosity
ϑ	angle, especially scattering angle
θ	torsional angle (conformational angle)
θ	temperature in °C (T if in K)
Θ	theta temperature
κ	isothermal (cubic) compressibility
λ	wavelength (λ_o = wavelength of incident light)
λ	heat conductivity
λ	draw ratio
Λ	aspect ratio
μ	moment of a distribution
μ	chemical potential
μ	Poisson ratio
ξ	frictional coefficient
Ξ	zip length
Π	osmotic pressure
ρ	density
ρ	volume resistivity
σ	tensile stress (= σ_{11})
σ	steric factor
σ	electrical conductance
σ_n	standard deviation with respect to numbers or amounts
ς	degree of coupling of chains
τ	bond angle, valence angle
τ	shear stress (= σ_{21})
Y	cohesion energy density
ϕ	volume fraction; ϕ_f = free volume fraction
Φ	Flory parameter; Φ_Θ = Flory constant
χ	Flory–Huggins interaction parameter
ψ	parameter in an entropy quantity
ω	angular velocity
Ω	thermodynamic probability

Contents

Preface	
List of Symbols for Physical Quantities	
Contents	

1. Introduction	1
1.1. Fundamental Terms	1
1.2. History	4

Chemistry

2. Chemical Structure	10
2.1. Constitution	10
2.1.1. Nomenclature	10
2.1.2. Monomers for Polymers	12
2.1.3. Process-Based Terms	12
2.1.4. Structure-Based Terms	14
2.1.5. One-, Two- and Three-Dimensional Macromolecules	16
2.1.6. Branched Macromolecules	20
2.2. Molar Mass and Molar Mass Distribution	23
2.2.1. Degree of Polymerization	23
2.2.2. Molecular Mass, Molecular Weight, Molar Mass	24
2.2.3. Distribution Functions	27
2.2.4. Experimental Methods	31
Mass Spectrometry	31
Size-Exclusion Chromatography	32
2.3. Configuration	34
2.3.1. Stereoisomers	34
2.3.2. Ideal Tacticity	35
2.3.3. Real Tacticity	40
2.3.4. Experimental Methods	41
2.4. Conformation	43
2.4.1. Microconformation	43
2.4.2. Macroconformation in Crystals	45
2.4.3. Macroconformation in Melts and Solutions	46
3. Chain-Growth Polymerizations	50
3.1. Overview of Polymerizations	50

3.1.1.	Classes of Polymerizations	50
3.1.2.	Examples of Polymerizations	52
3.1.3.	Functionality	53
3.1.4.	Experimental Investigations	53
3.1.5.	Kinetics and Statistics	54
3.2.	Thermodynamics of Polymerizations	54
3.2.1.	Polymerization Equilibria	54
3.2.2.	Critical Polymerization Temperatures	55
3.2.3.	Ceiling and Floor Temperatures	56
3.2.4.	Polymerization Enthalpies and Entropies	57
3.2.5.	Chain and Ring Formation	58
3.3.	Statistics of Chain Polymerizations	59
3.4.	Anionic Polymerizations	63
3.4.1.	Ion Equilibria	63
3.4.2.	Monomers	64
3.4.3.	Initiators	65
3.4.4.	Living Polymerizations	66
3.4.5.	Termination and Chain Transfer	68
3.4.6.	Stereocontrol	70
3.5.	Cationic Polymerizations	71
3.5.1.	Monomers	71
3.5.2.	Initiators	72
3.5.3.	Propagation	74
3.5.4.	Termination and Chain Transfer	75
3.6.	Insertion Polymerizations	77
3.6.1.	Introduction	77
3.6.2.	Ziegler–Natta Polymerizations	78
	Heterogeneous Ziegler Catalysts	79
	Homogeneous Ziegler Catalysts	81
	Kinetics	82
3.6.3.	Metathesis Polymerizations	83
	Metatheses	83
	Polyelimination of Aliphatic Olefins	84
	Ring-Opening Polymerization of Cycloolefins	84
3.6.4.	Group Transfer Polymerizations	85
3.7.	Free-Radical Polymerizations	86
3.7.1.	Introduction	86
3.7.2.	Formation of Free Radicals	86
	Self-Initiated Polymerizations	86
	Thermal Initiators	88
	Redox Initiators	90
	Photo Initiators	90

3.7.3.	Initiation, Propagation and Termination	90
3.7.4.	Steady State	92
3.7.5.	Ideal Kinetics	93
3.7.6.	Allyl Polymerizations	96
3.7.7.	Kinetic Chain Transfer	96
3.7.8.	Non-Ideal Kinetics	100
3.7.9.	Industrial Polymerizations	102
	Reactors	102
	Polymerization in Bulk	103
	Polymerization in Solution and by Precipitation	104
	Polymerization in Suspension	104
	Polymerization in Emulsion	105
3.8.	Copolymerizations	107
3.8.1.	Introduction	107
3.8.2.	Copolymerization Equation	107
3.8.3.	Sequence Statistics	110
3.8.4.	Kinetics of Radical Copolymerizations	111
3.8.5.	<i>Q,e</i> -Scheme	112
3.8.6.	Ionic Copolymerizations	114
Appendix to Chapter 3		115
A 3-1:	Equilibria	115
A 3-2:	Poisson Distribution	116
A 3-3	Stationary State	116
A 3-4:	Schulz-Flory Distribution	117
4.	Step-Growth Polymerizations and Polymer Reactions	120
4.1.	Polycondensations and Polyadditions	120
4.1.1.	Introduction	120
4.1.2.	Chemistry of Bifunctional Polycondensations	121
4.1.3.	Equilibria of Bifunctional Polycondensations	124
	Equilibrium Constants	124
	Number-Average Degrees of Polymerization	124
	Distributions of Degrees of Polymerization	126
4.1.4.	Kinetics of Bifunctional Reactions	127
4.1.5.	Diffusion-Controlled Polycondensations	129
4.1.6.	Activated Polycondensations	130
4.1.7.	Cyclizations	131
	Intramolecular Cyclizations	131
	Intramolecular Cyclizations	132
4.1.8.	Polyadditions	135
	Polyurethanes PUR	135
	Epoxy Resins EP	137
4.1.9	Branching Polycondensations	138

	Hyperbranched Polymers	139
	Dendritic Polymers	139
	Gel Point	139
	Alkyd Resins	142
	Phenol-Formaldehyde Resins (Phenolic Resins) PF	142
	Melamine Resins MF and Urea Resins UF	144
4.2.	Biological Polymerizations	145
4.2.1.	Introduction	145
4.2.2.	Nucleic Acids	146
4.2.3.	Proteins	148
	Structure	148
	Protein Syntheses	150
	Enzymes	152
	Silk	153
	Wool	153
	Collagen and Elastin	154
4.2.4.	Lignins	155
4.2.5.	Polysaccharides	156
	Nomenclature	157
	Biosyntheses	157
	Celluloses	158
	Amylose and Amylopectin	159
	Other Polysaccharides	160
4.2.6.	Polyesters	161
4.2.7.	Polyprenes	161
4.3.	Reactions of Macromolecules	162
4.3.1.	Polymer Analog Reactions	162
4.3.2.	Chain Extensions	163
	Block Formation	163
	Grafting Reactions	164
4.3.3.	Cross-Linking Reactions	165
4.3.4.	Degradation	166
	Chain Scission	166
	Depolymerization	167

Physical Chemistry

5	Size and Shape of Molecules	170
5.1.	Introduction	170
5.2.	Scattering Methods	170
5.2.1.	Static Light Scattering	171
	Infinite Dilution	171
	Concentration Dependence	173

	Angular Dependence	173
5.2.2.	Small Angle X-Ray and Neutron Scattering	175
5.3.	Ideal Coil Molecules	176
5.3.1.	Macroconformations	176
5.3.2.	Random Coils	179
5.3.3.	Steric Factor and Hindrance Parameter	181
5.3.4.	Radius of Gyration	183
5.3.5.	Coil Density	184
5.4.	Worm-Like Chains	185
5.5.	Real Coil Molecules	186
5.5.1	Excluded Volume	186
5.5.2.	Dependence on Molar Mass	187
5.5.3.	Branched Polymers	189
5.5.4.	Tethered Chains	191
5.6.	Euclidian Bodies	191
5.6.1.	Spheres and Spheroids	191
5.6.2.	Rods	192
5.6.3.	Excluded Volume	193
5.7.	Scaling	195
5.7.1.	Self-Similarity	195
5.7.2.	Overlap of Coils	196
5.7.3.	Fractals	198
5.8.	Viscosimetric Dimensions	200
5.8.1.	Introduction	200
5.8.2.	Concentration Dependence	201
5.8.3.	Molar Mass Dependence	203
5.8.4.	Hydrodynamic Volumes	205
5.9.	Interpretation of $[\eta] = f(M)$	206
5.9.1.	Unperturbed Coils	206
5.9.2.	Flory Constant of Flexible Molecules	207
5.9.3.	Perturbed Coils	207
5.9.4.	Rods	207
5.9.5.	Branched Polymers	207
	Appendix to Chapter 5	21
	A 5-1: End-to-End Distances of Freely Rotating Chains	213
	A 5-2: End-to-End Distance and Radius of Gyration	214
	A 5-3: Chains with Persistence	216
6	Solution Thermodynamics	218
6.1.	Phenomena	218

6.1.1.	Introduction	218
6.1.2.	Concentration Ranges	219
6.1.3.	Solubility Parameters	220
6.2.	Statistical Thermodynamics	223
6.2.1.	Types of Solutions	223
6.2.2.	Lattice Theory	224
	Enthalpy of Mixing	225
	Entropy of Mixing	226
	Gibbs Energy of Mixing	227
6.2.3.	Phase Separation	227
	Solutions of Amorphous Polymers	227
	Polymer Blends	230
	Critical Solution Temperatures	231
	Solutions of Crystalline Polymers	232
6.3.	Osmotic Pressure	233
6.3.1.	Fundamentals	233
6.3.2.	Membrane Osmometry	235
6.3.3.	Vapor Phase Osmometry	236
6.3.4.	Virial Coefficients	237
6.3.5.	Overlap Concentrations	239
6.4.	Association	241
6.4.1.	Open Associations	242
6.4.2.	Closed Associations	243
6.4.3.	Gels	245
7.	Polymer Hydrodynamics	247
7.1.	Introduction	247
7.2.	Diffusion in Solution	247
7.2.1.	Mutual Diffusion	247
7.2.2.	Frictional Coefficients	248
7.2.3.	Spring-and-Bead Models	250
7.3.	Sedimentation in Solution	252
7.3.1.	Fundamentals	252
7.3.2.	Sedimentation Rate	253
7.3.3.	Sedimentation Equilibrium	255
7.4.	Viscosity of Solutions and Melts	256
7.4.1.	Introduction	256
7.4.2.	Viscometry	256
7.4.3.	Newtonian Viscosities	259
7.4.4.	Non-Newtonian Viscosities	261
7.4.5.	Flow Curves	263
7.4.6.	Extensional Viscosities	265