

# Contents

---

<b>1 DETERMINATION OF STRUCTURE-PROPERTY RELATIONSHIPS IN POLYMERS</b>	<b>1</b>
1.1 Structure-Property Relationships of Polymer Chains, 1	
1.2 The Problem of Polymer Characterization, 2	
1.3 Approach, 4	
References, 8	
<b>2 PROBABILITY APPLIED TO POLYMERIZATION</b>	<b>9</b>
2.1 Elements of Probability Theory (1), 9	
2.2 Bernoulli or Random Chain Processes, 15	
2.2.1 Probability Applied to the Addition Polymerization Process, 15	
2.2.2 Distribution Function of the Polymer Molecules, 17	
2.2.3 Average Chain Length in the Polymerization Mixtures, 19	
2.2.4 Number of n-mers in the Polymer Mixture, 20	
2.2.5 Weight Fraction of x-mers in the Polymer Mixture, 21	
2.2.6 Molecular Weight Averages and Polydispersity, 21	
2.2.7 Calculation of Parameters from Probability Distributions, 23	
2.2.8 Real Distributions and Generalized Molecular Weight Distributions, 26	

**2.3 Statistics of Markov Chains, 27**

2.3.1 Definition, 27

2.3.2 Initial Probability Vectors, 28

2.3.3 Stationary Probability Vectors, 29

**References, 31****3 THEORY OF THE CHARACTERIZATION OF POLYMER MICROSTRUCTURE**

32

**3.1 Introduction, 32****3.2 General Statistical Relations (1), 32****3.3 Microstructure of Instantaneous Binary Copolymerization Models, 39**

3.3.1 Terminal Copolymerization Model, 39

3.3.2 Penultimate Copolymerization Model, 45

3.3.3 Generalized Approach to Calculation of Microstructure for Effects of Remote Units, 51

3.3.4 Terminal Complex Copolymerization Model (8), 59

3.3.5 Copolymerization Model with Depropagation, 62

3.3.6 Other Polymerization Mechanisms, 66

**3.4 Microstructure for Integral Copolymerization (13), 67**

3.4.1 Composition for Integral Copolymerization, 67

3.4.2 Copolymer Microstructures for Integral Copolymerization, 71

**References, 74****4 MULTICOMPONENT COPOLYMERIZATION THEORY**

75

**4.1 Composition of Terpolymers with Terminal Propagation, 75**

4.1.1 General Case, 75

4.1.2 One of Three Comonomers Cannot Homopolymerize, 79

4.1.3 Two of the Termonomers Cannot Homopolymerize, 79

4.1.4 Two Termonomers Cannot Add to Themselves or to Each Other, 80

4.1.5 Two Termonomers Can Only Add to Third  
Monomer, 80

4.2 Sequence Distribution in Terpolymers (2), 80

4.3 Multicomponent Copolymerization with  $n$  Monomers (4), 85  
References, 87

5 COPOLYMER MICROSTRUCTURE AND ITS  
EXPERIMENTAL TREATMENT

88

5.1 Introduction, 88

5.2 Experimental Methods of Distinguishing Polymerization  
Models, 89

5.2.1 Copolymer Composition Measurements, 90

5.2.2 Copolymer Sequence Measurements, 98

5.3 Copolymerization Reactivity Ratios from Composition, 105

5.3.1 Preliminary Considerations, 105

5.3.2 Linear Least Squares Methods, 107

5.3.3 Nonlinear Least Squares Methods (9), 109

5.3.4 Methods for Integrated Copolymerization  
Equation, 115

5.3.5 Penultimate Reactivity Ratios from  
Composition, 116

5.3.6 Charge Transfer Reactivity Ratios from  
Composition Copolymerization Model, 116

5.4 Use of Preliminary Data to Design Copolymerization  
Experiments, 116

References, 119

6 CHEMICAL AND PHYSICAL METHODS OF DETERMINING  
POLYMER MICROSTRUCTURE

120

6.1 Introduction, 120

6.2 Preparation and Selection of Sample, 121

6.3 Extraction, 121

6.4 Dissolution Techniques for Polymers, 122

6.5 Separation Procedures (4), 123

- 6.6 Identification Procedures for Polymers (2, 7), 124**
- 6.7 Chemical Analysis of Gross Composition, 125**
  - 6.7.1 Elemental Analysis, 125
  - 6.7.2 Functional Group Analysis, 126
- 6.8 Chemical Methods of Determining Polymer Microstructures (14), 126**
  - 6.8.1 Selective Degradation for Microstructure Determination, 127
  - 6.8.2 Cyclization Reactions, 136
  - 6.8.3 Sequence Analysis by Cooperative Reactions, 137
- 6.9 Physical Methods of Determining Microstructure of Polymers, 138**
  - 6.9.1 Ultraviolet (UV) and Visible Spectroscopy, 139
  - 6.9.2 Mass Spectroscopy (32), 142
  - 6.9.3 Electron Spectroscopy for Chemical Applications (ESCA) (35), 145
- References, 147**

## **7 VIBRATIONAL SPECTROSCOPY OF POLYMERS**

149

- 7.1 Introduction, 149**
- 7.2 Basic Theory, 150**
  - 7.2.1 Basic IR Spectroscopy (1), 150
  - 7.2.2 Basic Raman Spectroscopy (3), 153
  - 7.2.3 Basis of Raman and IR Spectroscopy, 157
  - 7.2.4 Method of Structure Determination with Raman and IR Spectroscopy (6), 160
  - 7.2.5 Selection of Vibrational Spectroscopic Method (7), 162
- 7.3 Sampling Techniques for Polymers, 165**
  - 7.3.1 IR Spectroscopy, 165
  - 7.3.2 Raman Sampling (7), 168
- 7.4 Instrumentation for Vibrational Spectroscopy, 172**
  - 7.4.1 IR Dispersion Instruments, 172
  - 7.4.2 FT IR Spectrometer (14), 174
  - 7.4.3 Raman Spectroscopy, 177

7.5	Identification Techniques Using Vibrational Spectroscopy, 179	
7.6	Determination of the Chemical Functionality of Polymers Using Vibrational Spectroscopy, 181	
7.7	Effect of Chain and Sequence Length in Vibrational Spectroscopy (25, 26), 189	
7.8	Quantitative Spectroscopic Methods for Polymers, 200	
7.8.1	IR Spectroscopy (1), 200	
7.8.2	Raman Spectroscopy, 206	
7.9	Stereochemical Configuration of Polymer Chains (7), 206	
7.10	Conformation of the Polymer Chain, 209	
7.10.1	The Solid State, 209	
7.10.2	Conformation of Polymers in Liquid and Solution, 211	
7.11	Summary, 214	
	References, 215	
8	<b>NUCLEAR MAGNETIC RESONANCE OF POLYMER CHAINS</b>	217
8.1	Introduction, 217	
8.2	Basic Theory of NMR (8), 218	
8.2.1	Nuclear Spin, 218	
8.2.2	Spin-Lattice Relaxation, 219	
8.2.3	Chemical Shift for $^1\text{H}$ and $^{13}\text{C}$ Nuclei, 220	
8.2.4	Dipole-Dipole Interaction, 225	
8.2.5	Electron Coupled Spin-Spin Interaction, 227	
8.3	Instrumentation for NMR, 232	
8.3.1	Field Sweep NMR (20), 232	
8.3.2	Experimental NMR of $^{13}\text{C}$ Nuclei, 234	
8.3.3	FT NMR (23), 234	
8.3.4	High Resolution $^{13}\text{C}$ NMR of Solids, 235	
8.4	Experimental Techniques (5), 240	
8.4.1	Sample Preparation, 240	

- 8.4.2 Spin Decoupling, 240
- 8.4.3 Isotopic Substitution, 243
- 8.4.4 Use of Model Compounds, 244
- 8.4.5 Effects of High Magnetic Field, 245
- 8.4.6 Computer Analysis of NMR Spectra, 247
- 8.5 Applications of NMR to Polymers (5), 250
  - 8.5.1 Introduction, 250
  - 8.5.2 Determination of Chemical Functionality, 251
  - 8.5.3 Determination of Steric Configuration in Homopolymers, 254
  - 8.5.4 Determination of Structural and Geometric Isomerism in Polymer Chains, 263
  - 8.5.5 Determination of Conformation of Polymer Chains, 264
  - 8.5.6 Determination of Copolymer Microstructure, 266
- References, 270
- 9 CHAIN ISOMERISM THROUGH MONOMER ENCHAINMENT 273
  - 9.1 Terminology, 273
  - 9.2 General Considerations, 276
  - 9.3 Preparation of Model Head-to-Head and Tail-to-Tail Polymers, 277
  - 9.4 Theoretical Microstructure of Polymers with Positional Isomerism (7), 277
    - 9.4.1 Homopolymers, 277
    - 9.4.2 Theory of Monomer Inversion in Copolymers (8), 281
  - 9.5 Methods of Determining the Nature of Chemical Linkage Between Monomers, 284
    - 9.5.1 Chemical Methods, 284
    - 9.5.2 Physical Methods, 288
  - References, 303
- 10 CHAIN ISOMERISM INVOLVING STEREOCONFIGURATION
  - 10.1 Introduction, 304

- 10.2 Effect of Stereoregulation, 307**
- 10.3 Designation of Sequence Types (1), 309**
- 10.4 General Relations for Stereoregular Sequences (3), 311**
  - 10.4.1 Homopolymers, 311
  - 10.4.2 Copolymer Microstructure with Stereoregular Polymerization (1), 315
- 10.5 Microstructure of Polymers Exhibiting Stereoregularity (1), 316**
  - 10.5.1 Terminal or Bernoulli Model, 316
  - 10.5.2 Penultimate Model, 319
  - 10.5.3 Penpenultimate Model, 321
  - 10.5.4 Two State Propagation or Coleman-Fox Model (4, 5), 323
  - 10.5.5 Stereoconfiguration for Copolymers, 325
- 10.6 Determination of Stereopolymerization Mechanisms, 327**
  - 10.6.1 Terminal or Bernoullian Stereopolymerization Model, 328
  - 10.6.2 Penultimate Stereopolymerization Model, 328
  - 10.6.3 Penpenultimate Stereopolymerization Model, 330
  - 10.6.4 Two Stage Model, 333
- 10.7 Methods of Determining Stereoregularity, 334**
  - 10.7.1 NMR Measurement of Stereoregularity (1), 334
  - 10.7.2 IR Methods, 341
- 10.8 Molecular Mechanism of Stereospecific Polymerization, 347**
  - 10.8.1 Free Radical Polymerization, 347
  - 10.8.2 Anionic Polymerization, 348
  - 10.8.3 Mechanism of Ziegler-Natta Catalyst, 349
  - 10.8.4 Effect of Polymerization Conditions on Stereoregularity of Polymers, 352
- References, 354**

## **11 CHAIN ISOMERISM DUE TO BRANCHING IN POLYMERS 356**

- 11.1 Introduction, 356**
- 11.2 Short Chain Branching in Polymers, 357**
  - 11.2.1 Mechanism of Formation, 357
  - 11.2.2 Characterization of Short Chain Branching in Polymers, 361

**11.3 Long Chain Branching in Polymers, 373**

11.3.1 Mechanisms of Long Branch Formation, 374

11.3.2 Branching Factors for Model Branched Polymers, 390

11.3.3 Characterization of Long Chain Branching (27, 28), 396

11.3.4 Characterization of Cross-Linked Structures, 402

**References, 407**

**INDEX**