



## CONTENTS

CONTRIBUTORS	xi
FOREWORD	xiii
PREFACE	xv
CONTENTS OF VOLUME 16, PARTS B AND C . . . . .	xvii
CONTRIBUTORS TO VOLUME 16, PARTS B AND C . . . . .	xxi
VOLUMES IN SERIES . . . . .	xxiii

### 1. Introduction by R. A. FAVA

1.1. Historic Development . . . . .	1
1.2. Definitions . . . . .	3
1.3. Formation and Conformation . . . . .	4
1.4. The Solid State . . . . .	6
1.4.1. Amorphous Polymers . . . . .	6
1.4.2. Crystalline Polymers . . . . .	7
1.5. Orientation . . . . .	8
1.6. Impurities . . . . .	9

### 2. Polymer Molecular Weights by DOROTHY J. POLLOCK AND ROBERT F. KRATZ

2.1. Definitions of Molecular Weight . . . . .	13
2.1.1. Introduction . . . . .	13
2.1.2. The Moments of Molecular Weight . . . . .	14

2.2.	Intensive Properties of Polymers . . . . .	16
2.2.1.	Solution Viscosity . . . . .	16
2.2.2.	Colligative Properties . . . . .	22
2.2.3.	Light Scattering . . . . .	27
2.3.	Fractionation. . . . .	30
2.3.1.	Introduction . . . . .	30
2.3.2.	Polydispersity and Fractionation . . . . .	30
2.3.3.	Fractionation Techniques. . . . .	32
2.4.	Gel Permeation Chromatography . . . . .	41
2.4.1.	Introduction . . . . .	41
2.4.2.	Theory of Separation . . . . .	46
2.4.3.	Instrumentation and Operation . . . . .	48
2.4.4.	Molecular Weight Evaluations . . . . .	53
2.4.5.	Applications . . . . .	61
2.4.6.	Conclusions. . . . .	64
2.5.	Miscellaneous Methods . . . . .	65
2.5.1.	Sedimentation Analysis . . . . .	65
2.5.2.	End-Group Analysis . . . . .	69

### 3. Spectroscopic Methods

#### 3.1. Infrared and Raman Spectra of Polymers

by R. G. SNYDER

3.1.1.	Introduction . . . . .	73
3.1.2.	Experimental . . . . .	77
3.1.3.	Vibrational Theory for Molecules . . . . .	89
3.1.4.	Vibrations of a Periodic Chain Molecule . . . . .	98
3.1.5.	Ordered Polymer Systems . . . . .	116
3.1.6.	Disordered Polymer Systems . . . . .	134

#### 3.2. Inelastic Electron Tunneling Spectroscopy

by H. W. WHITE AND T. WOLFRAM

3.2.1.	Introduction . . . . .	149
3.2.2.	Experimental Methods . . . . .	154

3.2.3.	Experimental Results . . . . .	158
3.2.4.	Theory . . . . .	162
3.2.5.	Applications . . . . .	164
3.2.6.	Summary . . . . .	169
3.3.	Rayleigh–Brillouin Scattering in Polymers by G. D. PATTERSON	
3.3.1.	Introduction . . . . .	170
3.3.2.	Theory . . . . .	172
3.3.3.	Experimental . . . . .	181
3.3.4.	Applications . . . . .	188
3.4.	Inelastic Neutron Scattering Spectroscopy by C. V. BERNEY AND SIDNEY YIP	
3.4.1.	Introduction . . . . .	205
3.4.2.	Basic Principles . . . . .	212
3.4.3.	Experimental Techniques . . . . .	218
3.4.4.	Selected Applications . . . . .	229
3.4.5.	Prospects and Perspectives . . . . .	239
4.	High-Resolution Nuclear Magnetic Resonance Spectroscopy by J. R. LYERLA	
4.1.	Nuclear Magnetic Resonance Spectroscopy . . . . .	241
4.1.1.	Introduction . . . . .	241
4.1.2.	The NMR Experiment . . . . .	242
4.1.3.	NMR Parameters . . . . .	245
4.1.4.	Experimental Methods and Instrumentation . . . . .	265
4.1.5.	Measurement of NMR Parameters . . . . .	278
4.2.	HR-NMR as a Probe of Polymer Structure . . . . .	284
4.2.1.	Polymerization Mechanism . . . . .	285
4.2.2.	Polymer Chain Stereochemistry . . . . .	288
4.2.3.	Copolymer Sequence Distribution . . . . .	294
4.2.4.	Polymer Chain Conformation . . . . .	299
4.3.	HR-NMR as a Probe of Polymer Molecular Dynamics . . . . .	302
4.3.1.	Chain Segmental Motion . . . . .	303
4.3.2.	Sidechain Reorientational Motions . . . . .	309

4.3.3.	Distribution of Correlation Times . . . . .	312
4.3.4.	Other Nuclei . . . . .	319
4.4.	HR-NMR of the Solid State . . . . .	320
4.4.1.	The Resolution Problem: Sources of Line- Broadening and Methods for Their Removal . . . . .	323
4.4.2.	The Sensitivity Problem . . . . .	331
4.4.3.	Experimental Implementation of DD/CP/MAS . . . . .	338
4.4.4.	Applications of $^{13}\text{C}$ NMR to the Solid State of Macromolecules . . . . .	343
4.5.	Summary . . . . .	368

## 5. Probe and Label Techniques

### 5.1. Positron Annihilation

by J. R. STEVENS

5.1.1.	Introduction . . . . .	371
5.1.2.	Positrons and Positronium . . . . .	372
5.1.3.	Theoretical Considerations . . . . .	377
5.1.4.	Experimental Techniques . . . . .	380
5.1.5.	Methods of Data Analysis . . . . .	390
5.1.6.	The Positron and Positronium in Polymers . . . . .	393
5.1.7.	Conclusion . . . . .	403

### 5.2. Fluorescence Probe Methods

by L. LAWRENCE CHAPOY AND DONALD B. DUPRÉ

5.2.1.	Introduction . . . . .	404
5.2.2.	The Fluorescence Phenomenon . . . . .	405
5.2.3.	Fluorescence Quenching Techniques . . . . .	407
5.2.4.	Fluorescence Polarization Techniques . . . . .	412
5.2.5.	Energy Transfer Probes . . . . .	436
5.2.6.	Probe Selection . . . . .	437
5.2.7.	Instrumentation . . . . .	439

### 5.3. Paramagnetic Probe Techniques

by PHILIP L. KUMLER

5.3.1.	ESR Spectroscopy—Theory . . . . .	442
5.3.2.	ESR Spectroscopy—Instrumentation . . . . .	452

5.3.3. Paramagnetic Probes . . . . .	457
5.3.4. Spin-Probe and Spin-Label Applications to Synthetic Polymers . . . . .	465
5.4. Small-Angle Neutron Scattering by J. S. KING	
5.4.1. Introduction . . . . .	480
5.4.2. Elastic Neutron Scattering Cross Section at Small Angles . . . . .	481
5.4.3. SANS Spectrometer Design . . . . .	485
5.4.4. Experimental Results . . . . .	497
AUTHOR INDEX FOR PART A. . . . .	507
SUBJECT INDEX FOR PART A. . . . .	527
AUTHOR INDEXES FOR PARTS B AND C. . . . .	537
SUBJECT INDEXES FOR PARTS B AND C. . . . .	569