

*CHAIN STRUCTURE  
AND CONFORMATION  
OF MACROMOLECULES*

**Frank A. Bovey**  
Bell Laboratories  
Murray Hill, New Jersey

with a chapter by  
**Lynn W. Jelinski**  
Bell Laboratories  
Murray Hill, New Jersey

ACADEMIC PRESS



1982

A Subsidiary of Harcourt Brace Jovanovich, Publishers

New York London

Paris San Diego San Francisco São Paulo Sydney Tokyo Toronto

# CONTENTS

*Preface*

ix

## CHAPTER 1 The Structure of Polymer Chains

1.1	Introduction	1
1.2	History of the Macromolecular Concept	2
1.3	Isomerism in Vinyl Polymer Chains	3
1.4	Isomerism in Diene Polymer Chains	8
1.5	Vinyl Polymers with Optically Active Side Chains	12
1.6	Polymers with Asymmetric Centers in the Main	14
1.7	Other Types of Isomerism	16
	References	16

## CHAPTER 2 The Spectroscopy of Macromolecules

2.1	Introduction	19
2.2	Vibrational Spectroscopy	19
2.3	Nuclear Magnetic Resonance Spectroscopy	32
	General References	38

## CHAPTER 3 Stereochemical Configuration and Its Observation

3.1	Introduction	39
3.2	Model Compounds for Vinyl Polymer Chains	40
3.3	Polymer Chains	47
3.4	The Effect of Polymerization Temperature on Stereochemical Configuration	60
3.5	More Complex Proton Spectra; Computer Simulation	63

3.6	Carbon-13 Spectroscopy	78
3.7	Fluorine Spectroscopy	91
	Appendix	94
	References	98
 <b>CHAPTER 4 Geometrical Isomerism in Diene Polymers</b>		
4.1	Introduction	101
4.2	Polybutadiene	101
4.3	Polyisoprene	113
4.4	Polychloroprene	116
	References	121
 <b>CHAPTER 5 Copolymerization and Copolymer Structure</b>		
5.1	Introduction	123
5.2	Copolymer Composition; The Copolymer Equation	124
5.3	Reactivity Ratios	128
5.4	Determination of Reactivity Ratios	133
5.5	Monomer Sequences and Their Observation	137
	References	155
 <b>CHAPTER 6 Regioregularity and Branching in Vinyl Polymer Chains</b>		
6.1	Introduction	157
6.2	Head-To-Tail Versus Head-To-Head:Tail-To-Tail Isomerism; Regioregularity	158
6.3	Branching in Vinyl Polymers	172
	References	183
 <b>CHAPTER 7 Chain Conformations of Macromolecules</b>		
7.1	Introduction	185
7.2	The Freely Jointed Chain	187
7.3	The Freely Rotating Chain	188
7.4	Chains with Restricted Rotation	188
7.5	Experimental Observation of Polymer Chain Conformations in Solution	203

7.6	Experimental Observation of Polymer Chain Conformations in the Crystalline State	206
7.7	Experimental Observation of Polymer Chain Conformations in the Amorphous Solid State	215
7.8	Chain Conformation and Chemical Shift	217
	References	219
	General References	220

## CHAPTER 8 Solid State NMR of Macromolecules

L. W. JELINSKI

8.1	Introduction	223
8.2	Pulsed Fourier Transform Nmr and Relaxation	224
8.3	Dipolar Broadening in Solids	227
8.4	High Power Proton Decoupling	228
8.5	Chemical Shift Anisotropy	230
8.6	Magic Angle Spinning	232
8.7	$^1\text{H}$ - $^{13}\text{C}$ Cross Polarization	234
8.8	Solid State Carbon-13 NMR of Polymers	238
	References	248