## CONTENTS

## Preface

1	The Chemical Basis of Polymers	
	Introduction	1
	Typical Addition Polymers	2
	The Methods of Addition Polymerization	4
	Radical polymerization	
	Cationic polymerization	6
	Anionic polymerization	7
	Polymerization on heterogeneous catalysts	10
	Typical Condensation Polymers	10
	Polymers from Stepwise Reactions	13
	Copolymers	13
	References	15
2	The Microstructure of Chain Molecules	17
	Chemical Linkage between Monomer Units	17
	Steric Regularity of Polymer Chains	20
	The Determination of Tacticity	26
	Crystallinity and melting point	26
	Infra-red spectra	27
	NMR spectra	29
	Solution properties	31
	The Microstructure of Polydienes	32
	Determination of the Microstructure of Polydienes	33
	Stereoregularity of Addition Polymerization	36
	Free radical propagation	36
	Ionic propagation	37
	Heterogeneous polymerization	40
	Optical Activity in Polymers	40
	The Conformation of Isolated Chain Molecules	44
	References	47
	Symbols	50
3	Molecular Weight and Branching	51
	Average Molecular Weight	51
	The Distribution of Molecular Weights	52
	Determination of $\overline{M}_n$	55
	End-group analysis	55

CONTENTS

	$\overline{M}_n$ from solution properties	56
	Osmotic pressures	57
	Determination of $\overline{M}_{w}$	59
	Light scattering by solutions	59
	Sedimentation analysis	62
	Viscosity of solutions	65
	Determination of Molecular Weight Distributions	67
	Control of Molecular Weights and Distributions	69
	Condensation polymerization	69
	Stepwise polymerization	70
	Radical polymerization	70
	Cationic polymerization	71
	Anionic polymerization	72
	Polymerization on heterogeneous catalysts	75
	Chain Branching	76
	References	82
	Symbols	84
		0-
4	The Crystallinity of Polymers	86
	Molecular Aggregation	86
	Aggregation of Macromolecules	89
	Structural Features of Crystallizable Polymers	92
	Molecular Arrangement in Crystallites	94
	Polyethylene	94
	Syndiotactic vinyl polymers	97
	Polytetrafluoroethylene	97
	Polyvinyl alcohol	98
	Isotactic vinyl polymers	98
	Polyesters	105
	Polyamides	106
	Polydienes	108
	The Principles of Crystallite Structure	110
	Single Crystals of Polymers	112
	The Morphology of Polymers Crystallized from Melts	116
	References	122
	Symbols	124
5	The Fusion and Crystallization of Polymers	125
	Determination of the Crystalline/Amorphous Ratio	125
	The Fusion of Polymer Crystallites	131
	The Mechanism of Crystallization	140
	The Kinetic Treatment of Crystallization	142
	The Experimental Study of Crystallization in Polymers	144
	General Kinetic Features of Crystallization	145

	CONTENTS	ix
	Microscopic Studies of Growth Rates	147
	Microscopic Studies of Nucleation Rates	148
	Measurements of Overall Rates of Crystallization	149
	Applications of the Avrami Equation	151
	Temperature Dependence of Crystallization Rates	152
	The Orientation of Crystallites	154
	References	157
	Symbols	159
6	Elastomers and the Thermodynamics of Rubberlike Elasticity	160
	The Mechanical Properties of Rubber	160
	Synthetic Elastomers	163
	Polyisoprenes	163
	Polybutadienes	164
	Polychloroprene	164
	Butadiene and styrene copolymers	164
	Butadiene and acrylonitrile copolymers	165
	Butyl rubber	165
	Polysulphide elastomers	166
	Silicone elastomers	166
	The Structure and Formation of Polymer Networks	167
	The Thermodynamics of Stress and Strain	172
	Experimental Thermodynamic Data	177
	The Elastic Moduli and Types of Strain	179
	References	182
	Symbols	183
7	The Statistical Thermodynamic Theory of High Elasticity	184
	Introduction	184
	The Statistics of a Freely-jointed Chain	185
	Extension to Real Chains	191
	The Equation of State of a Single Chain	194
	The Configurations of a Molecular Network	197
	The Stress/Strain Equation of a Network	201
	Network Structure and Defects	205
	References	210
	Symbols	211
8	Practical Aspects of Elasticity Theory	212
	Introduction	212
	Testing the Stress/Strain Equation	212
	The Thermo-elastic Phenomena	214
	The Ratio of Stress to Strain	217
	The Effect of Molecular Weight	220

CONTEN	ſΤ	S

	Behaviour of Elastomers at Large Deformations	225
	The Effect of Crystallization	226
	Complex Networks	230
	Fillers and Plasticizers	232
	References	234
	Symbols	235
	Bymoois	
9	The Nature of Visco-Elasticity	237
	Introduction	237
	Classification of the Mechanical States of Polymers	238
	Molecular Interpretation of Stress/Strain Behaviour	243
	References	250
	Symbols	250
10	The Glassy State and Glass Transition	251
10	Mechanical Properties of Polymeric Glasses	251
	The Glass Transition and its Observation	254
	The Effects of Polymer Structure on $T_a$	257
	Chemical structure and $T_{c}$	258
	T of copolymers	261
	Microstructure and $T_{-}$	262
	Molecular weight and $T_{-}$	263
	Branching cross-linking and $T_{c}$	265
	The Effect of Diluents on $T_{\rm eff}$	266
	Theories of the Glass Transition	267
	References	273
	Symbols	274
	Symbols	
11	Retarded High Elasticity	276
	General Characteristics of the Retarded Highly Elastic	
	State	276
	Mechanical Models of Visco-Elastic Behaviour	278
	The Voigt model	278
	Three element models	281
	Four element models and secondary creep	286
	Generalized models	287
	Visco-elastic Measurements	290
	Temperature Dependence of Visco-elastic Phenomena	293
	Derivation of Distribution Functions from Experimental	
	Data	297
	Molecular Interpretation of Visco-elasticity	301
	Results and Interpretation of Visco-elastic Studies	304
	References	310
	Symbols	311

х

	CONTENTS	xi
12	Diffusion of Gases and Vapours in Polymers	313
	Introduction	313
	The Study of Diffusion in Polymers	314
	Diffusion through Polymer Membranes	315
	Kinetics of Sorption by Polymers	318
	Diffusion in Elastomers	321
	Diffusion of Vapours above $T_{q}$	327
	Diffusion of Vapours in the Region of $T_{a}$	331
	Diffusion of Gases in the Region of $T_{a}$	335
	Diffusion in Crystalline Polymers	340
	References	344
	Symbols	346
13	Irreversible Deformations	347
	Introduction	347
	The Effect of Temperature on Viscosity	3/8
	The Effect of Molecular Weight on Viscosity	351
	Theoretical Treatment of Bulk Viscosity	351
	Non-Newtonian Flow	352
	Permanent Set in Cross-linked Polymers	353
	References	364
	Symbols	365
	· · · · · · · · · · · · · · · · · · ·	505
	Author Index	367
	Subject Index	375