

Contents

1. The Constitution and Architecture of Chains	1
1.1 Further Reading	11
2. Single Chain Conformations	13
2.1 Rotational Isomeric States	13
2.2 Helices	17
2.3 Coils	20
2.3.1 Ideal Chains	23
2.3.2 Expanded Chains	43
2.4 The Ising-Chain	53
2.5 Further Reading	61
3. Liquid Equilibrium States	63
3.1 Dilute and Semi-Dilute Polymer Solutions	64
3.1.1 Osmotic Pressure	65
3.1.2 Screening Effect	76
3.2 Polymer Mixtures	83
3.2.1 Flory-Huggins Treatment of Compatibility	83
3.2.2 Phase Separation Mechanisms	100
3.2.3 Critical Fluctuations and Spinodal Decomposition	107
3.3 Block Copolymers	129
3.3.1 Phase Behavior	129
3.3.2 Layered Structures	133
3.3.3 Pretransitional Phenomena	135
3.4 Further Reading	141
4. Metastable Partially Crystalline States	143
4.1 Structure Characteristics	145
4.2 Primary Crystallization	157
4.2.1 Spherulite Nucleation and Growth	158
4.2.2 Spinodal Mode	173
4.3 Secondary Crystallization	176
4.3.1 Insertion Mode	181

4.3.2	Surface Crystallization and Melting	185
4.4	Further Reading	189
5.	Mechanical and Dielectric Response	191
5.1	Response Functions	192
5.1.1	Viscoelasticity	192
5.1.2	Orientational Polarization	196
5.1.3	General Relationships	197
5.2	Relaxatory Modes	204
5.2.1	Single-Time Relaxation Process	205
5.2.2	Retardation and Relaxation Time Spectra	209
5.3	Specific Relaxation Processes and Flow Behavior	213
5.3.1	Local Processes	214
5.3.2	Glass-Rubber Transition and Melt Flow	217
5.3.3	Glass Transition Temperature	237
5.3.4	Relaxation in Partially Crystalline Systems	244
5.4	Further Reading	255
6.	Microscopic Dynamical Models	257
6.1	The Fluctuation-Dissipation Theorem	257
6.2	The Rouse-Model	262
6.2.1	Stress Relaxation	269
6.2.2	Dielectric Normal Mode	274
6.3	Entanglement Effects	277
6.3.1	The Reptation Model	282
6.4	Hydrodynamic Interaction in Solutions	287
6.4.1	Intrinsic Viscosity	293
6.5	Further Reading	296
7.	Non-linear Mechanical Behavior	297
7.1	Rubber Elasticity	301
7.1.1	The Fixed Junction Model of Ideal Rubbers	304
7.1.2	The Cauchy Strain Tensor	311
7.1.3	Finger's Constitutive Equation	315
7.2	Non-Newtonian Melt Flow	325
7.2.1	Rheological Material Functions	325
7.2.2	The Lodge Liquid	332
7.2.3	Stress-Optical Rule and Network Model	339
7.3	Further Reading	348
8.	Yield Processes and Fracture	349
8.1	Shear Yielding	353
8.1.1	Mechanics of Neck Formation	353
8.1.2	Structure Changes on Cold-Drawing	359

8.2 Crazing	368
8.3 Brittle Fracture	374
8.3.1 Linear Fracture Mechanics	376
8.3.2 Slow Mode of Crack Growth	380
8.4 Further Reading	385
Appendix: Scattering Experiments	387
A.1 Fundamentals	387
A.1.1 Basic Equations	387
A.1.2 Time-Resolved Scattering Experiments	392
A.2 Absolute Intensities	395
A.3 Low Angle Scattering Properties	398
A.3.1 Guinier's Law	398
A.3.2 Forward Scattering	400
A.4 Special Polymer Systems	401
A.4.1 Binary Mixtures and Block Copolymers	401
A.4.2 Two-Phase Layer Systems	408
A.5 Further Reading	415
Glossary of Symbols	417
Figure References	425
Bibliography	429
Subject Index	433