

Contents

Preface to the Second Edition	V
Preface to the First Edition	VII
1 Introduction	1
1.1 Melt Structure and Its Effect on Rheology	1
1.2 Overview of This Book	2
1.3 Applications of the Information Presented.....	4
1.4 Supplementary Sources of Information	4
References.....	5
2 Structure of Polymers	7
2.1 Molecular Size.....	7
2.1.1 The Freely-Jointed Chain	7
2.1.2 The Gaussian Size Distribution.....	8
2.1.2.1 Linear Molecules	8
2.1.2.2 Branched Molecules	12
2.1.3 The Dilute Solution and the Theta State.....	14
2.1.4 Polymer Molecules in the Melt	16
2.2 Molecular Weight Distribution	17
2.2.1 Monodisperse Polymers	17
2.2.2 Average Molecular Weights and Moments of the Distribution....	18
2.2.3 Continuous Molecular Weight Distribution	20
2.2.4 Distribution Functions	22
2.2.5 Narrow Distribution Samples	26
2.2.6 Bimodality	27
2.3 Tacticity	28
2.4 Branching.....	29
2.5 Intrinsic Viscosity.....	31
2.5.1 Introduction.....	31
2.5.2 Rigid Sphere Models.....	32

2.5.3	The Free-Draining Molecule.....	34
2.5.4	Non-Theta Conditions and the Mark-Houwink-Sakurada Equation.....	35
2.5.5	Effect of Polydispersity.....	36
2.5.6	Effect of Long-Chain Branching.....	37
2.5.7	Effects of Short-Chain Branching	38
2.5.8	Determination of Intrinsic Viscosity—Extrapolation Methods	40
2.5.9	Effect of Shear Rate.....	41
2.6	Other Structure Characterization Methods	41
2.6.1	Membrane Osmometry.....	41
2.6.2	Light Scattering.....	42
2.6.3	Gel Permeation Chromatography	44
2.6.3.1	MWD of Linear Polymers	44
2.6.3.2	GPC with Branched Polymers.....	47
2.6.3.3	GPC with LDPE	48
2.6.3.4	Interactive Chromatography.....	49
2.6.3.5	Field Flow Fractionation	50
2.6.4	Mass Spectrometry (MALDI-TOF).....	50
2.6.5	Nuclear Magnetic Resonance.....	51
2.6.6	Separations Based on Crystallizability: TREF, CRYSTAF, and CEF	52
2.6.7	Bivariate (Two-Dimensional) Characterizations	54
2.6.8	Molecular Structure from Rheology	54
2.7	Summary	55
	References.....	57
3	Polymerization Reactions and Processes	65
3.1	Introduction.....	65
3.2	Classifications of Polymers and Polymerization Reactions	67
3.3	Structural Characteristics of Polymers.....	68
3.3.1	Introduction.....	68
3.3.2	Chemical Composition—Role of Backbone Bonds in Chain Flexibility.....	69
3.3.3	Chemical Composition—Copolymers.....	69
3.3.4	Tacticity	69
3.3.5	Branching.....	70
3.4	Living Polymers Having Prescribed Structures.....	71
3.4.1	Anionic Polymerization	73
3.4.2	Living Free-Radical Polymerization (Reversible Deactivation Radical Polymerization—RDRP).....	75
3.4.3	Model Polyethylenes for Research.....	75

3.5	Industrial Polymerization Processes	76
3.6	Free-Radical Polymerization of Low-Density Polyethylene (LDPE)	78
3.6.1	Shear Modification	79
3.7	Linear Polyethylene via Complex Coordination Catalysts	79
3.7.1	Catalyst Systems	79
3.7.2	Branching in High-Density Polyethylene	80
3.7.3	Ultrahigh Molecular Weight Polyethylene	81
3.8	Linear Low-Density Polyethylene via Ziegler-Natta Catalysts	81
3.9	Single-Site Catalysts	82
3.9.1	Metallocene Catalysts	83
3.9.2	Long-Chain Branching in Metallocene Polyethylenes	84
3.9.3	Post-Metallocene Catalysts	89
3.10	Polypropylene	90
3.11	Reactors for Polyolefins	91
3.12	Polystyrene	93
3.13	Summary	94
	References	95
4	Linear Viscoelasticity—Fundamentals	105
4.1	Stress Relaxation and the Relaxation Modulus	105
4.1.1	The Boltzmann Superposition Principle	105
4.1.2	The Maxwell Model for the Relaxation Modulus	110
4.1.3	The Generalized Maxwell Model and the Discrete Relaxation Spectrum	113
4.1.4	The Continuous Relaxation Spectrum	114
4.2	The Creep Compliance and the Retardation Spectrum	115
4.3	Experimental Characterization of Linear Viscoelastic Behavior	119
4.3.1	Oscillatory Shear	120
4.3.2	Experimental Determination of the Storage and Loss Moduli	123
4.3.3	Creep Measurements	125
4.3.4	Other Methods for Monitoring Relaxation Processes	127
4.4	Calculation of Relaxation Spectra from Experimental Data	127
4.4.1	Discrete Spectra	127
4.4.2	Continuous Spectra	128
4.5	Time-Temperature Superposition	130
4.5.1	Time/Frequency (Horizontal) Shifting	130
4.5.2	The Modulus (Vertical) Shift Factor	131
4.5.3	Validity of Time-Temperature Superposition	135
4.6	Time-Pressure Superposition	136
4.7	Alternative Plots of Linear Viscoelastic Data	137
4.7.1	Van Gurp-Palmen Plot of Loss Angle Versus Complex Modulus	137

4.7.2	Cole-Cole Plots.....	139
4.8	Summary	141
	References.....	141
5	Linear Viscoelasticity—Behavior of Molten Polymers.....	147
5.1	Introduction.....	147
5.2	Zero-Shear Viscosity of Linear Polymers	147
5.2.1	Effect of Molecular Weight.....	148
5.2.2	Effect of Polydispersity.....	150
5.3	The Relaxation Modulus.....	152
5.3.1	General Features.....	152
5.3.2	How Can a Melt Act like a Rubber?.....	154
5.4	The Storage and Loss Moduli.....	154
5.5	The Creep and Recoverable Compliances.....	158
5.6	The Steady-State Compliance.....	160
5.7	The Plateau Modulus	162
5.7.1	Determination of G_N^0	162
5.7.2	Effects of Short Branches and Tacticity	164
5.8	The Molecular Weight between Entanglements, M_e	165
5.8.1	Definitions of M_e	165
5.8.2	Molecular Weight between Entanglements (M_e) Based on Molecular Theory	167
5.9	Rheological Behavior of Copolymers.....	170
5.10	Effect of Long-Chain Branching on Linear Viscoelastic Behavior	172
5.10.1	Introduction.....	172
5.10.2	Ideal Branched Polymers	173
5.10.2.1	Zero-Shear Viscosity of Ideal Stars and Combs	173
5.10.2.2	Steady-State Compliance of Model Star Polymers	176
5.10.3	Storage and Loss Moduli of Model Branched Systems	178
5.10.4	Randomly Branched Polymers.....	181
5.10.5	Low-Density Polyethylene	184
5.11	Use of Linear Viscoelastic Data to Determine Branching Level.....	186
5.11.1	Introduction.....	186
5.11.2	Correlations Based on the Zero-Shear Viscosity	187
5.12	Summary	188
	References.....	189
6	Tube Models for Linear Polymers—Fundamentals	197
6.1	Introduction.....	197
6.2	The Rouse-Bueche Model for Unentangled Polymers	199
6.2.1	Introduction.....	199

6.2.2	The Rouse Model for the Viscoelasticity of a Dilute Polymer Solution	200
6.2.3	Bueche's Modification for an Unentangled Melt	203
6.3	Entanglements and the Tube Model	208
6.3.1	The Critical Molecular Weight for Entanglement M_C	209
6.3.2	The Plateau Modulus G_N^0	211
6.3.3	The Molecular Weight Between Entanglements M_e	213
6.3.4	The Tube Diameter a	214
6.3.5	The Equilibration Time τ_e	218
6.3.6	Identification of Entanglements and Tubes in Computer Simulation	218
6.4	Modes of Relaxation	224
6.4.1	Reptation	224
6.4.2	Primitive Path Fluctuations	226
6.4.3	Reptation Combined with Primitive Path Fluctuations	228
6.4.4	Constraint Release—Double Reptation	231
6.4.4.1	Monodisperse Melts	232
6.4.4.2	Bidisperse Melts	233
6.4.4.3	Polydisperse Melts	239
6.4.5	Rouse Relaxation within the Tube	242
6.5	An Alternative Picture for Entangled Polymers: Slip-Links	244
6.6	Summary	249
	References	250
7	Tube Models for Linear Polymers—Advanced Topics	255
7.1	Introduction	255
7.2	Limitations of Double Reptation Theory	256
7.3	Constraint-Release Rouse Relaxation in Bidisperse Melts	259
7.3.1	Non-Self-Entangled Long Chains in a Short-Chain Matrix	259
7.3.2	Self-Entangled Long Chains in a Short-Chain Matrix	263
7.3.3	Thin Tubes, Fat Tubes, and the Viovy Diagram	265
7.4	Polydisperse Melts and “Dynamic Dilution”	272
7.4.1	Polydisperse Chains	272
7.4.2	Tube Dilation or “Dynamic Dilution”	274
7.5	Input Parameters for Tube Models	277
7.6	Summary	287
	References	288
8	Determination of Molecular Weight Distribution Using Rheology	291
8.1	Introduction	291
8.2	Viscosity Methods	291

8.3	Empirical Correlations Based on the Elastic Modulus	293
8.4	Methods Based on Double Reptation.....	294
8.5	Generalization of Double Reptation.....	298
8.6	Dealing with the Rouse Modes	298
8.7	Models that Account for Additional Relaxation Processes	299
8.8	Determination of Polydispersity Indexes	302
8.9	Summary	303
	References.....	303
9	Tube Models for Branched Polymers.....	307
9.1	Introduction.....	307
9.2	General Effect of LCB on Rheology	309
9.2.1	Qualitative Description of Relaxation Mechanisms in Long-Chain-Branched Polymers	314
9.3	Star Polymers	317
9.3.1	Deep Primitive Path Fluctuations	317
9.3.2	Dynamic Dilution	319
9.3.3	Comparison of Milner-McLeish Theory to Linear Viscoelastic Data	322
9.3.3.1	Monodisperse Stars	322
9.3.3.2	Bidisperse Stars.....	327
9.3.3.3	Star/Linear Blends.....	328
9.4	Multiply Branched Polymers	330
9.4.1	Dynamic Dilution for Polymers with Backbones.....	330
9.4.2	Branch Point Motion.....	332
9.4.3	Backbone Relaxation.....	336
9.5	Tube Model Algorithms for Polydisperse Branched Polymers.....	339
9.5.1	“Hierarchical” and “BoB” Dynamic Dilution Models.....	340
9.5.2	The “Time-Marching” Algorithm.....	344
9.5.3	Data and Predictions for Model Polymers and Randomly Branched Polymers.....	345
9.6	Slip-Link Models for Branched Polymers	353
9.6.1	Symmetric Star Polymers and Blends with Linear Polymers ..	354
9.6.2	Branch Point Hopping in Slip-Link Simulations	358
9.7	Summary	360
	References.....	362
10	Nonlinear Viscoelasticity	369
10.1	Introduction.....	369
10.2	Nonlinear Phenomena—A Tube Model Interpretation.....	369
10.2.1	Large Scale Orientation—The Need for a Finite Strain Tensor ..	370

10.2.2	Chain Retraction and the Damping Function.....	370
10.2.3	Convective Constraint Release and Shear Thinning.....	373
10.3	Constitutive Equations	374
10.3.1	Boltzmann Revisited	375
10.3.2	Integral Constitutive Equations.....	377
10.3.3	Differential Constitutive Equations.....	381
10.4	Nonlinear Stress Relaxation.....	382
10.4.1	Doi and Edwards Predictions of the Damping Function	383
10.4.2	Estimating the Rouse Time of an Entangled Chain.....	385
10.4.3	Damping Functions of Typical Polymers	386
10.4.4	Normal Stress Relaxation.....	388
10.4.5	Double-Step Strain	391
10.5	Dimensionless Groups Used to Plot Rheological Data.....	392
10.5.1	The Deborah Number	392
10.5.2	The Weissenberg Number	393
10.6	Transient Shear Tests at Finite Rates	393
10.6.1	Stress Growth and Relaxation in Steady Shear	393
10.6.2	Large- and Medium-Amplitude Oscillatory Shear	398
10.7	The Viscometric Functions	402
10.7.1	Dependence of Viscosity on Shear Rate	402
10.7.1.1	Empirical Viscosity Models	403
10.7.1.2	Viscosity Function in Terms of Tube Models	405
10.7.1.3	Effect of Molecular Weight Distribution on Viscosity ..	406
10.7.1.4	Effect of Long-Chain Branching on Viscosity	407
10.7.2	Normal Stress Differences in Steady Simple Shear.....	409
10.8	Experimental Methods for Shear Measurements	413
10.8.1	Rotational Rheometers	413
10.8.1.1	Generating Step Strain	414
10.8.1.2	Flow Irregularities in Cone-Plate Rheometers	415
10.8.1.3	Measurement of the Second Normal Stress Difference ..	416
10.8.2	Sliding Plate Rheometers.....	417
10.8.3	Optical Methods—Flow Birefringence	418
10.8.4	Capillary and Slit Rheometers.....	419
10.8.5	The Cox-Merz Rule	421
10.9	Extensional Flow Behavior of Melts and Concentrated Solutions	422
10.9.1	Introduction.....	422
10.9.2	Solutions versus Melts	429
10.9.3	Linear, Monodisperse Polymers	429
10.9.4	Effect of Polydispersity.....	430
10.9.5	Linear Low-Density Polyethylene	430
10.9.6	Model Branched Systems	431

10.9.7 Long-Chain Branched Metallocene Polyethylenes.....	433
10.9.8 Randomly Branched Polymers and LDPE.....	434
10.9.9 Stress Overshoot in Extensional Flow.....	436
10.10 Experimental Methods for Extensional Flows	437
10.10.1 Introduction.....	437
10.10.2 Rheometers for Uniaxial Extension.....	438
10.10.3 Uniaxial Extension—Approximate Methods	442
10.10.4 Rheometers for Biaxial and Planar Extension	443
10.11 Summary	443
References.....	446
11 Tube Models for Nonlinear Viscoelasticity of Linear and Branched Polymers.....	461
11.1 Introduction.....	461
11.2 Relaxation Processes Unique to the Nonlinear Regime	462
11.2.1 Retraction.....	462
11.2.2 Convective Constraint Release.....	464
11.3 Monodisperse Linear Polymers.....	465
11.3.1 No Chain Stretch: The Doi-Edwards Equation	465
11.3.2 Chain Stretch: The Doi-Edwards-Marrucci-Grizzuti (DEMG) Theory	469
11.3.3 Convective Constraint Release (CCR) and the GLaMM Model	474
11.3.4 Toy Models Containing CCR and Chain Stretch.....	476
11.3.4.1 “Rolie-Poly” Model for CCR.....	476
11.3.4.2 Differential Model of Ianniruberto and Marrucci.....	478
11.3.5 Comparison of Theory with Data for Monodisperse Linear Polymers: Shearing Flows	480
11.3.6 Extensional Flows of Melts and Solutions of Linear Polymers	484
11.3.7 Constitutive Instabilities and Slip.....	490
11.3.8 Entanglement Stripping and Chain Tumbling.....	492
11.3.9 Processing Flows.....	493
11.4 Polydisperse Linear Polymers	494
11.5 Polymers with Long-Chain Branching	497
11.5.1 The Pom-Pom Model	502
11.5.2 Revisions to the Pom-Pom Model	508
11.5.2.1 Drag-Strain Coupling.....	508
11.5.2.2 Correction for Reversing Flows	509
11.5.2.3 Second Normal Stress Difference and Other Corrections: The Extended Pom-Pom Model	509
11.5.2.4 Stress Overshoots, Accelerated Relaxation, and Entanglement Stripping	510

11.5.3 Empirical Multi-Mode Pom-Pom Equations for Commercial Melts.....	511
11.6 Towards Prediction of Nonlinear Viscoelasticity from Molecular Parameters.....	515
11.6.1 Seniority and Priority.....	515
11.6.2 Computational Prediction of Nonlinear Rheology for Polydisperse Branched Polymers	517
11.7 Summary	522
References.....	525
12 State of the Art and Challenges for the Future.....	535
12.1 State of the Art	535
12.2 Progress and Remaining Challenges.....	539
Appendix A: Structural and Rheological Parameters for Several Polymers...	547
Appendix B: Some Tensors Useful in Rheology.....	549
Nomenclature	555
Author Index	563
Subject Index.....	581