

# Contents

<b>Acknowledgments</b> .....	<b>VII</b>
<b>Preface</b> .....	<b>IX</b>
<b>Chapter Abstracts</b> .....	<b>XVII</b>
<b>1 Preamble</b> .....	<b>1</b>
1.1 Introduction .....	1
1.1.1 The Classical View of Polymer Visco-elasticity, Shear-Thinning, and Entanglements .....	2
1.1.2 The Dual-Split Statistics View of Polymer Visco-elasticity, Shear-Thinning, and Entanglements .....	3
1.2 Introduction to the Dual-Phase Model of Polymer Interactions and to the Cross-Dual-Phase Model of Entanglements .....	4
1.2.1 A New Model of Polymer Interactions (Summary) .....	4
1.2.1.1 Conformers: The b and F Types of Conformers .....	6
1.2.1.2 The Dual-Split Statistics of the Conformers: [b/F ↔ (c,g,t)] .....	8
1.2.1.3 Crossed Dual-Phase Statistics for Long Chains .....	13
1.2.2 A New Understanding of Polymer Melt Molecular Interactions and Flow Properties .....	15
<b>2 Trouble with Polymer Physics: “Sustained-Orientation”: Ground-Breaking Experimental Research Shakes the Current Understanding of the Liquid State of Polymers</b> .....	<b>21</b>
2.1 Introduction .....	21
2.2 Experimental Description .....	22
2.2.1 The Rheo-Fluidification Processor .....	22
2.2.2 Sustained-Orientation .....	23
2.3 Results .....	25
2.4 Discussion .....	27

2.5	Summary and Conclusions .....	29
2.6	Note .....	29
<b>3</b>	<b>The Great Myths of Polymer Rheology: Comparison of Theory with Experimental Data .....</b>	<b>31</b>
3.1	Introduction .....	32
3.2	Shear-Thinning: Non-Newtonian Viscous Behavior .....	34
3.3	Description of the Data Sources .....	36
3.4	Analysis Protocol .....	40
3.5	Accuracy Consideration .....	40
3.6	Critical Analysis of the Equations of Rheology .....	44
3.6.1	Universality of WLF Constants at $T_g$ .....	44
3.6.2	Validity of the 3.4 Power Exponent for $M > M_c$ .....	48
3.6.3	For $M < M_c$ , Viscosity Is Not Proportional to $M$ , Contrary to Rouse's Model .....	52
3.6.4	Accuracy in the Determination of the Newtonian Viscosity .....	54
3.6.5	Time-Temperature Superposition .....	59
3.6.6	The Upper Melt Temperature Departure from Superposition .....	63
3.6.7	The Lower Melt Temperature Departure from Superposition .....	67
3.6.8	Is the Superposition Principle Ever Valid? .....	71
3.7	The Question of Understanding Rheology with a Spectrum of Relaxation .....	73
3.8	Conclusions .....	85
<b>4</b>	<b>The Great Myths of Polymer Rheology: Transient and Steady State. The Question of Melt Entanglement Stability .....</b>	<b>89</b>
4.1	Introduction .....	89
4.1.1	Transient and Steady State Behavior .....	89
4.1.2	Step Strain Experiment in the Non-linear Region .....	90
4.1.3	Step Strain Rate Experiments under Non-linear Conditions .....	94
4.1.4	Strain-Induced Transients under Oscillatory Shear .....	96
4.1.5	Combining Rotation and Oscillation Shear Modes .....	98
4.1.5.1	The Work of Osaki et al. ....	98
4.1.5.2	Effect of Combining Rotation and Oscillation in the Non-linear Regime: Shear-Refinement under Dynamic Conditions .....	100
4.1.6	Melt Fracture. Edge Fracture in Parallel Plate Experiments .....	113
4.1.7	Objectives of This Chapter .....	114

4.2	Experimental Procedure, Polymer Characterization, Definition of Parameters	116
4.2.1	Experimental Procedures	116
4.2.1.1	Type 1A: The Simple Time Sweep at Given T, $\omega$ , and Strain	116
4.2.1.2	Type 1B: The Simple Time Sweep at Given T, $\omega$ , and Strain % Immediately Followed by a Cooling Ramp Test Performed in the Linear Range	116
4.2.1.3	Type 2: The Three-Step Experiment of Type FTF (Frequency–Time–Frequency) in a Dynamic Rheometer	117
4.2.1.4	Type 3: The Four-Step Experiment of Type FT1–FT2–FT1–FT2 in a Dynamic Rheometer	117
4.2.1.5	Type 4: Pure Viscometry	117
4.2.1.6	Type 5: Pure Viscometry Followed by a Frequency Sweep	117
4.2.1.7	Type 6: Viscosity Measurement under Extrusion Flow Conditions	118
4.2.1.8	Type 7: In-line Viscosity Measurement at the End of a “Treatment Processor”	118
4.2.2	Rheometers Used	118
4.2.3	Materials	119
4.2.4	Initial State and Sample Molding Procedure	121
4.2.5	Definition of the Rheological Parameters to Analyze the Stability of the Melt	122
4.3	Results	127
4.3.1	Linear PC (Lexan 141). Time Sweeps at Various Temperatures, Frequencies, 50% Strain	127
4.3.2	Viscosimetric Experiments on LLDPE	130
4.3.2.1	Pure Rotation. Type 4 Experiment	130
4.3.2.2	Pure Rotation Followed by Frequency Sweep. Type 5 Experiments	142
4.3.2.3	Type 4 Experiments on Melts with Prior Mechanical History	146
4.3.2.4	Transients Created in Dynamic Conditions by an Increase of Strain	150
4.3.3	Dynamic Type 2 Experiments (FS–TS–FS) on PC	153
4.3.3.1	Effect of Strain at Constant Low Frequency (0.1 Hz)	153
4.3.3.2	Effect of Frequency during Time Sweep (at a Constant Strain of 5%)	173
4.3.3.3	Effect of Increased Energy Input during Time Sweep: T = 225 °C, Frequency = 5 Hz, and $\gamma$ = 20%	185
4.3.3.4	Effect of Annealing the Melt after Treatment and Type 3 Experiments	191

4.3.4	Long-Term Entanglement Network Instability for a PMMA Melt . . .	199
4.3.5	Entanglement Network Instability for a Polystyrene Melt . . . . .	202
4.3.5.1	PS 1070 . . . . .	202
4.3.5.2	PS2: Thermal-mechanical History to Create Out-of-Equilibrium Melt Properties . . . . .	206
4.4	Discussion . . . . .	210
4.4.1	The Question of the Origin of the Time Dependency of the Viscoelastic Parameters . . . . .	210
4.4.2	Challenging Interpretations . . . . .	211
4.4.2.1	Viscous Heating . . . . .	211
4.4.2.2	Shear Degradation . . . . .	211
4.4.2.3	Drooling of the Melt Outside the Rheometer Plates . . . . .	213
4.4.2.4	Plastification Due to an Increase of the Monomer Concentration by the Shear Process . . . . .	215
4.4.2.5	Shear-Thinning . . . . .	216
4.4.2.6	Edge Fracture Explanation . . . . .	216
4.5	Summary . . . . .	249
4.6	Conclusion . . . . .	250
<b>5</b>	<b>The Great Myths of Polymer Rheology: Elasticity of the Network of Entanglements . . . . .</b>	<b>257</b>
5.1	Background . . . . .	257
5.2	Introduction . . . . .	259
5.3	The Cross-Dual-Phase Network of Entanglement . . . . .	264
5.4	The Static and Dynamic Frequency of the Phase-Wave . . . . .	265
5.5	The Influence of $T_g(\omega, \gamma)$ on the Rheology Data . . . . .	280
5.6	The Cohesive Network Energy . . . . .	292
5.7	Effect of Temperature . . . . .	296
5.7.1	T Ramp Down Experiments . . . . .	296
5.7.2	Frequency Sweeps at T Constant . . . . .	301
5.7.3	Diversity of the Temperature Dependence Depending on the Polymer Type . . . . .	313
5.8	Effect of Strain % . . . . .	322
5.9	The Melt Behavior at Low Frequency . . . . .	359
5.10	Summary and Conclusions . . . . .	365

<b>6</b>	<b>The Elastic Dissipative State of Polymeric Melts. Solid-like Behavior in the Molten State</b>	<b>385</b>
6.1	Introduction	385
6.2	Noirez et al. Solid-like Results	388
6.3	Why Narrowing the Gap Makes $\chi_1$ Increase (The Melt Is More “Glassy-like”)	397
6.4	Is There a Surface Effect in the Experiments Reported by Noirez et al.?	398
6.5	The Question of the Nature of the Elasticity in the Solid-like Melt	400
6.6	Conclusion	401
<b>7</b>	<b>Shear-Thinning of Polymeric Melts: The Failure of the Reptation Model</b>	<b>403</b>
7.1	Rheo-SANS Results of Watanabe et al. (2007)	403
7.2	Rheo-SANS Results of Noirez et al. (2009)	404
7.3	New Rheo-SANS Evidence by Zhe Wang et al.: “Fingerprinting Molecular Relaxation in Deformed Polymers”	405
7.4	Discussion and Conclusions	409
<b>8</b>	<b>Conclusions – Entanglements: A New Interpretation and Perspectives in Science and Technology</b>	<b>417</b>
8.1	Summary of the Book’s Previous Chapters	417
8.2	Industrial Applications: Improve the Processability of Existing and New Resins	419
8.3	A New Paradigm: Future Achievements	422
8.4	Appendix A	426
	<b>Index</b>	<b>427</b>