

## Contents

### List of Contributors XI

- 1 Introduction 1**  
*John A. Pojman and Qui Tran-Cong-Miyata*
- 1.1 Overview 1  
 1.2 What Follows 2  
 1.3 The Future 4  
 References 4
- 2 What Is Nonlinear Dynamics and How Does It Relate to Polymers? 5**  
*Irving R. Epstein, John A. Pojman, and Qui Tran-Cong-Miyata*
- 2.1 Introduction 5  
 2.2 Nonlinear Dynamics 5  
 2.3 Some Key Ideas of Nonlinear Chemical Dynamics 6  
 2.3.1 Chemical Oscillations 7  
 2.3.2 Waves and Patterns 7  
 2.3.3 More Complex Phenomena 8  
 2.4 Polymeric Systems 9  
 2.4.1 What Is Special about Polymers? 10  
 2.4.2 Challenges 10  
 2.4.3 Sources of Feedback 10  
 2.4.4 Nonlinear Dynamics and Phase Separation of Reacting Systems 12  
 2.4.5 Spatial Structures in Polymeric Systems 13  
 2.4.6 Approaches to Nonlinear Dynamics in Polymeric Systems 13  
 2.4.6.1 Oscillations in a CSTR 16  
 2.5 Conclusions 16  
 References 16
- 3 Evolution of Nonlinear Rheology and Network Formation during Thermoplastic Polyurethane Polymerization and Its Relationship to Reaction Kinetics, Phase Separation, and Mixing 21**  
*I. Sedat Gunes, Changdo Jung, and Sadhan C. Jana*
- 3.1 Introduction 21

3.2	Brief Overview of Evolution of Nonlinear Rheological Properties during Polymerization	22
3.2.1	The Relationship between Nonlinear Rheology and the Extent of Polymerization during the Growth of Linear Chains	22
3.2.2	Relationship between Nonlinear Rheology and the Extent of Polymerization during the Growth of Nonlinear Chains	24
3.2.3	Chemical Structure of the Monomers and Polymerization Mechanism in Polyurethane Polymerization	25
3.2.4	Evolution of Nonlinear Rheology during Polyurethane Polymerization	26
3.2.5	Basic Reactions and Phase Separation Kinetics in Synthesis of Polyurethanes and Their Relationship to the Evolution of Nonlinear Rheology	27
3.3	Evolution of Nonlinear Rheology and Network Formation during Thermoplastic Polyurethane Polymerization: Effects of Mixer Design, Mixing Protocol, Catalyst Concentration, and Timescales	27
3.3.1	Effects of Mixing	29
3.3.1.1	Mechanism of Mixing	29
3.3.1.2	Laminar Mixing under Shear and Extensional Flow with Constant Shear and Elongation Rates	30
3.3.1.3	Dispersive and Distributive Mixing	30
3.3.1.4	Chaotic Mixing	31
3.3.1.5	Effect of Mixing on Systems Undergoing Chemical Reactions	32
3.3.2	Analysis of Timescale of Mixing and Chemical Reactions during TPU Polymerization	32
3.3.3	Simultaneous Effects of Mixing, Chemical Reaction, and Molecular Diffusion on the Evolution of Nonlinear Rheological Properties	36
3.4	Conclusions	38
	References	40
<b>4</b>	<b>Frontal Polymerization</b>	<b>45</b>
	<i>John A. Pojman</i>	
4.1	Introduction	45
4.1.1	Requirements for Frontal Polymerizations	45
4.1.2	Types of Systems	46
4.1.3	Characteristics of Frontal Polymerization	47
4.2	Applications	49
4.2.1	Cure-On-Demand Putty	49
4.2.2	Adhesive	50
4.2.3	Coatings	51
4.3	Motivation for Studying Nonlinear Dynamics with Frontal Polymerization	51
4.4	Convective Instabilities	52
4.4.1	Buoyancy-Driven Convection	52
4.4.2	Effect of Surface-Tension-Driven Convection	55

4.5	Thermal Instabilities	56
4.5.1	Effect of Complex Kinetics	57
4.5.2	Effect of Bubbles	58
4.5.3	Effect of Buoyancy	59
4.5.4	Other Factors	59
4.6	Snell's Law	59
4.7	Three-Dimensional Frontal Polymerization	60
4.8	Impact on Applications	61
4.9	Conclusions	62
	References	62
<b>5</b>	<b>Isothermal Frontal Polymerization</b>	<b>69</b>
	<i>Lydia L. Lewis and Vladimir A. Volpert</i>	
5.1	Introduction	69
5.1.1	A Comparison between TFP and IFP: Their Mechanisms and Front Properties	69
5.1.2	Background	71
5.2	Mathematical Models	74
5.3	Experimental IFP	79
5.4	Comparison of Experimental and Mathematical IFP	85
5.5	Conclusions	87
	Acknowledgments	88
	References	88
<b>6</b>	<b>Reaction-Induced Phase Separation of Polymeric Systems under Stationary Nonequilibrium Conditions</b>	<b>91</b>
	<i>Hideyuki Nakanishi, Daisuke Fujiki, Dan-Thuy Van-Pham, and Qui Tran-Cong-Miyata</i>	
6.1	Introduction	91
6.2	Overview of Theoretical Studies on Phase Separation Kinetics of Nonreactive and Reactive Binary Mixtures	92
6.2.1	Phase Separation of Nonreacting Mixtures	92
6.2.2	Phase Separation of Reacting Mixtures	94
6.3	Chemical Reactions in Polymeric Systems: the Non-Mean-Field Kinetics	97
6.3.1	Reaction Kinetics in the Bulk State of Polymer	97
6.3.2	Reaction Kinetics in the Liquid State of Polymer Mixtures	98
6.4	Reaction-Induced Elastic Strain and Its Relaxation Behavior	99
6.5	Phase Separation under Nonuniform Conditions in Polymeric Systems	101
6.5.1	Polymers with Spatially Graded Continuous Structures	101
6.5.2	Morphology with Arbitrary Symmetry and Distribution of Length Scales	105
6.5.2.1	The Computer-Assisted Irradiation Method	105

6.5.2.2	Polymers with an Arbitrary Distribution of Characteristic Length Scales	106
6.6	Conclusions	109
	Acknowledgments	110
	References	110
<b>7</b>	<b>Gels Coupled to Oscillatory Reactions</b>	<b>115</b>
	<i>Ryo Yoshida</i>	
7.1	Introduction	115
7.2	Design of Self-Oscillating Gel	116
7.3	Self-Oscillating Behaviors of the Gel	117
7.3.1	Self-Oscillation of the Miniature Bulk Gel	117
7.3.2	Control of Oscillating Behaviors	119
7.3.3	Peristaltic Motion of Gels with Propagation of Chemical Wave	119
7.3.4	Self-Oscillation with Structural Color Changes	121
7.4	Design of Biomimetic Micro-/Nanoactuator Using Self-Oscillating Polymer and Gel	122
7.4.1	Self-Walking Gel	122
7.4.2	Mass Transport Surface Utilizing Peristaltic Motion of Gel	124
7.4.3	Microfabrication of Self-Oscillating Gel for Microdevices	124
7.4.4	Control of Chemical Wave Propagation in Self-Oscillating Gel Array	126
7.4.5	Self-Oscillating Polymer Chains as “Nano-Oscillators”	127
7.4.6	Self-Flocculating/Dispersing Oscillation of Microgels	128
7.4.7	Fabrication of Microgel Beads Monolayer	129
7.4.8	Attempts of Self-Oscillation under Physiological Conditions	131
7.5	Conclusion	132
	References	132
<b>8</b>	<b>Self-Oscillating Gels as Biomimetic Soft Materials</b>	<b>135</b>
	<i>Olga Kuksenok, Victor V. Yashin, Pratyush Dayal, and Anna C. Balazs</i>	
8.1	Introduction	135
8.2	Methodology	137
8.2.1	Continuum Equations	137
8.2.2	Formulation of the Gel Lattice Spring Model (gLSM)	140
8.3	Sensitivity to Mechanical Deformation	143
8.3.1	Capturing Effects of Local Mechanical Impact on Homogeneous BZ Gels	143
8.3.2	Straining Heterogeneous BZ Gels	147
8.4	Sensitivity to Light	154
8.5	Conclusions	160
	Acknowledgments	160
	References	161

<b>9</b>	<b>Chemoelastodynamics of Responsive Gels</b>	<b>163</b>
	<i>Jacques Boissonade, Pierre Borckmans, Patrick De Kepper, and Stéphane Métais</i>	
9.1	Introduction	163
9.2	Elastodynamics of Responsive Gels: a Brief Survey	164
9.3	Oscillatory Gel Dynamics Using an Oscillating Chemical Reaction	166
9.3.1	The Approach	166
9.3.2	Coupling to the Oscillating Belousov–Zhabotinsky Reaction	169
9.3.3	Numerical Integration Results	171
9.4	Chemodynamic Oscillations Induced by Geometric Feedback	174
9.4.1	Spatial Bistability and Related Chemomechanical Instabilities	174
9.4.2	Simple Models	175
9.4.3	A More Realistic Model: The Polyelectrolyte Model	177
9.5	Experimental Observations	181
9.5.1	Experimental Results	182
9.5.1.1	Case of the Chlorite–Tetrathionate Reaction	182
9.5.1.2	Case of the Bromate–Sulfite Reaction	184
9.6	Conclusions and Perspectives	185
	References	186
<b>10</b>	<b>Oscillatory Systems Created with Polymer Membranes</b>	<b>189</b>
	<i>Ronald A. Siegel</i>	
10.1	Introduction	189
10.2	Survey of Synthetic Membrane Oscillators	191
10.2.1	Teorell Oscillator	191
10.2.2	Polyelectrolyte Membrane-Based Oscillators	193
10.2.3	Thermofluidic Oscillator	194
10.2.4	Lipid/Organic Membrane Analogs	196
10.2.5	Membrane/Enzyme Oscillators	196
10.2.6	General Discussion	198
10.3	Hydrogel–Enzyme Oscillator for Rhythmic Hormone Delivery	199
10.3.1	General Scheme	200
10.3.2	Bistability of Hydrogel Membrane Permeability	201
10.3.3	Oscillator Operation	204
10.3.4	Oscillator Prototype	205
10.3.5	Analysis of Factors Affecting Oscillations Over Time	207
10.3.6	Tuning pH Range of Oscillations	208
10.3.7	Discussion and Conclusion	211
	Acknowledgments	212
	References	212
	Further Reading	217

<b>11</b>	<b>Structure Formation in Inorganic Precipitation Systems</b>	<b>219</b>
	<i>Oliver Steinbock and Jason Pagano</i>	
11.1	Introduction	219
11.2	Permanent Patterns from Inorganic Precipitation and Deposition Processes	220
11.3	Tube Formation in Precipitation Systems and Silica Gardens	221
11.4	Historic and Cultural Links	222
11.5	Some Recent Developments	223
11.6	Experimental Methods	224
11.7	Growth Regimes	225
11.8	Wall Composition and Morphology	228
11.9	Relaxation Oscillations	230
11.10	Radius Selection	233
11.11	Bubbles as Templates	235
11.12	Toward Applications	237
11.13	Outlook and Conclusions	238
	Acknowledgments	239
	References	239
	<b>Index</b>	<b>243</b>