

## Contents

### List of Contributors ix

- 1 Introduction 1**  
*Christopher Barner-Kowollik*
- 2 Quantum-Chemical Studies of RAFT Polymerization: Methodology, Structure-Reactivity Correlations and Kinetic Implications 5**  
*Michelle L. Coote, Elizabeth H. Krenske, Ekaterina I. Izgorodina*
- 2.1 Introduction 5
- 2.2 Methodology 7
- 2.3 Computational Modeling of RAFT Kinetics 19
- 2.4 Structure–Reactivity Studies 34
- 2.5 Abbreviations 45
- 3 The Mechanism and Kinetics of the RAFT Process: Overview, Rates, Stabilities, Side Reactions, Product Spectrum and Outstanding Challenges 51**  
*Graeme Moad, Christopher Barner-Kowollik*
- 3.1 History 51
- 3.2 Preequilibrium Kinetics and Mechanism 59
- 3.3 Main Equilibrium Kinetics and Mechanism 83
- 3.4 Mechanisms for Rate Retardation/Inhibition – Outstanding Questions 90
- 3.5 RAFT Copolymerization: Block and Statistical Copolymers 91
- 3.6 The Kinetics and Mechanism of Star and Graft Polymer Formation Processes 94
- 3.7 Mechanism and Kinetics as a Guide for the Synthetic Polymer Chemist 97
- 4 The RAFT Process as a Kinetic Tool: Accessing Fundamental Parameters of Free Radical Polymerization 105**  
*Thomas Junkers, Tara M. Lovestead, Christopher Barner-Kowollik*
- 4.1 Introduction 105
- 4.2 Chain-Length-Dependent Termination: A Brief Overview 107

## vi | Contents

- 4.3 RAFT Chemistry as a Tool for Elucidating the Chain Length  
Dependence of  $k_t$  109
- 4.4 Chain-Length-Dependent Propagation Rate Coefficients 144
- 5 The Radical Chemistry of Thiocarbonylthio Compounds: An Overview 151**  
*Samir Z. Zard*
- 5.1 Historical Overview and Early Chemistry 151
- 5.2 The Barton–McCombie Deoxygenation 153
- 5.3 A Minor Mechanistic Controversy 154
- 5.4 A New Degenerative Radical Process 156
- 5.5 Synthetic Routes to Thiocarbonylthio Derivatives 160
- 5.6 Some Synthetic Applications of the Degenerative Radical  
Transfer to Small Molecules 168
- 5.7 Applications to Controlled Radical Polymerizations 177
- 5.8 Concluding Remarks 185
- 6 RAFT Polymerization in Bulk Monomer or in (Organic) Solution 189**  
*Ezio Rizzardo, Graeme Moad, San H. Thang*
- 6.1 Introduction 189
- 6.2 RAFT Agents 192
- 6.3 RAFT Polymerization 205
- 6.4 RAFT Polymerization Conditions 222
- 6.5 Abbreviations 225
- 7 RAFT Polymerization in Homogeneous Aqueous Media: Initiation Systems,  
RAFT Agent Stability, Monomers and Polymer Structures 235**  
*Andrew B. Lowe, Charles L. McCormick*
- 7.1 Introduction 235
- 7.2 Initiation Systems 236
- 7.3 RAFT Agent Stability 241
- 7.4 Suitable Monomers 248
- 7.5 Examples of Experimental Procedures 276
- 8 RAFT-Mediated Polymerization in Heterogeneous Systems 285**  
*Carl N. Urbani, Michael J. Monteiro*
- 8.1 Introduction 285
- 8.2 Effect of  $C_{tr,RAFT}$  on  $M_n$  and PDI in Homogeneous Systems 292
- 8.3 Raft in Heterogeneous Systems 293
- 8.4 Conclusion 311
- 9 Complex Architecture Design via the RAFT Process: Scope,  
Strengths and Limitations 315**  
*Martina H. Stenzel*
- 9.1 Complex Polymer Architectures 315
- 9.2 Block Copolymers 315
- 9.3 Star Polymers via RAFT Polymerization 343

9.4	Comb Polymers	359
9.5	Other Complex Architectures	364
9.6	Conclusions	367
<b>10</b>	<b>Macromolecular Design by Interchange of Xanthates: Background, Design, Scope and Applications</b>	<b>373</b>
	<i>Daniel Taton, Mathias Destarac, Samir Z. Zard</i>	
10.1	Introduction	373
10.2	History of MADIX Polymerization	374
10.3	Mechanism of MADIX Polymerization	379
10.4	Kinetics of MADIX Polymerization	383
10.5	Choice of MADIX Agents	387
10.6	Synthesis of MADIX Agents	390
10.7	Experimental Conditions in MADIX	391
10.8	Monomers Polymerizable by MADIX	393
10.9	MADIX Polymerization in Waterborne Dispersed Media	399
10.10	Macromolecular Engineering by MADIX	403
10.11	Methodologies to Remove the Dithiocarbonate End Groups	412
10.12	Applications of MADIX (co)polymers	414
<b>11</b>	<b>Surface and Particle Modification via the RAFT Process: Approach and Properties</b>	<b>423</b>
	<i>Yu Li, Linda S. Schadler, Brian C. Benicewicz</i>	
11.1	Introduction	423
11.2	Approach	424
11.3	Properties	444
11.4	Conclusions	449
11.5	Abbreviations	450
11.6	Acknowledgment	451
<b>12</b>	<b>Polymers with Well-Defined End Groups via RAFT – Synthesis, Applications and Postmodifications</b>	<b>455</b>
	<i>Leonie Barner, Sébastien Perrier</i>	
12.1	Introduction	455
12.2	Terminal Functionalities Introduced via the CTA	456
12.3	RAFT in Combination with Other Polymerization Techniques	467
12.4	Stability of the Thiocarbonylthio End Group and Its Modification Postpolymerization	471
12.5	Conclusion	478
12.6	Abbreviations	478
<b>13</b>	<b>Toward New Materials Prepared via the RAFT Process: From Drug Delivery to Optoelectronics?</b>	<b>483</b>
	<i>Arnaud Favier, Bertrand de Lambert, Marie-Thérèse Charreyre</i>	
13.1	Introduction	483

viii | *Contents*

13.2	Bio-Related Applications	485
13.3	Polymer-Based Materials for Various Applications	508
13.4	Conclusions	526

<b>Subject Index</b>	<b>537</b>
----------------------	------------