Contents

List of Contributors  xi

1  Introduction  1
   Mitra S. Ganewatta, Chuanbing Tang, and Chang Y. Ryu
   1.1  Introduction  1
   1.2  Sustainable Polymers  2
   1.3  Biomass Resources for Sustainable Polymers  4
       1.3.1  Natural Biopolymers  4
       1.3.2  Monomers and Polymers from Biomass  6
   1.4  Conclusions  8
       References  8

2  Polyhydroxyalkanoates: Sustainability, Production, and Industrialization  11
   Ying Wang and Guo-Qiang Chen
   2.1  Introduction  11
   2.2  PHA Diversity and Properties  14
       2.2.1  PHA Diversity  14
       2.2.2  PHA Properties  15
   2.3  PHA Production from Biomass  16
       2.3.1  PHA Production Strains  16
       2.3.2  PHA Synthesis Pathways  17
       2.3.3  PHA Production from Unrelated Carbon Sources  17
           2.3.3.1  Production of P3HB4HB from Unrelated Carbon Sources  19
           2.3.3.2  PHBV Production from Various Substrates  24
           2.3.3.3  PHA Production Under Seawater-Based Open and Continuous Conditions from Mixed Substrates  25
   2.4  PHA Application and Industrialization  26
   2.5  Conclusion  28
       Acknowledgment  28
       References  28

3  Polylactide: Fabrication of Long Chain Branched Polylactides and Their Properties and Applications  35
   Zhigang Wang and Huagao Fang
   3.1  Introduction  35
5.2 Rosin Based Polyurethane Foams 92
5.3 Rosin-Based Polyurethane Elastomers 95
5.4 Terpene-Based Polyurethanes 95
5.5 Terpene-Based Waterborne Polyurethanes 97
5.6 Rosin-Based Shape Memory Polyurethanes 99
5.7 Conclusions 100
References 101

6 Rosin-Derived Monomers and Their Progress in Polymer Application 103
Jifu Wang, Shaofeng Liu, Juan Yu, Chuanwei Lu, Chunpeng Wang, and Fuxiang Chu
6.1 Introduction 103
6.2 Rosin Chemical Composition 104
6.3 Rosin Derived Monomers for Main-Chain Polymers 105
6.3.1 Rosin-Derived Main-Chain Polymers from MPA and its Derivatives 105
6.3.2 Rosin-Derived Polymers from APA and its Derivatives 107
6.3.3 Ketonic Type Rosin-Derived Macro-Monomers 110
6.3.4 Others 111
6.4 Rosin-Derived Monomers for Side-Chain Polymers 112
6.4.1 Rosin Derived Monomers 112
6.4.2 Side-Chain Linear Homopolymers 114
6.4.2.1 Side-Chain Linear Homopolymers Prepared by ATRP 114
6.4.2.2 Side-Chain Linear Homopolymer Prepared by RAFT 115
6.4.3 Side-Chain Linear Copolymers 116
6.4.3.1 Side-Chain Linear Rosin Acid-Caprolactone Block Copolymers 116
6.4.3.2 Side-Chain Linear Rosin Acid-PEG Amphiphilic Block Copolymers 118
6.4.4 Side-Chain Grafted Copolymers 120
6.4.4.1 Side-Chain Grafted Copolymer by Click Chemistry 120
6.4.4.2 Side-Chain Grafted Copolymer by ATRP 124
6.4.4.3 Side-Chain Grafted Copolymer by Other Method 130
6.5 Rosin-Derived Monomers for Three-Dimensional Rosin-Based Polymer 131
6.5.1 Three-Dimensional Rosin-based Polymer by Condensation Polymerization 132
6.5.1.1 Rosin Modified Phenolic Resins 132
6.5.1.2 Rosin-based Polyurethane 133
6.5.1.3 Rosin-based Thermoset Resin from Epoxy Resin 134
6.5.2 Three-Dimensional Rosin-based Polymer by Free Radical Polymerization 136
6.5.2.1 Rosin-based UV Curing Resin 136
6.5.2.2 Rosin-based Thermal Curing Resin 138
6.6 Outlook and Conclusions 140
Acknowledgments 141
References 141
7 Industrial Applications of Pine-Chemical-Based Materials 151
Lien Phun, David Snead, Phillip Hurd, and Feng Jing

7.1 Pine Chemicals Introduction 151
7.2 Crude Tall Oil 151
7.3 Terpenes 153
7.3.1 Terpene Resins 153
7.4 Tall Oil Fatty Acid 159
7.4.1 TOFA-Based Alkyds 160
7.4.2 TOFA for Polyamides 160
7.4.3 Oxidized Tall Oil 161
7.4.4 Polyurethanes 162
7.4.5 Epoxy Resin Esters 164
7.4.6 Amidoamine Epoxy Resins 166
7.5 Rosin 167
7.5.1 Adhesives-Polyesters 168
7.5.2 Coatings 169
7.5.3 Epoxies 169
7.5.4 Modified Rosin Polymers 170
7.5.5 Insulation 170
7.5.6 Inks 170
7.5.7 Plastics 171
7.5.8 Paper Size 172
7.5.9 Surfactants 172
7.5.10 Other 172
7.6 Miscellaneous Products 173
References 178

8 Preparation and Applications of Polymers with Pendant Fatty Chains from Plant Oils 181
Liang Yuan, Zhongkai Wang, Nathan M. Trenor, and Chuanbing Tang

8.1 Introduction 181
8.2 (Meth)acrylate Monomers Preparation and Polymerization 182
8.2.1 From Fatty Acid Methyl Esters 182
8.2.2 From Fatty Acids 184
8.2.3 From Fatty Alcohols 186
8.2.3.1 Anionic Polymerization 186
8.2.3.2 Group Transfer Polymerization 187
8.2.3.3 Atom Transfer Radical Polymerization (ATRP) 187
8.2.3.4 Reversible Addition-Fragmentation Chain-Transfer Polymerization (RAFT) 191
8.2.4 From N-Alkylhydroxyl Amides 191
8.3 Norbornene Monomers and Polymers for Ring Opening Metathesis Polymerization (ROMP) 194
8.4 2-Oxazoline Monomers for Living Cationic Ring Opening Polymerization 195
8.5 Vinyl Ether Monomers for Cationic Polymerization 200
8.6 Conclusions and Outlook 203
References 204

9 Structure–Property Relationships of Epoxy Thermoset Networks from Photoinitiated Cationic Polymerization of Epoxidized Vegetable Oils 209
Zheqin Yang, Jananee Narayanan, Matthew Ravalli, Brittany T. Rupp, and Chang Y. Ryu

9.1 Introduction 209
9.2 Photoinitiated Cationic Polymerization of Epoxidized Vegetable Oils 213
9.2.1 Epoxidized Vegetable Oils (EVOs) 213
9.2.2 Photo-initiated Cationic Polymerization of ESO: Structure–Property Relationship 214
9.2.3 Photo-initiated Cationic Polymerization of ELO: Thickness Control 221
9.3 Conclusions 224
Acknowledgment 225
References 225

10 Biopolymers from Sugarcane and Soybean Lignocellulosic Biomass 227
Delia R. Tapia-Blácido, Bianca C. Maniglia, and Milena Martelli-Tosi

10.1 Introduction 227
10.2 Lignocellulosic Biomass Composition and Pretreatment 229
10.3 Lignocellulosic Biomass from Soybean 233
10.4 Production of Polymers from Soybean Biomass 234
10.5 Lignocellulosic Biomass from Sugarcane 242
10.6 Production of Polymers from Sugarcane Bagasse 242
10.7 Conclusion and Future Outlook 246
Acknowledgments 247
References 247

11 Modification of Wheat Gluten-Based Polymer Materials by Molecular Biomass 255
Xiaoping Zhang

11.1 Introduction 255
11.2 Modification of Wheat Gluten Materials by Molecular Biomass 257
11.2.1 Modification of WG by Natural Phenolics 258
11.2.2 Modification by Epoxidized Vegetable Oil 264
11.3 Biodegradation of Wheat Gluten Materials Modified by Biomass 269
11.4 Biomass Fillers for WG Biocomposites 271
11.5 Conclusion and Future Perspectives of WG-Based Materials 272
References 273
12 Copolymerization of C1 Building Blocks with Epoxides 279
Ying-Ying Zhang and Xing-Hong Zhang
12.1 Introduction 279
12.2 CO2/Epoxide Copolymerization 280
12.2.1 Heterogeneous Zn—Co(III) DMCC 281
12.2.1.1 Structure of Zn—Co(III) DMCC 282
12.2.1.2 CO2/Epoxide Copolymerization via Zn—Co(III) DMCC Catalysis 286
12.2.1.3 Copolymerization of CO2 with Biomass Monomers 288
12.3 CS2/Epoxide Copolymerization 295
12.4 COS/Epoxide Copolymerization 299
12.5 Properties of C1-Based Polymers 304
12.5.1 Thermal Property 304
12.5.2 Mechanical Property 306
12.5.3 Biodegradability 306
12.5.4 Optical Property 306
12.6 Conclusions and Outlook 307
References 307

13 Double-Metal Cyanide Catalyst Design in CO2/Epoxide Copolymerization 315
Joby Sebastian and Darbha Srinivas
13.1 Introduction 315
13.2 Polycarbonates and Their Synthesis Methods 317
13.3 Copolymerization of CO2 and Epoxides 318
13.4 Double-Metal Cyanides and Their Structural Variation 319
13.5 Methods of DMC Synthesis 322
13.6 Factors Influencing Catalytic Activity of DMCs 323
13.6.1 Hexacyanometallate 323
13.6.2 Complexing Agent 325
13.6.3 Co-complexing Agent 326
13.6.4 Zinc Precursor/Halide Precursor 329
13.6.5 Cobalt Precursor 331
13.7 Role of Co-catalyst on the Activity of DMC Catalysts 332
13.8 Copolymerization in the Presence of Hybrid DMC Catalysts 334
13.9 Copolymerization with Nano-lamellar DMC Catalysts 335
13.10 Effect of Crystallinity and Crystal Structure of DMC on Copolymerization 337
13.11 Effect of Method of Preparation of DMC Catalysts on Their Structure and Copolymerization Activity 337
13.12 Reaction Mechanism of Copolymerization 340
13.12.1 Polymerization in the Presence of Initiators 340
13.12.2 Polymerization in the Absence of Initiators 341
13.13 Conclusions 342
References 343

Index 347