

Contents

About the Editor *xiii*

Preface *xv*

1 Transition Metal-catalyzed Polycondensation 1

Takaki Kanbara and Junpei Kuwabara

- 1.1 Introduction 1
- 1.2 Ni-catalyzed Polycondensation 2
- 1.3 Pd-catalyzed Polycondensation 4
- 1.4 Pd-catalyzed Polycondensation via C—H Bond Functionalization 6
- 1.5 Cu- and Fe-catalyzed Polycondensation 13
- 1.6 Other Transition Metal-catalyzed Polymerization 15
- 1.7 Summary 19
- References 19

2 Living Conjugated Polymers 31

Kevin J. T. Noonan

- 2.1 Introduction 31
- 2.2 Metal π -Binding in CTP 32
- 2.3 Catalysts for CTP 34
- 2.4 Kumada–Corriu Catalyst-transfer Polymerization 35
- 2.5 Catalyst-transfer Polymerization with Organolithium Reagents 39
- 2.6 Negishi Catalyst-transfer Polymerization 41
- 2.7 Suzuki–Miyaura Catalyst-transfer Polymerization 42
- 2.8 Stille Catalyst-transfer Polymerization (Stille CTP) 44
- 2.9 Buchwald–Hartwig Amination and Direct Arylation Polymerization (C—H Activation) 45
- 2.10 Chain-growth Polymerization of Aromatics Without Metal Catalysts 46
- 2.11 Conclusion 47
- Acknowledgment 47
- Abbreviations 47
- Polymers 47
- Metal Catalysts 48
- Ligands 48

Miscellaneous Reagents and Terms 48

References 48

3 Optically Active Through-space Conjugated Polymers Based on Planar Chiral [2.2]Paracyclophane 61

Yasuhiro Morisaki

3.1 Introduction 61

3.2 Through-space Conjugation of [2.2]Paracyclophane-based Conjugated Polymers 62

3.3 Optically Active Through-space Conjugated Polymers Based on Planar Chiral [2.2]Paracyclophane 65

3.4 Optically Active Through-space Conjugated Cyclic Oligomers Based on Planar Chiral [2.2]Paracyclophane 73

3.5 Conclusion 76

References 76

4 Development of Solid-state Luminescent Conjugated Polymers Containing Boron Element-blocks and Their Applications 81

Kazuo Tanaka, Masayuki Gon, and Shunichiro Ito

4.1 Introduction 81

4.2 Boron Ketoiminates 83

4.2.1 Transformation of the Conventional Luminescent Complex to AIE-active One 83

4.2.2 Modulation of the Direction of Color Changes in Mechanochromic Luminescence Behaviors by the Substituent Effect 85

4.2.3 Requirement of Heat-insensitive Mechanochromic Luminescent Materials 86

4.2.4 Development of Heat-insensitive Mechanochromic Luminescent Materials 87

4.2.5 Development of AIE-active Conjugated Polymers 89

4.2.6 Enhancement of Solid-state Luminescent Properties 90

4.2.7 Development of the Thermochromic and Mechanochromic Luminescent Polymers 93

4.2.8 Enhancement of Environmental Sensitivity 94

4.2.9 Mechanochromic Luminescent Sensor for Marking a Tiny Spot 95

4.3 Rational Design for AIE-active Molecules Based on Excitation-driven Complexes 97

4.3.1 Idea of Excitation-driven Complexes and Logical Design from Scratch 97

4.3.2 Design for Planar AIE-active Molecules 98

4.3.3 Development of Solid-state Luminescent Polymers 99

4.3.4 Stimuli-responsive Materials Based on Regioregular Conjugated Polymer 101

4.3.5 Injection of Stimuli-responsiveness into Conjugated Polymer by Element Replacement 102

4.4 AIE-active Materials Possessing NIR Luminescent Properties 103

4.4.1	Transformation to NIR-luminescent Materials by Aza-substitution at “the Isolated LUMO”	103
4.4.2	NIR–AIE Molecules and Polymers and Their Applications	104
4.5	Conclusion	106
	References	107
5	Arsenic-containing Conjugated Polymers	111
	<i>Hiroaki Imoto and Kensuke Naka</i>	
5.1	Introduction	111
5.2	Arsenic in Organic Compounds	112
5.3	As–C Bond Formation	112
5.3.1	Conventional Methodologies	112
5.3.2	In Situ Generation of Organoarsenic Electrophile from Arsenic Homocycles	113
5.3.3	In Situ Generation of Organoarsenic Nucleophile from Arsenic Homocycles	114
5.3.4	Preparation and Utilization of Tribromoarsine	114
5.4	Arsenic-containing π -conjugated Systems	115
5.4.1	Arsole Derivatives	115
5.4.2	Other Arsenic-containing π -conjugated Systems	119
5.5	Poly(vinylene-arsine)s	121
5.5.1	Synthesis of Poly(vinylene-arsine)s	121
5.5.2	Properties of Poly(vinylene-arsine)s	125
5.5.3	Poly(vinylene-phosphine)s and Poly(vinylene-stibine)s	127
5.5.4	Cross-linked Poly(vinylene-arsine)s	128
5.6	Arsole Polymers	129
5.7	π -Conjugated Polymers with Other Arsenic Units	133
5.8	Conclusion	134
	References	135
6	Carborane-containing Conjugated Polymers and Their Applications for Optoelectronic Materials	141
	<i>Kazuo Tanaka</i>	
6.1	Introduction	141
6.2	Advanced Functional Materials	142
6.2.1	Hydrogen Storage	142
6.2.2	Enhancement of Thermal Stability of Composites	142
6.3	Electronic Properties of Carborane-containing Conjugated Polymers	143
6.3.1	Electrochemical Polymerization	143
6.3.2	Electric Devices	145
6.3.3	Applications for OPV	146
6.4	Luminescent Materials	148
6.4.1	Luminescent Materials and Devices	148
6.4.2	Aggregation-induced Emission	149
6.5	Photochemistry of <i>o</i> -carboranes	150
6.5.1	Demands for Solid-state Luminescent Materials	150

6.5.2	Experimental Proofs for Emission Annihilation Through the Bond Elongation at the Carbon–Carbon Bond in <i>o</i> -carborane	151
6.5.3	CT Emission of Aryl-modified <i>o</i> -carboranes	153
6.5.4	Angular Dependency of Electron Acceptor Properties of the <i>o</i> -carborane Unit	155
6.5.5	Twisted intramolecular Charge Transfer in the Crystalline State	156
6.6	Applications for Solid-state Luminescent Materials	158
6.6.1	Development of Highly Efficient Solid-state Luminescent Materials	158
6.6.2	High Emission Efficiency of Bis- <i>o</i> -carborane-modified Aromatic Systems	160
6.6.3	Solid-state Luminescence of <i>Nido</i> -carborane	161
6.6.4	Enhancement to Luminescent Efficiencies by Thermal Rearrangement from <i>Ortho</i> - to <i>Meta</i> -carborane	162
6.7	Stimuli-responsive Luminochromic Materials	164
6.7.1	Multi-stimuli-responsiveness of Bis- <i>o</i> -carborane-modified Anthracene	164
6.7.2	Real-time Thermochromic Luminescent Properties of Bis- <i>o</i> -carborane-modified Benzodithiophenes	164
6.7.3	Constant Luminescent Properties During Phase Changes and Luminochromic Behaviors	165
6.7.4	Aggregation-caused Luminochromic Properties in the Polymer Film for Constructing Film-type Sensors	167
6.7.5	Thermochromic Luminescence by the Regulation of Rotation of <i>o</i> -carborane	168
6.8	Conclusion	170
	References	171
7	Low-bandgap Conjugated Polymers	177
	<i>Yi Zhang, Chunchen Liu, and Fei Huang</i>	
7.1	Introduction	177
7.2	Design Principles of LBG-CPs	178
7.2.1	D–A Interaction for Bandgap Reduction	178
7.2.2	Stabilized Quinoidal Resonance for Bandgap Reduction	179
7.3	Synthesis of LBG-CPs	181
7.3.1	Stille Coupling for Constructing LBG-CPs	181
7.3.1.1	Synthesis of LBG-CPs Based on Thieno[3,4- <i>b</i>]Thiadiazole (TT) and Its Derivatives	183
7.3.1.2	Synthesis of LBG-CPs Based on Benzothiadiazole (BT) and Its Derivatives	183
7.3.1.3	Synthesis of LBG-CPs Based on Benzobisthiadiazole (BTT) and Its Derivatives	184
7.3.1.4	Synthesis of LBG-CPs Based on Diketopyrrolopyrrole (DPP) and Its Derivatives	185
7.3.1.5	Synthesis of LBG-CPs Based on Isoindigo (IID) and Its Derivatives	185

7.3.1.6	Synthesis of LBG-CPs Based on Benzofurandione (BFDO) and Its Derivatives	187
7.3.1.7	Synthesis of LBG-CPs Based on 4,4'-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY) and Its Derivatives	188
7.3.2	Other Polymerization Methods for Constructing LBG-CPs	188
7.3.2.1	Suzuki Coupling	188
7.3.2.2	Aldol Condensation	190
7.4	Application of LBG-CPs	193
7.4.1	Application in OPDs	193
7.4.2	Application in OTEs	197
7.4.3	Application in Bioimaging and PTT	199
7.5	Conclusions and Perspective	200
	Acknowledgments	201
	References	201
8	Polymers with Three-dimensional Conjugated Molecules	207
	<i>Satoru Hiroto</i>	
8.1	Introduction	207
8.2	Corannulene-containing Polymer	208
8.3	Supramolecular Polymers Based on Bowl-shaped π -conjugated Molecules	214
8.4	Helicene-based Polymers	220
8.5	Conclusion and Outlook	225
	Acknowledgment	227
	References	227
9	Conjugated Polymers for Energy Storage Devices	231
	<i>Bharat S. Mantripragada, Sameer N. Mishra, Kottisa S. Patnaik, Uday S. Reddi, Pavithra Kasthurirangan, Bipashna Pradhan, Saibrata Punyasloka, and Noriyoshi Matsumi</i>	
9.1	Introduction	231
9.2	Conjugated Polymers as Binder Materials in LIBs	234
9.2.1	Graphite Anodes	234
9.2.2	Si Anodes	236
9.3	Conjugated Polymers as Anodic Active Materials	239
9.3.1	Organic Anodes	239
9.3.2	Hard Carbons	241
9.4	Polymerizable Conjugated Molecules as Electrolyte Additives	247
9.5	π -Conjugated Polymers as Electrocatalysts	249
9.6	Conclusion	251
9.6.1	Binders	251
9.6.2	Active Materials	251
9.6.3	Electrolyte Additives	252
9.6.4	Catalysts in Li-O ₂ Batteries	252
	References	252

10 Conjugated Polymers and Their Applications in Organic Field Transistors, Organic Electrochemical Transistors, and Organic Thermoelectrics 257

Yifei He, Isha Sanskriti, Nivedha Velmurugan, Tom Wilfling, and Christine K. Luscombe

- 10.1 Introduction 257
 - 10.1.1 What Makes the CP Semiconducting? 257
 - 10.1.2 What Are the Charge Carriers? 258
 - 10.1.3 Formation of Charge Carriers 258
 - 10.1.4 Band Structure 261
 - 10.1.5 Ion Transport 262
 - 10.1.6 Morphology and Multilevel Microstructures 262
 - 10.2 Polymers for Organic Field Effect Transistors 264
 - 10.2.1 Introduction 264
 - 10.2.2 Example p-type Polymers 264
 - 10.2.2.1 Thiophene-based Polymers 264
 - 10.2.2.2 Indacenodithiophene-based Polymers 264
 - 10.2.2.3 Isoindigo-based Polymers 266
 - 10.2.2.4 Cyclopentadithiophene-based Polymers 267
 - 10.2.3 Example n-type Polymers 267
 - 10.2.4 Example Ambipolar Polymers 268
 - 10.2.4.1 Isoindigo-based Polymers 268
 - 10.2.5 Key Approaches to Improve OFET Performance 269
 - 10.2.5.1 Backbone Modifications 270
 - 10.2.5.2 Side Chain Modifications 270
 - 10.2.5.3 Device Architecture 270
 - 10.2.6 Application and Future Outlook 270
 - 10.3 Organic Electrochemical Transistors 271
 - 10.3.1 Design Principle 271
 - 10.3.2 Example Polymers 271
 - 10.3.2.1 P-type 271
 - 10.3.3 N-type 274
 - 10.3.3.1 Imide-based 275
 - 10.3.3.2 Isoindigo 276
 - 10.3.3.3 Diketopyrrolopyrrole 276
 - 10.3.3.4 Ladder Type 276
 - 10.3.3.5 Acceptor–Acceptor 277
 - 10.3.4 Summary Tables of Reviewed p- and n-type Materials 278
 - 10.3.4.1 P-type Materials 278
 - 10.3.4.2 N-type Materials 279
- 10.4 Organic Thermoelectrics 280
 - 10.4.1 Introduction 280
 - 10.4.2 TE Figure-of-merit 280
 - 10.4.3 Progress in TE Properties of CPs 280
 - 10.4.3.1 P-type TE CPs 281

10.4.3.2	N-type TE CPs	283
10.4.4	Applications and Outlook	285
	References	286
11	π-Conjugated Polymers with Controlled Higher-order Structures: Poly(acetylene)s and Poly(aryleneethynylene)s	299
	<i>Fumio Sanda</i>	
11.1	Introduction	299
11.2	Helical Substituted Poly(acetylene)s	300
11.3	Poly(aryleneethynylene)s	303
11.4	Platinum-containing Poly(aryleneethynylene)s	306
11.5	Summary and Outlook	314
	References	314
12	Advances in Organic Solar Cell Performance Involving Anthracene and Anthanthrone Core Polycyclic Aromatic Materials	323
	<i>Vivian S. John-Denk, Morongwa E. Ramoroka, and Emmanuel I. Iwuoha</i>	
12.1	Introduction	323
12.2	Anthracene-containing Materials for OSCs Applications	325
12.3	Anthanthrone-containing Materials for OSCs Applications	328
12.4	Hole-transporting Materials	330
12.5	Conclusion	334
	Acknowledgment	335
	Conflict of Interest	335
	References	335
13	Conjugated Polymers for Biomedical Applications	339
	<i>Qi Shen and Shu Wang</i>	
13.1	Introduction	339
13.2	Biosensing and Biological Detection	341
13.2.1	Fluorescence Signal Amplification Based on CPs	341
13.2.1.1	DNA Detection	341
13.2.1.2	RNA Detection	344
13.2.1.3	Protein Detection	345
13.2.2	Electrochemical Sensing Based on CPs	346
13.2.3	Colorimetric Sensing Based on CPs	349
13.3	Biological Imaging	350
13.3.1	Fluorescence Imaging	351
13.3.2	NIR Imaging	353
13.3.2.1	CPs for NIR-II Fluorescence Imaging	354
13.3.2.2	CPs for NIR Two-photon Imaging	355
13.3.2.3	CPs for NIR PA Imaging	356
13.4	Therapeutic Applications	357
13.4.1	Antimicrobial Therapy	357
13.4.2	Anti-tumor Therapy	359

xii | *Contents*

13.4.3 Antiviral Therapy 361

13.5 Conclusion 363

References 363

Index 373