

Contents

List of Contributors ix

1	Stille Polycondensation: A Versatile Synthetic Approach to Functional Polymers	1
	<i>Tianyue Zheng, Alexander M. Schneider, and Luping Yu</i>	
1.1	Introduction	1
1.1.1	History of the Stille Reaction (and Polycondensation)	2
1.2	Reaction Mechanism	3
1.2.1	Simplified Mechanism	3
1.3	Reaction Conditions	6
1.3.1	Catalyst and Ligand	7
1.3.2	Solvent	9
1.3.3	Additive	10
1.3.4	Temperature	11
1.4	Examples of Functional Materials Synthesized by Stille Polycondensation	12
1.4.1	Nonlinear Optical (NLO) polymers	13
1.4.1.1	Background	13
1.4.1.2	Examples of NLO Polymers Synthesized by Stille Polycondensation	13
1.4.2	Organic Photovoltaic Polymers	16
1.4.2.1	Background	16
1.4.2.2	Examples of Donor Polymers	17
1.4.2.3	Examples of Acceptor Materials	23
1.4.3	Organic Field Effect Transistor (OFET) Polymers	28
1.4.3.1	Background	28
1.4.3.2	Examples of FET Polymers Synthesized by Stille Polycondensation	32
1.4.4	Organic Light-Emitting Diode (OLED) Polymers	35
1.4.4.1	Background	35
1.4.4.2	Examples of OLED Polymers Synthesized by Stille Polycondensation	36
1.4.5	Other Functional Materials	38
1.5	Challenge and Outlook	42
1.5.1	Advantages of the Stille Reaction	42
1.5.2	Disadvantages of Stille Reaction	44
1.6	Summary	47
	References	48

2	Suzuki Polycondensation	59
	<i>Anurag Krishna, Andrey V. Lunchev, and Andrew C. Grimsdale</i>	
2.1	Introduction	59
2.2	Mechanism of Suzuki Coupling and Suzuki Polycondensation	60
2.3	Catalysts	62
2.4	Reaction Conditions for Suzuki Coupling	65
2.4.1	Bases, Water, Solvents	66
2.4.2	Microwave-Assisted Reactions	67
2.5	Side Reactions	67
2.6	AB versus AA/BB Suzuki Polycondensation	71
2.7	Monomer Purity, Stoichiometry, and Solvents	73
2.8	Monomers for SPC	75
2.8.1	Boron Monomers	75
2.8.2	Halide and Other Monomers	80
2.9	Chain Growth SPC	81
2.10	Scope and Applications of SPC	82
2.11	Conclusion	85
	References	86
3	Controlled Synthesis of Conjugated Polymers and Block Copolymers	97
	<i>Tine Hardeman, Marie-Paule Van Den Eede, Lize Verheyen, and Guy Koeckelberghs</i>	
3.1	Introduction	97
3.2	Approaches to Controlled Polymerizations	97
3.2.1	Catalyst Transfer Polymerizations	97
3.2.1.1	Mechanism	97
3.2.1.2	Kumada Catalyst Transfer Polycondensation	99
3.2.1.3	Negishi Catalyst Transfer Polycondensation	102
3.2.1.4	CTP Based on Suzuki–Miyaura Couplings	102
3.2.1.5	CTP Based on Other Coupling Reactions	103
3.2.2	Controlled Polymerizations Based on Deactivation of the Monomer	103
3.2.2.1	Mechanism	103
3.2.2.2	Pd(RuPhos) Protocol	104
3.2.2.3	Miscellaneous	104
3.3	End-Functionalized Polymers	106
3.3.1	Introduction	106
3.3.2	External Functionalized Initiators	106
3.3.2.1	Principle	106
3.3.2.2	External Initiators with Ni as Catalyst	106
3.3.2.3	External Initiators with Pd as Catalyst	109
3.3.2.4	Grafting-from	110
3.3.3	End-Capping	111
3.3.3.1	Principle	111
3.3.3.2	End-Capping with Ni as Catalyst	111
3.3.3.3	End-Capping with Pd as Catalyst	112
3.3.4	Heterobifunctional Conjugated Polymers	112
3.4	Block Copolymers	112

- 3.4.1 Grafting-to Method 112
- 3.4.2 End-Functional Polymer Copolymerization Method 113
- 3.4.3 Grafting-from Method 114
- 3.4.4 Sequential Monomer Addition 114
- 3.5 Other Copolymers 117
- References 117

- 4 Direct (Hetero)arylation Polymerization 131**
Mario Leclerc and Serge Beaupré
- 4.1 Introduction 131
- 4.2 First Examples of Direct (Hetero)arylation Polymerization 134
- 4.3 Selectivity and Reactivity Problems 138
- 4.4 En Route to Defect-Free Conjugated Polymers 142
- 4.5 Outlook 150
- References 150

- 5 Continuous Flow Synthesis of Conjugated Polymers and Carbon Materials 159**
Valerie D. Mitchell and Wallace W.H. Wong
- 5.1 Introduction to Flow Chemistry 159
- 5.2 Conjugated Polymers 161
- 5.3 Carbon Materials 173
- 5.4 Material Processing 177
- 5.5 Summary 178
- References 178

- 6 Synthesis of Structurally Defined Nanographene Materials through Oxidative Cyclodehydrogenation 183**
Akimitsu Narita
- 6.1 Introduction 183
- 6.2 Synthesis of Nanographene Molecules through Oxidative Cyclodehydrogenation 186
- 6.2.1 Solution Synthesis of Extended Nanographene Molecules with FeCl_3 and AlCl_3 186
- 6.2.2 Complementary Cyclodehydrogenation Methods for the Solution Synthesis of Nanographene Molecules 188
- 6.2.3 Synthesis of Nanographene Molecules with Seven- and Eight-Membered Rings 195
- 6.2.4 Synthesis of Heteroatom-Doped Nanographene Molecules 198
- 6.2.5 Nanographene Molecules through Surface-Assisted Cyclodehydrogenation 202
- 6.3 Bottom-Up Synthesis of Graphene Nanoribbons 204
- 6.3.1 Graphene Nanoribbons from Solution-Mediated Cyclodehydrogenation 205
- 6.3.2 Graphene Nanoribbons from Surface-Assisted Cyclodehydrogenation 208
- 6.4 Conclusions 217
- References 218

7	Photochemical and Direct C–H Arylation Routes toward Carbon Nanomaterials	229
	<i>Jean-Francois Morin, Maxime Daigle, and Maude Desroches</i>	
7.1	Introduction	229
7.2	Photochemical Routes toward PAHs and Carbon Nanomaterials	231
7.2.1	Photochemical Dehydrogenation	231
7.2.2	Photochemical Dehydrohalogenation (CDH)	237
7.2.3	Miscellaneous Photocyclization Reaction	242
7.3	Intramolecular Direct Arylation C–H	243
7.3.1	Conclusion and Perspective	249
	References	250
8	Carbon-Rich Materials from sp-Carbon Precursors	255
	<i>Dominik Prenzel and Rik R. Tykwinski</i>	
8.1	Introduction	255
8.2	Carbyne	256
8.3	Solid-State Reactions of Polyynes: Topochemical Polymerizations	261
8.4	Diyne Polymerization	261
8.5	Tubular Structures	264
8.6	Beyond Diynes – Topochemical Polymerization of Polyynes	268
8.7	Toward “Nanographene”	272
8.8	Pentalenes	274
8.9	Modification of sp-Precursors with Tetracyanoethylene (TCNE)	275
8.10	Thermal Dimerization of Cumulenes	278
8.11	Outlook: From Solution to Surface?	278
8.12	Summarizing Comments	282
	Acknowledgments	286
	References	286
	Index	293