

## Contents

Preface *xi*

- 1 Current Status and Future Perspectives of Functional and Smart Materials in Daily Life 1**  
*Rudolf Pietschnig*
  - 1.1 Introduction 1
  - 1.2 Properties and Applications 1
    - 1.2.1 Applications Based on Mechanical and Rheological Properties 1
    - 1.2.2 Applications Based on Electronic Excitation 2
    - 1.2.3 Applications Based on Optical Features 6
    - 1.2.4 Applications Based on Supramolecular Recognition 9
    - 1.2.5 Applications Based on Chemical Reactivity 10
    - 1.2.6 Further Applications 12
  - 1.3 Perspective 13

Acknowledgments 13  
References 13
- 2 Boron-Containing Polymers 17**
  - 2.1 Group 13–Group 15 Element Bonds Replacing Carbon–Carbon Bonds in Main Group Polyolefin Analogs 19**  
*Anne Staubitz, Jonas Hoffmann, and Philipp Gliese*
    - 2.1.1 Introduction 19
    - 2.1.2 Group 13–Group 15 Element-Containing Polyolefin Analogs with the Heteroatoms in the Main Chain 20
      - 2.1.2.1 Poly(phosphinoboranes) 20
        - 2.1.2.1.1 Metal Complexes as Catalysts for the Dehydrocoupling of Phosphine–Boranes 21
          - 2.1.2.1.2 Lewis Acid Promoted Dehydrocoupling of Phosphine–Boranes 23
          - 2.1.2.1.3 Lewis Base Promoted Dehydrocoupling of Phosphine–Boranes 24
          - 2.1.2.1.4 Poly(phosphinoborane)-Based Materials 25
          - 2.1.2.1.5 Potential Applications of Poly(phosphinoboranes) 25
        - 2.1.2.2 Poly(aminoboranes) 27
      - 2.1.3 Group 13–Group 15 Element-Containing Polyolefin Analogs with the Heteroatoms in the Side Chain 32

2.1.3.1	Borazine-Containing PS Analogs	32
2.1.3.2	Azaborinine-Containing PS Analogs	33
2.1.4	Conclusion and Outlook	35
	Acknowledgments	36
	References	36
<b>2.2</b>	<b>Highlighting the Binding Behavior of Icosahedral Boron Clusters Incorporated into Polymers: Synthons, Polymers Preparation, and Relevant Properties</b>	<b>41</b>
	<i>Clara Viñas, Rosario Núñez, Isabel Romero, and Francesc Teixidor</i>	
2.2.1	Introduction	41
2.2.2	Conducting Organic Polymers Containing Icosahedral Boron Clusters	42
2.2.2.1	Icosahedral Boron Clusters as Doping Agents in COPs	43
2.2.2.2	Icosahedral Boron Clusters in COPs Side Chains to Modify the Chemical Composition and Act as Doping Agent	44
2.2.2.3	Icosahedral Boron Clusters Incorporated into the Polymer Main Chain of the COPs	45
2.2.3	Fluorescent Carborane-Containing Polymers	46
2.2.4	Thermally Resistant Carborane-Based Polymers	48
2.2.5	Coordination Polymers and Nanoparticles Incorporating <i>closo</i> -Carborane Clusters	50
2.2.5.1	Carboxylate-Functionalized Carboranes	50
2.2.5.2	Phosphinate- and Phosphino-Functionalized Carboranes	51
2.2.5.3	Nanohybrid Materials Based on Functionalized Carboranes	52
2.2.6	Conclusion and Outlook	55
	Acknowledgments	55
	References	55
<b>3</b>	<b>Synthesis of Group 14 Metal-Containing Polymers</b>	<b>61</b>
	<i>Ana Torvisco, Frank Uhlig, and David Scheschkewitz</i>	
3.1	Introduction	61
3.2	Organohydrides of Group 14, $R_nEH_{4-n}$	62
3.3	Diorganodihydrides of Group 14, $R_2EH_2$ , as Building Blocks for Chain-Type Polymers	65
3.3.1	Metal-Catalyzed Dehydropolymerization	65
3.3.2	Dehydrogenative Coupling Using an Amine Base	65
3.3.3	Solvent- and Catalyst-Free Dehydrogenative Coupling	67
3.3.4	Condensation	68
3.4	Monoorganotrihydrides of Group 14, $REH_3$ , as Building Blocks for 3D Polymers	68
3.4.1	Metal-Catalyzed Dehydropolymerization	68
3.4.2	Dehydrogenative Coupling Using an Amine Base	69
3.5	Applications	72
3.6	Conclusion and Outlook	74
	Acknowledgments	75
	References	75

<b>4</b>	<b>Synthesis of Polymers Containing Group 15 Elements</b>	<b>85</b>
	<i>Andreas Orthaber and Alejandro P. Soto</i>	
4.1	Introduction	85
4.2	Conjugated Polymers Containing Group 15 Elements	86
4.2.1	Phosphaalkenes, Arsaalkenes, and Diphosphenes	86
4.2.2	Group 15-Based Heteroles	89
4.3	Polymers with two Unsaturated Organic Moieties Adjacent to the Heteroelement Motif	93
4.3.1	Cross-Conjugated Group 15 Heteroalkene-Containing Materials	93
4.3.2	Group 15 Elements with two Adjacent Alkynes, Alkenes, or Arene Motifs of the Polymer Backbone	94
4.3.2.1	Ring-Opening Polymerization	95
4.4	Organic–Inorganic Hybrid Polymers Containing Saturated Phosphorus Centers	96
4.4.1	Miscellaneous Polymers	97
4.5	Polyphosphazene	97
4.6	Poly(phosphoester)s	104
4.7	Conclusion and Outlook	107
	Acknowledgments	107
	References	107
<b>5</b>	<b>Synthesis of Inorganic Dendrimers</b>	<b>115</b>
	<i>Anne-Marie Caminade</i>	
5.1	Introduction	115
5.2	Main Methods of Synthesis of Silicon-Containing Dendrimers	115
5.2.1	Synthesis of Carbosilane Dendrimers	115
5.2.2	Synthesis of Other Types of Silicon-Containing Dendrimers	118
5.3	Main Methods of Synthesis of Phosphorus-Containing Dendrimers	120
5.3.1	Synthesis of Phosphorhydrazone Dendrimers	120
5.3.2	Synthesis of Other Types of Phosphorus-Containing Dendrimers	121
5.4	Synthesis of Miscellaneous Types of Inorganic Dendrimers	129
5.4.1	Synthesis of Dendrimers Containing Main Group Elements Other than Si and P	129
5.4.2	Synthesis of Hybrid Dendrimers Containing at Least Two Types of Main Group Elements	132
5.5	Conclusion and Outlook	135
	Acknowledgments	135
	References	136
<b>6</b>	<b>Metallo-Supramolecular Polymers</b>	<b>141</b>
	<i>Jiří Vohlídal and Muriel Hissler</i>	
6.1	Introduction	141
6.2	Constitutional Dynamic Polymers: Dynamers	142
6.3	Main Types of Metallo-Supramolecular Polymers (MSPs) and Terminologies Related to Them	143
6.4	MSP Dynamers Derived from Unimers with Defined Structure	144

- 6.4.1 Synthesis of Unimers 144
- 6.4.2 Central Blocks of Conjugated Unimers 146
- 6.4.3 Assembly and Characterization of MSP Dynamers 148
- 6.4.4 Properties of Conjugated MSPs 151
- 6.5 Potential Applications and Outlook 155
- 6.5.1 Electrochromic Devices Based on the Modification of the Absorption Properties 155
- 6.5.2 Electrochromic Devices Based on the Modification of the Emission Properties 156
- 6.5.3 Ion Conductivity 157
- 6.5.4 Actuators 157
- 6.5.5 Outlooks 157
- Acknowledgments 158
- References 158
  
- 7 Applications of Heteroatom-Based Oligomers and Polymers in Optoelectronics 163**  
*Matthew P. Duffy, Pierre-Antoine Bouit, and Muriel Hissler*
- 7.1 Introduction 163
- 7.2 Organic Light-Emitting Diodes (OLEDs) 164
- 7.2.1 Application as Charge-Transport Layer 166
- 7.2.2 Application as Host for Phosphorescent Complexes 169
- 7.2.3 Application as Emitting Materials 171
- 7.3 Photovoltaic Cells (Organic Solar Cells [OSCs] and Dye-Sensitized Solar Cells [DSSCs]) 181
- 7.3.1 Dyes for Dye-Sensitized Solar Cells (DSSCs) 183
- 7.3.2 Donors in Organic Solar Cells (OSCs) 184
- 7.4 Application in Electrochromic Cells 188
- 7.5 Conclusion 189
- Acknowledgments 189
- Abbreviations 190
- References 192
  
- 8 Inorganic Polymers as Flame-Retardant Materials 197**  
*Raghvendra Kumar Mishra, Tarik Eren, and De-Yi Wang*
- 8.1 Introduction 197
- 8.2 Importance of Flame-Retardant Materials 198
- 8.3 Application of Inorganic Polymer as a Flame-Retardant Material 200
- 8.3.1 Polysiloxanes 201
- 8.3.2 Polyphosphazenes 210
- 8.3.3 Polysilane and Polysilynes 220
- 8.3.4 Ferrocene-Based Polymers 222
- 8.3.5 Carborane-Containing Polymers 225
- 8.3.5.1 Poly(carboranylenesiloxanes) 226
- 8.3.5.2 Carborane-Containing High-Performance Thermoplastics 229
- 8.3.5.3 Carboranes as Miscellaneous Polymers 230

8.4	Conclusion	233
	Acknowledgments	233
	References	233
<b>9</b>	<b>Inorganic Polymers for Potential Medicinal Applications</b>	<b>243</b>
	<i>Andreia Valente, Rafaella L. M. Precker, and Evamarie Hey-Hawkins</i>	
9.1	Introduction	243
9.2	Inorganic Polymers and Metal-Containing Polymers for Tissue Engineering and Drug Delivery	243
9.2.1	Inorganic Polymers	243
9.2.1.1	Polysiloxanes	244
9.2.1.2	Polyphosphazenes	247
9.2.2	Metal-Containing Polymers	250
9.2.2.1	Platinum–Polymer Conjugates	251
9.2.2.2	Ruthenium–Polymer Conjugates	251
9.2.2.3	Carborane–Polymer Conjugates	254
9.3	Emerging and Potential Applications for Metal–Organic Frameworks for Drug Delivery	255
9.3.1	Metal–Organic Frameworks (MOFs)	257
9.3.2	Application of MOFs in Drug Delivery Systems	257
9.3.2.1	Selected Examples of MIL- <i>n</i> Frameworks in Drug Delivery	258
9.3.2.2	Selected Other Metal–Organic Frameworks Used in Drug Delivery	262
9.3.3	Toxicity and Stability	263
9.3.3.1	Toxicity	263
9.3.3.2	Stability	265
9.3.4	Biodegradation	265
9.4	Final Remarks and Perspectives	266
	Acknowledgments	267
	References	267
<b>10</b>	<b>Inorganic Dendrimers and Their Applications</b>	<b>277</b>
	<i>Anne-Marie Caminade</i>	
10.1	Introduction	277
10.2	Inorganic Dendrimers as Catalysts	278
10.2.1	Overview of the Use of Inorganic Dendrimers as Catalysts	278
10.2.2	The Dendrimer Effect Illustrated with Catalytic Inorganic Dendrimers	280
10.2.3	The Recovery and Reuse of Catalytic Inorganic Dendrimers	283
10.3	Inorganic Dendrimers for Nanomaterials	287
10.3.1	Elaboration of Materials and Nano-objects Exclusively Composed of Inorganic Dendrimers	288
10.3.2	Hybrid Materials Incorporating Inorganic Dendrimers	291
10.3.3	Modification of the Surface of Materials with Inorganic Dendrimers Toward Biological Uses	293
10.4	Inorganic Dendrimers in Biology/Nanomedicine	296
10.4.1	Inorganic Dendrimers for Bioimaging	296

10.4.2	Inorganic Dendrimers for Gene Therapy	298
10.4.3	Inorganic Dendrimers Against Viruses	299
10.4.4	Inorganic Dendrimers in Brain Diseases	301
10.4.5	Inorganic Dendrimers Against Cancers	301
10.4.6	Inorganic Dendrimers Against Inflammatory Diseases	302
10.5	Conclusion and Outlook	304
	Acknowledgments	304
	References	305

## 11 Other Examples of Inorganic Polymers as Functional Materials 317

*Irene Weymuth and Walter Caseri*

11.1	Introduction	317
11.1.1	1,2,4-Triazole in Coordination Chemistry	317
11.1.2	Spin-Crossover	319
11.2	Coordination Polymers of 4-Aminotriazole and Iron(II)	322
11.2.1	Solutions	322
11.2.2	Solid State	324
11.3	Coordination Polymers of 4-Alkyltriazoles and Iron(II)	327
11.4	Coordination Polymers of 1,2,4-Triazoles and Other Metals	330
11.5	Conclusion and Outlook	332
	Acknowledgments	333
	References	333

**Index** 337