

Contents

1	Introduction of Organosilicon Materials	1
	<i>Huihui Shi, Jing Yang, Zibiao Li, and Chaobin He</i>	
1.1	Introduction	1
1.2	Synthesis of Polymeric Organosilicon Materials	2
1.2.1	Polysiloxanes	3
1.2.2	Polysilsesquioxanes	5
1.2.3	Other Polymeric Organosilicon Materials	7
1.3	Applications	10
1.3.1	Biomaterials	10
1.3.2	Optical and Electronic Materials	13
1.3.3	Surface Modification	15
1.4	Conclusion and Outlook	18
	References	18
2	Reactive Functionally Terminated Polyorganosiloxanes	23
	<i>Yuanyuan Pang, Junqiang Justin Koh, Zibiao Li, and Chaobin He</i>	
2.1	Types of Functionalized Polysiloxane and Their Synthesis	23
2.1.1	Types of Functional Polysiloxanes	23
2.1.2	Polysiloxane with Monofunctional Terminals	25
2.1.3	Polysiloxane with Difunctional Terminals	25
2.1.4	Polysiloxane with Functional Side Groups	27
2.2	Functionalized Polysiloxane as Macromers	30
2.2.1	Modifying Degree of Polymerization of Functionalized Polysiloxanes	30
2.2.2	Cross-Linking of Functionalized Polysiloxanes	30
2.2.3	Polysiloxane-Containing Block and Graft Copolymers	35
2.2.3.1	Polysiloxane-Containing Segmented and Multiblock Copolymers by Step-Growth Polymerization	35
2.2.3.2	Polysiloxane-Containing Graft Copolymers	41
2.2.3.3	Polysiloxane-Containing Copolymers by Hydrosilylation and Click Chemistry	42
2.3	Functionalized Polysiloxane as Macroinitiators and Macrochain Transfer Agents	43
2.3.1	Conventional Radical Polymerization	43
2.3.2	Controlled Radical Polymerization	45

- 2.3.2.1 Atom Transfer Radical Polymerization (ATRP) 45
- 2.3.2.2 Reversible Addition Fragmentation Chain Transfer (RAFT) Polymerization 47
- 2.3.2.3 Other Controlled Radical Polymerization Methods 50
- 2.3.3 Ring-Opening Polymerization (ROP) 50
- References 54

3 Functionalized Polyhedral Oligomeric Silsesquioxanes (POSS) and Copolymers: Methods and Advances 63

Huihui Shi, Jing Yang, Zibiao Li, and Chaobin He

- 3.1 Introduction 63
- 3.2 Synthetic Strategies for Functionalized POSS 64
 - 3.2.1 Octafunctional POSS 65
 - 3.2.1.1 Hydrolysis and Condensation from RSiX_3 Monomer 65
 - 3.2.1.2 Modification of Substituents 66
 - 3.2.2 Monofunctional POSS 71
 - 3.2.2.1 Corner Capping of $\text{T}_7\text{R}_7(\text{OH})_3$ 71
 - 3.2.2.2 Modification of Substituents 73
 - 3.2.3 Bifunctional POSS 73
 - 3.2.3.1 Some Special Cases 73
 - 3.2.3.2 Some Developing New Strategies 74
- 3.3 Synthetic Protocols for Hybrid POSS-containing Polymers 76
 - 3.3.1 Preparation from Monomers 78
 - 3.3.1.1 Radical Polymerization 79
 - 3.3.1.2 Ring-Opening Polymerization 81
 - 3.3.1.3 Step-Growth Polymerization 83
 - 3.3.1.4 Other Polymerization Methods 86
 - 3.3.2 Preparation from Polymers 87
 - 3.3.2.1 By Conventional Organic Reactions 87
 - 3.3.2.2 Some Advanced Methods 91
- 3.4 Conclusion 91
- References 91

4 Nanostructured Self-assemblies from Silicon-containing Hybrid Copolymers 97

Hong Chi, Beng Hoon Tan, Fuke Wang, Chaobin He, and Zibiao Li

- 4.1 Introduction 97
- 4.2 Mechanism in Self-assembly of POSS and PDMS-Based Copolymers 99
 - 4.2.1 Stimuli-Responsive Micelles 100
 - 4.2.1.1 pH-Sensitive Micelles 100
 - 4.2.1.2 Thermosensitive Micelles 103
 - 4.2.1.3 Photoactive Micelles 104
 - 4.2.2 Other Mechanisms in Different Assemblies 104
 - 4.2.2.1 Micelles 104
 - 4.2.2.2 Spheres 105
 - 4.2.2.3 Sheets 106

4.3	Application	107
4.3.1	Biomedical Applications	107
4.3.2	Photodynamic Therapy	109
4.3.3	Coating	111
4.3.4	Optical Sensors	112
4.4	Conclusions and Perspectives	113
	References	113
5	Superhydrophobic Materials Derived from Hybrid Silicon Copolymers	119
	<i>Lu Jiang, Xian Jun Loh, Chaobin He, and Zibiao Li</i>	
5.1	Introduction	119
5.2	Hybrid Silicon Copolymer Materials with Superhydrophobic Property	120
5.2.1	PDMS-Incorporated Hybrid Copolymer Materials	120
5.2.2	POSS-Incorporated Hybrid Copolymer Materials	122
5.3	Application of Superhydrophobic Silicon Copolymer Materials	128
5.3.1	Oil–Water Separation	128
5.3.1.1	PDMS-Based Superhydrophobic Materials	131
5.3.1.2	POSS-Based Superhydrophobic Materials	135
5.3.2	Self-cleaning and Antifouling	136
5.3.3	Anticorrosion	137
5.3.4	Other Applications	138
5.4	Conclusion	140
	References	140
6	Silicone Copolymers for Healthcare and Personal Care Applications	145
	<i>Weiren Cheng, Dan Kai, Xian Jun Loh, Chaobin He, and Zibiao Li</i>	
6.1	Silicone Copolymers for Biomedical and Healthcare Applications	145
6.1.1	Adsorption and Cell Interaction on Silicone Copolymer Surface	145
6.1.1.1	Antifouling Effect of Silicone Copolymer Surfaces	148
6.1.1.2	Antibacterial Effect of Silicone Copolymer Surfaces	148
6.1.1.3	Silicone Copolymers in Tissue Engineering and Regenerative Medicine	150
6.1.1.4	Silicone Copolymers Based Bio-coating	150
6.1.2	Self-assembly with Silicone Copolymers	152
6.1.2.1	Silicone Copolymers for Drug Delivery and Bioimaging	153
6.1.2.2	Silicone Copolymers in the Construction of Artificial Cells	154
6.2	Silicone for Personal Care Applications	157
6.2.1	Silicone Oil Emulsions	157
6.2.2	Silicone Copolymers as Surfactants	158
6.2.3	Silicone for Hair Care	159
6.2.4	Strategies for Depositing Silicone on Hair	160
6.2.5	Silicone for Skin Care Applications	161
6.3	Conclusions	162
	References	163

7	Construction of Organic Optoelectronic Materials by Using Polyhedral Oligomeric Silsesquioxanes (POSS) 167 <i>Fuke Wang, Xuehong Lu, Zibiao Li, and Chaobin He</i>
7.1	Unique Properties of POSS for Building Organic Optoelectronic Materials 167
7.2	POSS-Based Organic Electroluminescence Materials 171
7.3	POSS as a Building Block for Electrochromic Materials 181
7.4	Other Applications of POSS in Organic Optoelectronic Materials 189
7.5	Conclusions 195 References 196
8	Hybrid POSS Nanocomposites: An Overview of Material Toughening and Fire Retardancy 201 <i>Junhua Kong, Beng H. Tan, Xuehong Lu, Zibiao Li, and Chaobin He</i>
8.1	Introduction 201
8.2	Polypropylene/POSS Composites 202
8.3	Polycarbonate/POSS Composites 206
8.4	Polystyrene/POSS Composites 211
8.5	Polyester/POSS Composites 216
8.6	Polyepoxides/POSS Composites 220
8.7	Summary 233 References 233
9	3D Printing Silicone Materials and Devices 239 <i>Jayven Yeo, Junqiang Justin Koh, Fuke Wang, Zibiao Li, and Chaobin He</i>
9.1	Introduction 239
9.2	Extrusion-Based Printing 240
9.2.1	Fused Deposition Modeling (FDM) 240
9.2.2	Direct Ink Writing (DIW) 242
9.2.2.1	Rheology-Controlled Shape Retention 242
9.2.2.2	Coaxial Printing 245
9.2.2.3	Embedded 3D Printing 245
9.3	Jetting-Based Printing 247
9.3.1	Inkjet 3D Printing (IJP) 247
9.3.2	Aerosol Jet Printing (AJP) 249
9.4	Vat Photopolymerization/Light-Based/Photocurable 3D Printing 251
9.4.1	Stereolithography (SLA) 252
9.4.2	Digital Light Processing (DLP) 252
9.4.3	Photopolymerization Process 252
9.4.3.1	Photoinitiator 253
9.4.3.2	Photocurable Polymers 254
9.5	Potential Applications 260 References 261
	Index 265