

## Contents

|         |   |    |
|---------|---|----|
| 1       | <b>Introduction of Organosilicon Materials</b>  | 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       | <b>Reactive Functionally Terminated Polyorganosiloxanes</b>                               | 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        |
| <b>3</b> | <b>Functionalized Polyhedral Oligomeric Silsesquioxanes (POSS) and Copolymers: Methods and Advances</b> | <b>63</b> |
|          | <i>Huihui Shi, Jing Yang, Zibiao Li, and Chaobin He</i>   |           |
| 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 $\text{RSiX}_3$ 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        |
| <b>4</b> | <b>Nanostructured Self-assemblies from Silicon-containing Hybrid Copolymers</b>                         | <b>97</b> |
|          | <i>Hong Chi, Beng Hoon Tan, Fuke Wang, Chaobin He, and Zibiao Li</i>                                    |           |
| 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        |
| <b>5</b> | <b>Superhydrophobic Materials Derived from Hybrid Silicon Copolymers</b> | <b>119</b> |
|          | <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        |
| <b>6</b> | <b>Silicone Copolymers for Healthcare and Personal Care Applications</b> | <b>145</b> |
|          | <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       | <b>Construction of Organic Optoelectronic Materials by Using Polyhedral Oligomeric Silsesquioxanes (POSS)</b> | 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       | <b>Hybrid POSS Nanocomposites: An Overview of Material Toughening and Fire Retardancy</b>                     | 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       | <b>3D Printing Silicone Materials and Devices</b>   | 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 |