

Contents

1 Polyhedral Oligomeric Silsesquioxanes: From Early and Strategic Development through to Materials Application	1
Elda Markovic, Kristina Constantopolous and Janis G. Matisons	
1.1 Introduction.....	1
1.2 Early Synthesis of Polyhedral Oligosilsesquioxanes (POS).....	4
1.3 Hydrolysis and Condensation in Making Oligosilsesquioxanes.....	5
1.4 Synthesis of Hydrido-octasilsesquioxane, $H_8Si_8O_{12}$ (T_8H_8) and Octakis-(Hydridodimethylsiloxy)Octasilsesquioxane, $[H(CH_3)_2SiO]_8Si_8O_{12}$ ($Q_8M_8H_8$)	8
1.5 Hydrosilylation	10
1.6 Octa-Functionalized POS Macromonomers	11
1.6.1 Macromonomers Derived by the Hydrosilylation of Octahydrido-silsesquioxane ($H_8Si_8O_{12}$; T_8H_8).....	11
1.6.2 Macromonomers Derived by the Hydrosilylation of Octa(Hydridodimethylsiloxy)Octasilsesquioxane $[(HSiMe_2O)_8Si_8O_{12}; (Q_8M_8H_8)]$	13
1.7 Organic-Inorganic Hybrid Materials Prepared from POS: Octasilsesquioxane-containing Polymers.....	15
1.7.1 Hybrid Organic-Inorganic Crosslinked Materials Containing POS.....	15
1.7.2 Star-Shaped Hybrid Organic-Inorganic Materials Containing POS as a Macroinitiator	18
1.8 Mono-Substituted Polyhedral Oligomeric Silsesquioxane Macromonomers	20
1.8.1 Synthesis of Mono-Substituted Silsesquioxanes by Hydrolysis of Trifunctional Silanes	21
1.8.2 Synthesis of Mono-Substituted Silsesquioxanes by Hydrosilylation.....	22
1.8.3 Synthesis of Mono-substituted Silsesquioxanes by Corner-Capping Reactions	24
1.9 Chemistry of Incompletely Condensed Silsesquioxanes	25
1.9.1 Synthesis of Incompletely Condensed Silsesquioxanes.....	26

1.9.2	Chemistry of Incompletely Condensed Silsesquioxanes	31
1.9.3	Hybrid Organic-Inorganic Materials Derived from Mono-Substituted POS Monomers	32
1.10	Summary	36
1.11	References.....	37

2 Preparation and Characterization of Polyhedral

Oligosilsesquioxanes47

David B. Cordes and Paul D. Lickiss

2.1	General Comments.....	47
2.2	Synthesis of T_nR_n Compounds where R = H, Alkyl or Alkenyl.....	48
2.2.1	Hydrolysis	48
2.2.1.1	T_4 and T_6 Compounds.....	48
2.2.1.2	T_8 Compounds	49
2.2.1.3	T_{10} , T_{12} and Larger Compounds.....	51
2.2.2	Substitution	51
2.2.3	Cage Rearrangement	53
2.2.4	Modification of R	54
2.2.4.1	T_8 Compounds.....	54
2.2.4.2	T_{10} and T_{12} Compounds	59
2.2.5	Other Synthetic Methods.....	59
2.2.5.1	T_6 Compounds.....	59
2.2.5.2	T_8 Compounds.....	60
2.2.5.3	T_{10} and T_{12} Compounds	60
2.3	Synthesis of T_nR_n Compounds where R = Aryl	61
2.3.1	Hydrolysis	61
2.3.1.1	T_8 Compounds.....	61
2.3.1.2	T_{10} and T_{12} Compounds	62
2.3.2	Modification of R.....	62
2.3.2.1	T_8 Compounds.....	62
2.3.2.2	T_{10} and T_{12} Compounds	65
2.3.3	Other Synthetic Methods.....	65
2.4	Synthesis of T_nR_n Compounds where R = Alkoxy.....	66
2.5	Synthesis of T_nR_n Compounds where R = Siloxy	66
2.5.1	Corner Capping	66
2.5.2	Substitution	66
2.5.2.1	T_8 Compounds.....	66
2.5.2.2	T_{10} , T_{12} and T_{14} Compounds.....	67
2.5.3	Modification of R.....	67
2.5.3.1	T_6 Compounds.....	67
2.5.3.2	T_8 Compounds.....	67
2.5.3.3	T_{10} Compounds.....	70
2.6	Synthesis of T_nR_n Compounds where R = Metal Complex	70

2.6.1	Hydrolysis	70
2.6.2	Substitution	71
2.6.2.1	T_8 Compounds	71
2.6.2.2	T_{10} Compounds	71
2.6.3	Modification of R	71
2.7	Synthesis of Miscellaneous T_nR_n Compounds	74
2.7.1	Hydrolysis	74
2.7.1.1	T_6 Compounds	74
2.7.1.2	T_8 Compounds	74
2.7.1.3	T_{10} Compounds	75
2.7.2	Co-Hydrolysis	75
2.7.3	Substitution and Modification of Functional Groups	76
2.7.4	Other Synthetic Methods	76
2.7.4.1	T_4 Compounds	76
2.7.4.2	T_8 Compounds	76
2.7.4.3	T_{10} Compounds	77
2.8	Synthesis of Endohedral T_8R_8 Compounds	77
2.9	Introduction to the Physical Properties of POS Compounds	78
2.10	NMR and EPR Spectroscopy of POS Compounds	78
2.10.1	Solution ^{29}Si NMR Studies	78
2.10.2	Solid State NMR Studies	83
2.10.3	EPR Spectra	85
2.11	Vibrational Spectra of Polyhedral Oligomeric Silsesquioxane Compounds	85
2.12	Mass Spectra of POS Compounds	88
2.13	Electronic Spectra of POS Compounds	90
2.14	Structural Studies of POS Compounds	91
2.14.1	Single Crystal X-Ray Diffraction Studies	91
2.14.2	Structures Derived from Computational and Gas-Phase Electron Diffraction Studies	95
2.14.3	X-ray Diffraction Studies on Powders, Thin Films, etc.	96
2.14.3.1	T_8R_8 Compounds	97
2.14.3.2	T_8R_7R' Compounds	98
2.15	TGA, DSC and Related Studies of POS Compounds	99
2.15.1	T_8R_8 Compounds (R = H, Alkyl, Vinyl, Aryl or Silyl Derivatives)	99
2.15.2	T_8R_8 Compounds (R = Siloxy Derivatives)	100
2.15.3	T_8R_7R' Compounds	101
2.16	Microscopy Studies of T_8 POS Compounds	102
2.16.1	T_8R_8 Compounds	102
2.16.2	T_8R_7R' Compounds	102
2.17	X-Ray Photoelectron Spectra of POS Compounds	103
2.18	Electrochemistry of POS Compounds	103
2.19	Chromatographic Methods Applied to POS Compounds	104
2.20	Miscellaneous Physical Properties of POS Compounds	105

2.21	Acknowledgments.....	106
2.22	References	106

3 **Metallasilsesquioxanes: Molecular Analogues of Heterogeneous Catalysts**135

Antony J. Ward, Anthony F. Masters and Thomas Maschmeyer

3.1	Introduction.....	135
3.2	Metallasilsesquioxanes	136
3.2.1	Group 4 – Ti, Zr, Hf	136
3.2.2	Group 5 – V	145
3.2.3	Group 6 – Mo	147
3.2.4	Group 8 – Fe.....	148
3.2.5	Group 12 – Zn.....	149
3.2.6	Group 13 – Al.....	150
3.2.7	Group 14 – Si	151
3.2.8	Lanthanides – Nd	153
3.2.9	Hetero-bimetallic Systems	154
3.3	Phosphasilsesquioxanes as Ligands	156
3.4	Catalytic Materials Derived From Metalla-Silsesquioxanes	159
3.5	Conclusions and Future Prospects	162
3.6	References	163

4 **Polymers and Copolymers Containing Covalently Bonded Polyhedral Oligomeric Silsesquioxanes Moieties**167

Katherine Grace Williams, Samuel Paul Gido and Edward Bryan Coughlin

4.1	Introduction.....	167
4.2	Synthetic Strategies.....	168
4.2.1	Free Radical Polymerization.....	168
4.2.2	Living Radical Polymerization (ATRP, RAFT and NMP).....	169
4.2.3	Anionic Polymerization	172
4.2.4	Ring-Opening Metathesis Polymerization (ROMP)	172
4.2.5	Metallocene-Catalyzed Polymerization	174
4.2.6	Step-Growth Polymerization.....	175
4.2.7	Grafting	180
4.3	POS Pendant-Random Copolymers.....	182
4.3.1	Glass Transition Temperature.....	182
4.3.2	Mechanical Properties.....	183
4.3.3	Crystallinity in POS Pendant-Random Copolymers	183
4.4	POS Pendant-Block Copolymers	186

4.4.1	Diblocks	186
4.4.2	Triblocks.....	188
4.4.3	Hemitelechelic ('Tadpole'-Shaped) Polymers	189
4.4.4	Telechelic (Dumbbell-Shaped) Polymers	191
4.5	POS-Polyimide and POS-Urethanes.....	192
4.5.1	POS-Polyimide.....	192
4.5.2	POS-Urethane	193
4.6	Multifunctional POS in Network or Core Structures.....	195
4.6.1	Epoxy Networks.....	195
4.6.2	Other POS Networks.....	196
4.6.3	POS Star or Core Structures.....	198
4.7	Conclusion	199
4.8	References	200
5	Polyhedral Oligomeric Silsesquioxanes in Plastics.....	209
	Chris DeArmitt	
5.1	Introduction.....	209
5.2	POS are Molecules.....	210
5.3	POS as Plastics Additives	213
5.4	POS Solubility	214
5.5	Effects of POS on Polymer Properties.....	214
5.5.1	POS Solubilized in the Polymer.....	215
5.5.2	POS Insoluble Present at Concentrations Above the Solubility Limit	216
5.5.3	POS Chemically Attached to the Polymer	217
5.5.4	POS Network Thermosets.....	218
5.6	POS Dispersants.....	219
5.7	POS Metal Deactivators.....	223
5.8	New Applications and the Future.....	224
5.9	Conclusions.....	225
5.10	References	225
6	Fluorinated Polyhedral Oligosilsesquioxane Surfaces and Superhydrophobicity.....	229
	Scott T. Iacono, Andrew J. Peloquin, Dennis W. Smith, Jr. and Joseph M. Mabry	
6.1	Introduction.....	229
6.2	Experimental	231
6.2.1	Materials.....	231
6.2.2	Single Crystal X-Ray Structural Characterization	231
6.2.3	Fluorinated POS Coating and Composite Preparation.....	232

6.2.3.1	Spin Cast Fluorinated POS Coating	232
6.2.3.2	Fluorinated POS Solvent Blended Composites with 6F-BP PFCB Aryl Ether Polymer	232
6.2.3.3	Fluorinated POS Melt Blended PCTFE	232
6.2.4	Thermo-Mechanical Analysis	233
6.2.5	Microscopy.....	233
6.2.5.1	Atomic Force Microscopy (AFM)	233
6.2.5.2	Scanning Electron Microscopy (SEM)	233
6.2.6	Static and Dynamic Contact Angle	234
6.3	Results and Discussion	234
6.3.1	Fluorinated POS Synthesis.....	234
6.3.2	Fluorinated POS Properties.....	235
6.3.3	POS Fluoropolymers.....	238
6.3.3.1	Dispersion	238
6.3.3.2	Melt Processability.....	241
6.3.3.3	Thermo-Mechanical Analysis	242
6.3.3.4	Surface Properties	243
6.4	Conclusions.....	244
6.5	Acknowledgments.....	245
6.6	References	245

7 Polyhedral Oligomeric Silsesquioxanes in Electronics and Energy Applications247

Claire Hartmann-Thompson

	Introduction.....	247
7.1	Polyhedral Oligomeric Silsesquioxanes in Liquid Crystal Systems....	247
7.2	Polyhedral Oligomeric Silsesquioxanes in Electroluminescent (EL) Materials and Light Emitting Devices (LEDs)	261
7.2.1	Polyhedral Oligomeric Silsesquioxane End-capped EL Polymers.....	263
7.2.2	EL Polymers with Pendant Polyhedral Oligomeric Silsesquioxane Groups.....	264
7.2.3	EL Star Architectures with Polyhedral Oligomeric Silsesquioxane Cores	266
7.2.4	Polyhedral Oligomeric Silsesquioxane Iridium Complexes.....	270
7.2.5	Physical Blending of Polyhedral Oligomeric Silsesquioxanes into EL Polymers	273
7.3	Polyhedral Oligomeric Silsesquioxanes in Non-linear Optic (NLO), Optical Limiting (OL) and Laser Applications	274
7.4	Polyhedral Oligomeric Silsesquioxanes in Lithographic Applications	276
7.5	Polyhedral Oligomeric Silsesquioxanes in Sensor Systems	282

7.5.1	Fluorophore-Functionalized Polyhedral Oligomeric Silsesquioxanes as Sensors	283
7.5.2	Polyhedral Oligomeric Silsesquioxane Sensors for Gas and Vapor Detection.....	288
7.5.3	Polyhedral Oligomeric Silsesquioxanes in Conducting Composite and Electrochemical Sensors.....	292
7.6	Polyhedral Oligomeric Silsesquioxanes in Fuel Cell Applications	295
7.7	Polyhedral Oligomeric Silsesquioxanes in Battery Applications	304
7.8	Polyhedral Oligomeric Silsesquioxanes as Lubricants	308
7.9	References	309
8	Polyhedral Oligomeric Silsesquioxanes in Space Applications	327
	Henry W. Brandhorst, Jr.	
8.1	The Space Environment.....	327
8.2	Resistance of Siloxane Copolymers to Atomic Oxygen in Low Earth Orbit	330
8.3	Polyhedral Oligomeric Silsesquioxanes in Space Solar Power Systems	341
8.4	Summary	357
8.5	References	358
9	Biomedical Application of Polyhedral Oligomeric Silsesquioxane Nanoparticles	363
	Hossein Ghanbari, Sayed Mahdi Marashi, Yasmin Rafiei, Karla Chaloupka and Alexander M. Seifalian	
9.1	Introduction.....	363
9.2	Nanocomposites.....	364
9.3	Polyhedral Oligomeric Silsesquioxanes	365
9.4	Biomedical Applications of Polyhedral Oligomeric Silsesquioxane-Containing Polymers	368
9.4.1	Drug Delivery.....	368
9.4.2	Dental Nanocomposites	371
9.4.3	Biosensors	373
9.4.4	Cardiovascular Implants.....	374
	9.4.4.1 Mechanical Properties.....	376
	9.4.4.2 Degradative Resistance	377
	9.4.4.3 Biocompatibility and Biostability	378
	9.4.4.4 Endothelialization Property	379
	9.4.4.5 Anti-Thrombogenic Potential.....	382
	9.4.4.6 Resistance to Calcification and Fatigue	382
	9.4.4.7 Reduced In Vitro Inflammatory Response	383
9.4.5	Breast Implants.....	384
9.4.6	Coating Material for Quantum Dot Nanocrystals	385

9.4.7	Silver Nanoparticle-Containing Polyhedral Oligosilsesquioxane Polymers	387
9.4.8	Tissue Engineering	388
9.5	Other Applications	392
9.6	Future Prospects	392
9.7	References	393
Index		401
Abbreviations		415