Silsesquioxanes

Silsesquioxanes, or T- resins, are a class of compounds with the empirical formula $\text{RSiO}_{1.5}$. These compounds derive their name from the one and one half (1.5) or sesquistioichiometry of oxygen bound to silicon, with the alternate name “T- resin” derived from the presence of three oxygen substituents on silicon (tri-substituted). Several structural representations of silsesquioxanes with the empirical formula $\text{RSiO}_{1.5}$ are possible, with the two most common representations being a ladder-type structure (A) and a cubic structure (B) containing eight silicon atoms placed at the vertices of the cube. The cubic structure is commonly called the $T_8$ cube, and is usually drawn incorrectly with O-Si-O bond angles of 90°. The actual structure of a $T_8$ “cube” is more a Si-O cage framework, as illustrated in (C). However, the cubic structure (B) is easier to visualize and will be used hereafter to denote the silsesquioxane backbone.

Substituents on silicon can include hydrogen, alkyl, alkenyl, alkoxy and aryl. Due to organic substitution on silicon, many silsesquioxanes have reasonable solubility in common organic solvents.

Silsesquioxanes were first synthesized, but incorrectly identified, by Ladenburg in the late 1800s. In the early 1900s, Kipping further studied the hydrolysis and condensation reactions of trifunctional silanes and arrived at the conclusion that polycondensation of “siliconic acids” invariably leads to extremely complex mixtures of little synthetic value. Due to Kipping’s “discovery”, serious investigation into a controllable synthesis of silsesquioxanes was hindered for forty-five years until the work of Brown and Vogt in the 1960s.

Applications of Silsesquioxanes

Applications of Silsesquioxanes play an important role in the development of heterogeneous silica-supported transition metal catalyst systems. Octameric silsesquioxanes resemble skeletal frameworks found in crystalline forms of silica and zeolites, and their rigid framework makes silsesquioxanes suitable models for silica surfaces. Of particular interest are the incompletely condensed silsesquioxanes which have one silicon removed from a corner of the $T_8$ cube. This $T_7$ structure, commonly referred to as a trisilanol, possesses both structural and electronic similarities to hydroxylated silica surface sites.

The trisilanol 1 ($R = \text{c-C}_5\text{H}_9$ or $\text{c-C}_6\text{H}_{11}$) can undergo several corner capping reactions with transition-metal (Mo, W, V, Zr) and rare earth complexes to give a variety of substituted silsesquioxanes, 2. In solution, many of the resulting metallosilsesquioxanes exist in equilibrium with the corresponding dimer. In the case of the molybdenum metallo-silsesquioxane dimer 3 ($R = \text{c-C}_6\text{H}_{11}$), the triple bond between the molybdenum atoms is left intact. Metallosilsesquioxane compounds show activity as catalytic precursors for olefin metathesis and olefin polymerization.

![Diagram A](image1)

![Diagram B](image2)

![Diagram C](image3)
When the trisilanol 1 is reacted with a variety of Group 14 compounds of the type RMX₃ (R = alkyl, alkenyl, aryl, H; M = Si, Ge, or Sn; X = halogen or alkoxide), a wide variety of monomeric T₈ silsesquioxanes result.¹⁴,¹⁵ When R is an organic polymerizable or graftable group on silicon, a novel class of monomers called Polyhedral Oligomeric SilSesquioxanes, or POSS monomers results.¹⁶

<table>
<thead>
<tr>
<th>R'</th>
<th>Cat. No.</th>
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<tbody>
<tr>
<td>4a</td>
<td>allyl</td>
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<tr>
<td>4b</td>
<td>hydrogen</td>
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<tr>
<td>4c</td>
<td>propyl methacryl</td>
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<tr>
<td>4d</td>
<td>ethynorbornenyl</td>
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<tr>
<td>4e</td>
<td>vinylphenyl</td>
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<td>4f</td>
<td>methyl propionate</td>
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<td>4g</td>
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<td>4h</td>
<td>hydroxyl</td>
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<tr>
<td>4i</td>
<td>glycidyl</td>
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<tr>
<td>4j</td>
<td>3-chloropropyl</td>
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<tr>
<td>4k</td>
<td>3-cyanopropyl</td>
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<tr>
<td>4l</td>
<td>vinyl</td>
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<tr>
<td>4m</td>
<td>diphenylphosphinoethyl</td>
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</tbody>
</table>

The POSS monomers can be polymerized using standard techniques to yield inorganic-organic hybrid homopolymers and copolymers.¹⁷,¹⁸ The propylmethacryl-POSS monomer 4c undergoes free radical polymerization to give POSS macromers,¹⁹ and the hydrido-POSS monomer 4b can undergo hydrosilylation reactions to give oligomers and polymers.²⁰ The pendant silsesquioxane structures impart desirable mechanical properties to the polymers such as increased thermal stability to oxidation and resistance to degradation by ultraviolet light. Illustrated at left (5) is a syndiotactic segment of a polymer chain from the polymerization of the allyl-POSS monomer 4a.

There are numerous other applications of substituted silsesquioxanes, including their use as Wittig reagents,²¹ and precursors to silicon carbide (SiC) powders,²²-²⁴ nitrided glass (in combination with NH₃),²⁵ silicon oxyxnitride (SiₓONₓ),²⁶ low dielectric constant materials,²⁷-²⁹ alumino-³⁰,³¹ and galliosilicates,³² silica-reinforced composites,³³,³⁴ and a variety of microporous materials.²⁷,²⁸ The reader is urged to consult the literature³⁷-³⁹ for more information on these versatile building blocks for inorganic-organic hybrid polymers.
We offer a selection of specialty POSS monomers and the trisilanol-POSS (R = \(c\)-C\(_5\)H\(_9\)), which are listed below. For more information on silsesquioxanes or for compounds not listed here, please email us: aldrich@sial.com or visit us on the Web at www.sigma-aldrich.com. For more silicon-containing monomers, building blocks, and protecting groups, request your FREE copy of the Inorganics and Organometallics Catalog.

**Specialty POSS Monomers**

A 46,859-2 1-Allyl-3,5,7,9,11,13,15-heptacyclopentylpentacyclo-[9.5.1.1\(^3\),9\(^3\),15\(^5\),17\(^12\)]octasiloxane (Allyl-POSS); 1g, 5g

B 47,759-1 1-(3-Chloropropyl)-3,5,7,9,11,13,15-heptacyclopentylpentacyclo-[9.5.1.1\(^3\),9\(^3\),15\(^5\),17\(^12\)]octasiloxane (3-Chloropropyl-POSS); 1g, 5g

C 47,768-0 Ethyl-3,5,7,9,11,13,15-heptacyclopentylpentacyclo-[9.5.1.1\(^3\),9\(^3\),15\(^5\),17\(^12\)]octasiloxane-1-undecanoate (Ethyl undecanoate-POSS); 1g, 5g

D 47,765-6 1,3,5,7,9,11,13-Heptacyclopentyl-15-[2-(diphenylphosphino)-ethyl]pentacyclo[9.5.1.1\(^3\),9\(^3\),15\(^5\),17\(^12\)]octasiloxane (Diphenylphosphinoethyl-POSS); 1g, 5g

E 47,760-5 1,3,5,7,9,11,13-Heptacyclopentyl-15-glycidylpentacyclo-[9.5.1.1\(^3\),9\(^3\),15\(^5\),17\(^12\)]octasiloxane (Glycidyl-POSS); 1g, 5g

F 47,762-1 3,5,7,9,11,13,15-Heptacyclopentylpentacyclo[9.5.1.1\(^3\),9\(^3\),15\(^5\),17\(^12\)]octasiloxane-1-butyronitrile (Ethyl undecanoate-POSS); 1g, 5g

G 47,764-9 3,5,7,9,11,13,15-Heptacyclopentylpentacyclo[9.5.1.1\(^3\),9\(^3\),15\(^5\),17\(^12\)]octasiloxan-1-ol (Silanol-POSS); 1g, 5g

H 46,862-2 3-(3,5,7,9,11,13,15-Heptacyclopentylpentacyclo[9.5.1.1\(^3\),9\(^3\),15\(^5\),17\(^12\)]octasiloxane-1-yl)propyl methacrylate (Propyl methacryl-POSS); 1g, 5g

I 46,857-6 1,3,5,7,9,11,14-Heptacyclopentyltricyclo[7.3.3.1\(^5\),1\(^1\)]heptasiloxane-endos,7,14-triol (Trisilanol-POSS); 1g, 10g

J 47,761-3 1,3,5,7,9,11,13-Heptacyclopentyl-15-vinylpentacyclo-[9.5.1.1\(^3\),9\(^3\),15\(^5\),17\(^12\)]octasiloxane (Vinyl-POSS); 1g, 5g

K 46,858-4 1-Hydrido-3,5,7,9,11,13,15-heptacyclopentylpentacyclo-[9.5.1.1\(^3\),9\(^3\),15\(^5\),17\(^12\)]octasiloxane (Hydrido-POSS); 1g, 5g

L 47,766-4 Methyl-3,5,7,9,11,13,15-heptacyclopentylpentacyclo-[9.5.1.1\(^3\),9\(^3\),15\(^5\),17\(^12\)]octasiloxane-1-propionate (Methyl propionate-POSS); 1g, 5g

M 46,860-6 1-[2-(5-Norbornene-2-yl)ethyl]-3,5,7,9,11,13,15-heptacyclopentylpentacyclo[9.5.1.1\(^3\),9\(^3\),15\(^5\),17\(^12\)]octasiloxane (Norbornylethyl-POSS); 1g, 5g

N 47,654-4 1,3,5,7,9,11,13,15-Octakis(dimethylsililoxo)pentacyclo-[9.5.1.1\(^3\),9\(^3\),15\(^5\),17\(^12\)]octasiloxane [Octakis(dimethylsililoxo) silsesquioxane]; 1g, 5g

O 47,542-4 1,3,5,7,9,11,13,15-Octavinylpentacyclo[9.5.1.1\(^3\),9\(^3\),15\(^5\),17\(^12\)]octasiloxane (Octavinylsilsesquioxane); 1g, 5g

P 46,861-4 1-(4-Vinylphenyl)-3,5,7,9,11,13,15-heptacyclopentylpentacyclo-[9.5.1.1\(^3\),9\(^3\),15\(^5\),17\(^12\)]octasiloxane (Vinylphenyl-POSS); 1g, 5g

**SOLUBILITY**

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<th>Acetone</th>
<th>Acetonitrile</th>
<th>Chloroform</th>
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I = insoluble; S = soluble; s/ = slightly soluble

Silsequioxanes (continued)

Latest Additions

52,180-9 1-(4-Chlorobenzyl)-3,5,7,9,11,13,15-heptacyclpentylpentacyclo
[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane; 1g, 5g

52,229-5 1-[2-[{(Chloromethyl)phenyl}]-3,5,7,9,11,13,15-heptacyclpentylpentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane, mixture of isomers (Chloromethylphenyl)ethyl-POSS); 1g, 5g

52,182-5 1-(Chlorophenyl)-3,5,7,9,11,13,15-heptacyclpentylpentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane; 1g, 5g

51,754-2 1-[2-(3-Cyclohexen-1-yl)ethyl]-3,5,7,9,11,13,15-heptacyclpentylpentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane [(Cyclohexenyl)ethylPOSS]; 1g, 5g

52,103-5 1-(3-Cyclohexen-1-yl)-3,5,7,9,11,13,15-heptacyclpentylpentacyclo
[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (Cyclohexenyl-POSS); 1g, 5g

51,741-0 1-[2-(3,4-Epoxy cyclohexyl)ethyl]-3,5,7,9,11,13,15-heptacyclpentylpentacyclo
[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (Epoxy cyclohexyl-POSS); 1g, 5g

51,756-9 1-(Hydridodimethylsilyloxy)-3,5,7,9,11,13,15-heptacyclpentylpentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (Hydridodimethylsilyloxy-POSS); 1g, 5g

52,226-0 Octakis(tetramethylammonium)pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane-1,3,5,7,9,11,13,15-octakis(oxide)hydrate; 5g

52,104-3 endo-3,7,14-Tris(dimethylsilyloxy)heptacyclpentyltricycloheptasiloxane; 1g, 5g

References:

(1) Ladenburg, A. Annalen 1875, 179, 143.
(29) Miller, R.D. et al. ibid. 1997, 22(10), 44.
For reviews of the chemistry of silsesquioxanes, see: