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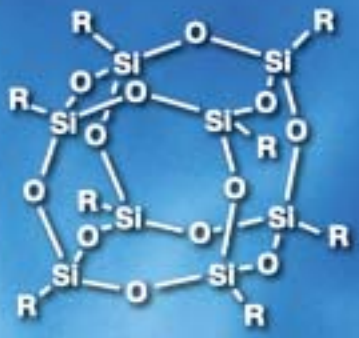

Silsesquioxanes

Bridging the Gap between Polymers & Ceramics

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POSS™ Monomers

POSS™ Polymers

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Silane Precursors

ALDRICH®

Silsesquioxanes

Bridging the Gap between Polymers & Ceramics

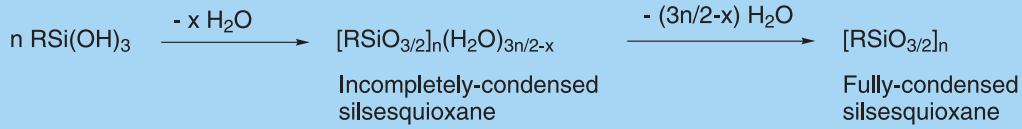
Hybrid inorganic–organic composites are an emerging class of new materials that hold significant promise.[1] Materials are being designed with the good physical properties of ceramics and the excellent choice of functional group chemical reactivity associated with organic chemistry. New silicon-containing organic polymers, in general, and polysilsesquioxanes, in particular, have generated a great deal of interest because of their potential replacement for, and compatibility with silicon-based inorganics in the electronics, photonics, and other materials technologies.[2-4]

Hydrolytic condensation of trifunctional silanes yields *network polymers or polyhedral clusters* having the generic formula $(RSiO_{1.5})_n$.[5,6] Hence, they are known by the "not quite on the tip of the tongue" name ***silsesquioxanes.*** Each silicon atom is bound to an average of one and a half (sesqui) oxygen atoms and to one hydrocarbon group (ane). Typical functional groups that may be hydrolyzed/condensed include alkoxy- or chlorosilanes, silanols, and silanolates.[7] Synthetic methodologies that combine pH control of hydrolysis/condensation kinetics, surfactant-mediated polymer growth, and molecular-templating mechanisms have been employed to control molecular–scale regularity and external morphology in the resulting inorganic-organic hybrids–from transparent nanocomposites, to mesoporous networks, to highly porous and periodic organosilica crystallites–all of which have the silsesquioxane (or $RSiO_{1.5}$) stoichiometry.[3,8-11] These inorganic–organic hybrids offer a unique set of physical, chemical, and size–dependent properties that could not be realized from just ceramics or organic polymers alone; thus, ***silsesquioxanes are depicted as bridging the property space between these two component classes of materials.*** Many of these silsesquioxane hybrid materials also exhibit an enhancement in properties such as solubility, thermal and thermomechanical stability, mechanical toughness, optical transparency, gas permeability, dielectric constant, and fire retardancy, to name just a few. A diverse range of applications have been reported in the recent literature and will be alluded to in the two sections below on ***polyhedral oligomeric silsesquioxane (POSS™) nanohybrids*** and ***mesoporous polysilsesquioxanes.***

Polyhedral Oligomeric Silsesquioxanes (POSS™) Nanohybrids

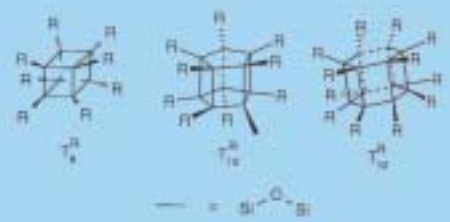
Since their discovery and isolation in 1946,[12] many stoichiometrically well-defined ***POSS™*** frameworks have been reported with synthetically useful functional groups.[5,6,13-17] They are most often prepared via hydrolytic condensation reactions of trifunctional organosilicon monomers, e.g., $RSiCl_3$ or $RSi(OMe)_3$, (***Scheme 1***).

Scheme 1



The structures of the POSS™ frameworks depend a great deal on the method of their preparation. They are uniquely sensitive to a highly interdependent combination of experimental factors, including product solubilities, initial monomer concentration, nature and stability of the solvent, temperature, pH, the amount of free water available, and the type of catalyst (acid or base) used to facilitate condensation. Careful hydrolysis leads to well-defined, fully condensed, prismatic, POSS™ structures T_8^R, T_{10}^R, T_{12}^R (***Scheme 2***).

Scheme 2



These nanosized synthetic platforms can be modified to contain groups for copolymerization, adhesion, light sensitization, binding catalysts, and liquid crystalline properties.[18-21] The chemistry of the apex silicon atoms, particularly, organic transformations at one of the eight apices in the T_8 structures, has been extensively reported,[22-23] yielding **1** where **R'≠ R**. If R' is a reactive functional group, while the other seven functional groups R are nonreactive, the resulting monofunctional *POSS™ monomer* can be copolymerized with standard organic monomers to yield nanocomposite copolymer alternatives to silica-reinforced plastics, allowing single-phase composite processing.[24] (Please see the section on *POSS™ Polymers* for further product information.) The T_8 structure has been suggested as a model for silica surfaces.[22,25] Polysilsesquioxane foams, which cannot be prepared directly because of low T_g's, have been prepared by a base-catalyzed disproportionation reaction of polyhydridosiloxanes that also generated a chemical blowing agent.[26]

Recently, a new class of dendrimer catalysts based on POSS™ cores has been reported.[27] These materials are expected to combine the traits of heterogeneous catalysts (i.e., easy separation from the reaction stream) with the high activity and precise control of catalytic sites normally associated with homogenous species. Metallodendrimers with a diphenylphosphino-POSS™ core and Ru-based chromophores show unique advantages.[28] A liquid crystalline silsesquioxane dendrimer exhibiting chiral nematic and columnar mesophases was synthesized.[29]

A second generation of porous, high–strength, spin-on dielectrics with $\kappa<3$ is being based on polyimide/polysilsesquioxane nanocomposites.[30] It has been noted that POSS™ frameworks are strong electron-withdrawing substituents.[31] Consequently, the nonlinear optical properties of H-POSS™ systems are being explored.[32] Also, it might be fruitful to explore the incorporation of POSS™

frameworks as pendants to conjugated polymer chains to tune the electronic bandgap and hence the light–emitting properties of the conjugated polymer. LEDs based on such inorganic–organic, hybrid, light–emitting polymers could offer significant performance and lifetime advantages over PLEDs. Numerous other applications of functionalized POSS™ frameworks are being proposed-membranes for gas separations, resists for EB lithography, and optical waveguides-leading to advances in multicomponent composite material systems.[1-3]

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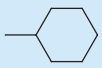
Fully Condensed POSS™ Frameworks: R'= R

1

51,771-2
Octa(chlorodimethylsilylethyl)-POSS™
$C_{32}H_{80}Cl_8O_{12}Si_{16}$
R= $-CH_2-CH_2-Si(CH_3)_2-Cl$
1g $39.60; 5g $132.00

56,056-1
Octa(dichloromethylsilylethyl)-POSS™
$C_{24}H_{56}Cl_{16}O_{12}Si_{16}$
R= $-CH_2-CH_2-Si(Cl)_2-CH_3$
1g $39.60; 5g $132.00

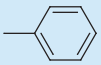
56,058-8
Octa(trichlorosilylethyl)-POSS™
$C_{16}H_{32}Cl_{24}O_{12}Si_{16}$
R= $-CH_2-CH_2-Si(Cl)_3$
1g $39.60; 5g $132.00

53,441-2
Octacyclohexyl-POSS™
$C_{48}H_{88}O_{12}Si_8$
R= 
1g $27.30; 10g $152.00

52,682-7
Octacyclopentyl-POSS™
$C_{40}H_{72}O_{12}Si_8$
R= 
1g $22.80; 5g $75.95

52,684-3
Octaisobutyl-POSS™
$C_{32}H_{72}O_{12}Si_8$
R= $-CH_2-CH(CH_3)-CH_3$
5g $22.75; 25g $75.75

52,683-5
Octamethyl-POSS™
$C_8H_{24}O_{12}Si_8$
R= $-CH_3$
5g $22.50; 25g $74.85

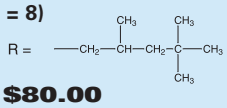
52,685-1
Octaphenyl-POSS™
$C_{48}H_{40}O_{12}Si_8$
R= 
5g $22.50; 25g $75.00

52,226-0
OctaTMA-POSS™ hydrate
$C_{32}H_{96}N_8O_{20}Si_8$
R= $-O^-$ $H_3C-N^{\pm}(CH_3)_2-CH_3$
5g $22.75; 25g $78.60

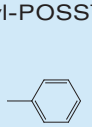
47,542-4
Octavinyl-POSS™
$C_{16}H_{24}O_{12}Si_8$
R= 
1g $47.40; 10g $263.30

47,654-4
Octasilane-POSS™
$C_{16}H_{56}O_{20}Si_{16}$
R= $-O-SiH(CH_3)_2$
1g $23.10; 10g $173.00

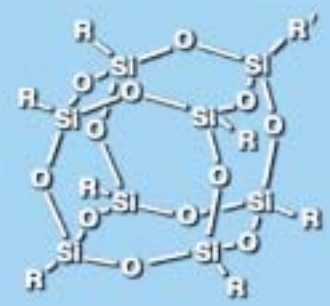
56,034-0
Methacryl-POSS™ cage mixture, n=8,10,12
$C_{56}H_{88}O_{28}Si_8$ **(for T_n = 8)**
R= $-CH_2-(CH_2)_2-O-C(=O)-C(CH_3)=CH_2$
1g $30.00; 5g $100.00

56,038-3
Isooctyl-POSS™ cage mixture, n=8,10,12
$C_{64}H_{136}O_{12}Si_8$ **(for T_n = 8)**
R = 
5g $24.00; 25g $80.00

56,035-9
Phenethyl-POSS™ cage mixture, n=8,10,12
$C_{64}H_{72}O_{12}Si_8$ **(for T_n = 8)**
R= $-CH_2-CH_2-C_6H_5$
1g $38.40; 5g $128.00

54,420-5
Dodecaphenyl-POSS™
$C_{72}H_{60}O_{18}Si_{12}$
R = 
5g $41.80

Fully Condensed POSS™ Frameworks: R′ ≠ R



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TMP Diol-Cyclopentyl-POSS™
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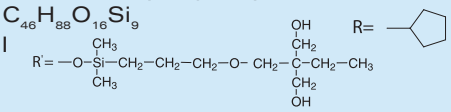
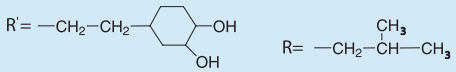


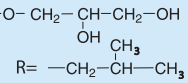
1g $63.00; 5g $210.00

56,028-6
trans-Cyclohexanediol-Isobutyl-POSS™ $C_{36}H_{78}O_{14}Si_8$



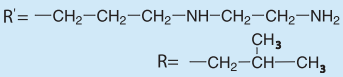
1g $26.40; 5g $88.00

56,030-8
1,2-Propanediol-Isobutyl-POSS™
$C_{34}H_{76}O_{15}Si_8$



1g $26.40; 5g $88.00

56,029-4
Aminoethylaminopropyl-Isobutyl-POSS™ $C_{33}H_{76}N_2O_{12}Si_8$



1g $26.40; 5g $88.00

51,740-2
MonoChloro-Cyclohexyl-POSS™
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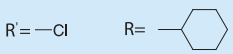

1g $39.60; 5g $132.00

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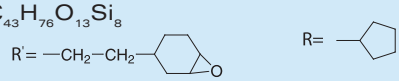
Epoxycyclohexylethyl-Cyclopentyl-POSS™
$C_{43}H_{76}O_{13}Si_8$



1g $63.00; 5g $210.00

56,031-6
Epoxycyclohexylethyl-Isobutyl-POSS™
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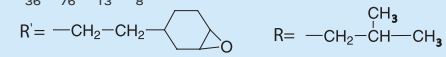
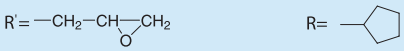


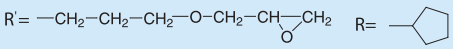
1g $24.00; 5g $80.00

47,760-5
Epoxypropyl-Cyclopentyl-POSS™
$C_{38}H_{68}O_{13}Si_8$



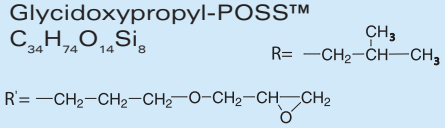
1g $62.00; 5g $206.55

52,727-0
Glycidyloxypropylcyclopentyl-POSS™ $C_{43}H_{80}O_{15}Si_9$



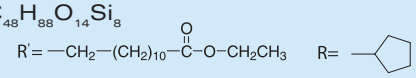
1mL $54.00; 5mLg $180.00

56,032-4
Glycidoxypropyl-POSS™
$C_{34}H_{74}O_{14}Si_8$



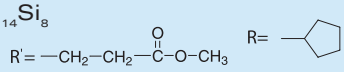
1g $24.00; 5g $80.00

47,768-0
Ethylundecanoate-Cyclopentyl-POSS™
$C_{48}H_{88}O_{14}Si_8$



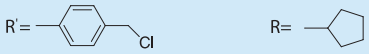
1g $70.90; 5g $236.40

47,766-4
Methylpropionate-Cyclopentyl-POSS™
$C_{39}H_{70}O_{14}Si_8$



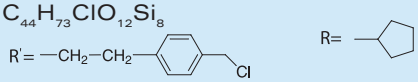
1g $70.90; 5g $236.25

52,180-9
4-Chlorobenzyl-Cyclopentyl-POSS™
$C_{42}H_{69}ClO_{12}Si_8$



1g $63.00; 5g $210.00

52,229-5
4-Chlorobenzylethyl-Cyclopentyl-POSS™
$C_{44}H_{73}ClO_{12}Si_8$



1g $54.00; 5g $180.00

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Chlorophenyl-Cyclopentyl-POSS™
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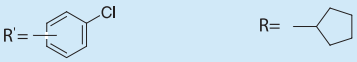

1g $64.80; 5g $216.00

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Chloropropyl-Cyclopentyl-POSS™
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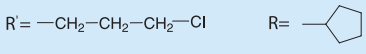

1g $39.50; 5g $175.65

56,033-2
Chloropropyl-Isobutyl-POSS™
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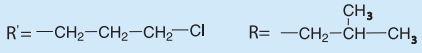
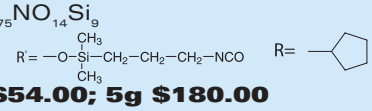


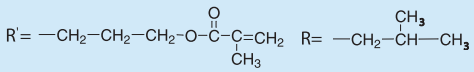
1g $21.60; 5g $72.00

52,734-3
Isocyanatopropyldimethylsilyloxy-Cyclopentyl-POSS™
$C_{41}H_{75}NO_{14}Si_9$



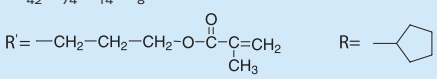
1g $54.00; 5g $180.00

53,463-3
Methacryl-Isobutyl-POSS™
$C_{35}H_{74}O_{14}Si_8$



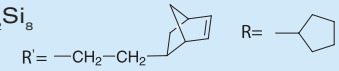
1g $20.80; 5g $70.00

46,862-2
Methacryl-Cyclopentyl-POSS
$C_{42}H_{74}O_{14}Si_8$



1g $55.44; 10g $308.00

46,860-6
Norbornenylethyl-Cyclopentyl-POSS™
$C_{44}H_{76}O_{12}Si_8$



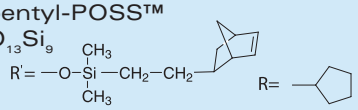
1g $80.20; 5g $267.30

Ready To Scale Up? For larger quantities, contact Sigma-Aldrich Fine Chemicals at 1-800-336-9719 (USA) or contact your local office

Fully Condensed POSS™ Frameworks: R' ≠ R

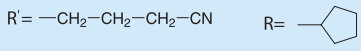
continued

51,753-4
Norbornenylethyldimethylsilyloxy-Cyclopentyl-POSS™
$C_{46}H_{82}O_{13}Si_9$



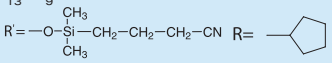
1g $59.40; 5g $198.00

47,762-1
Cyanopropyl-Cyclopentyl-POSS™
$C_{39}H_{69}NO_{12}Si_8$



1g $64.26; 5g $214.20

52,733-5
Cyanopropyldimethylsilyloxy-Cyclopentyl-POSS™
$C_{41}H_{75}NO_{13}Si_9$

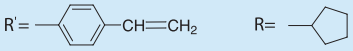


1g $54.00; 5g $180.00

52,103-5
Cyclohexenyl-Cyclopentyl-POSS™
$C_{41}H_{72}O_{12}Si_8$

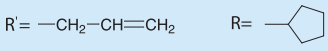
1g $64.00; 5g $213.30

46,861-4
4-Vinylphenyl-Cyclopentyl-POSS™
$C_{43}H_{70}O_{12}Si_8$



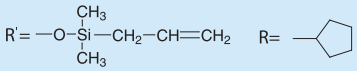
1g $79.80; 5g $265.95

46,859-2
Allyl-Cyclopentyl-POSS™
$C_{38}H_{68}O_{12}Si_8$



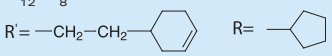
1g $64.70; 5g $215.60

52,731-9
Allyldimethylsilyloxy-Cyclopentyl-POSS™ $C_{40}H_{74}O_{13}Si_9$



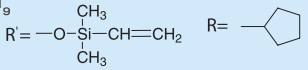
1g $54.00; 5g $180.00

51,754-2
3-Cyclohexenylethyl-Cyclopentyl-POSS™
$C_{43}H_{76}O_{12}Si_8$



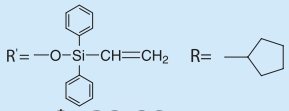
1g $63.00; 5g $210.00

52,413-1
Dimethylvinylsilyloxy-Cyclopentyl-POSS™
$C_{39}H_{72}O_{13}Si_9$



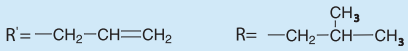
1g $58.50; 5g $195.00

52,730-0
Diphenylvinylsiloxy-Cyclopentyl-POSS™
$C_{49}H_{75}O_{13}Si_9$



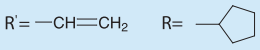
1g $54.00; 5g $180.00

53,442-0
Allyl-Isobutyl-POSS™
$C_{31}H_{68}O_{12}Si_8$



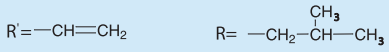
1g $20.80; 5g $63.00

47,761-3
Monovinyl-Cyclopentyl-POSS™
$C_{37}H_{66}O_{12}Si_8$



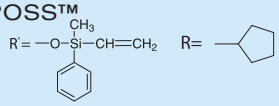
1g $41.50; 5g $184.45

56,036-7
Monovinyl-Isobutyl-POSS™
$C_{30}H_{66}O_{12}Si_8$



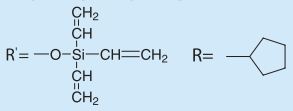
1g $24.00; 5g $80.00

52,729-7
Methylphenylvinylsilyloxy-Cyclopentyl-POSS™
$C_{44}H_{74}O_{13}Si_9$



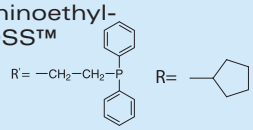
1g $54.00; 5g $180.00

52,732-7
Tris(vinylsilyloxy)-Cyclopenyl-POSS™
$C_{41}H_{72}O_{13}Si_9$



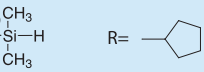
1g $54.00; 5g $180.00

47,765-6
Diphenylphosphinoethyl-Cyclopentyl-POSS™
$C_{49}H_{77}O_{12}PSi_8$



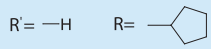
1g $79.40; 5g $264.65

51,756-9
Dimethylsilyloxy-Cyclopentyl-POSS™
$C_{37}H_{70}O_{13}Si_9$



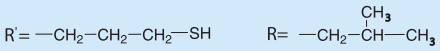
1g $62.55; 5g $208.50

46,858-4
Hydrido-Cyclopentyl-POSS™
$C_{35}H_{64}O_{12}Si_8$

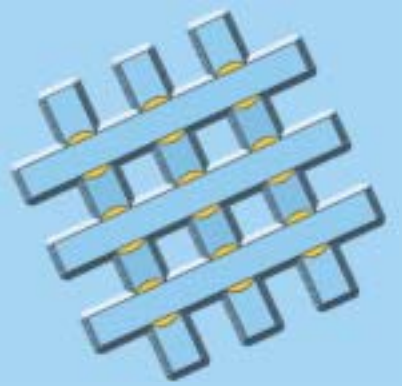


1g $59.18; 5g $197.25

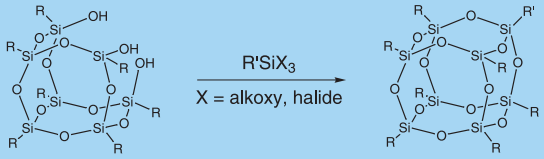
56,037-5
Mercaptopropyl-Isobutyl-POSS™
$C_{31}H_{70}O_{12}SSi_8$



1g $27.60; 5g $92.00



Incompletely Condensed POSS™ Frameworks: R'= R



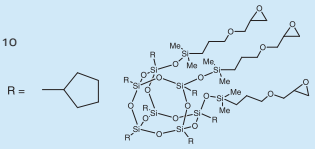
2

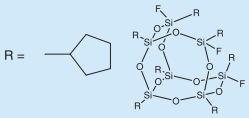
POSS™ Silanols are incompletely condensed frameworks possessing a hybrid inorganic–organic, three-dimensional structure and containing one–to–four silanol (Si–OH) groups. Unlike most other silanols that are generated in situ, the POSS™ silanols are stable towards condensation. The Si–OH groups in the POSS™ silanols are reactive enough to allow a wide range of applications; their chemistry has been extensively developed over the past 10–15 years. An example of their reactions is illustrated in ***Scheme 3***.

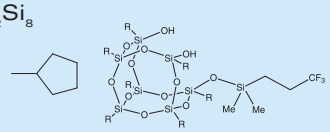
Scheme 3

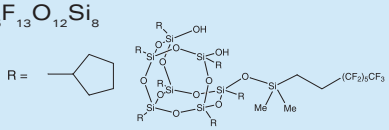
When trisilanol **2** is reacted with a variety of group 14 compounds of the type RMX_3 (R = alkyl, alkenyl, aryl, H; M = Si, Ge, or Sn; X = halogen or alkoxide), a wide variety of monomeric T_8 silsequioxanes results. A list of Si products is shown in the preceding pages in the table of Fully Condensed POSS™ Frameworks (R↑R′).[14,15]

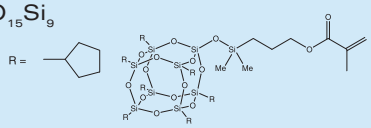
POSS™ Silanols

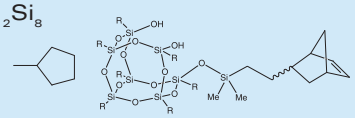
52,358-5
$C_{59}H_{114}O_{18}Si_{10}$

1g $63.00; 5g $210.00

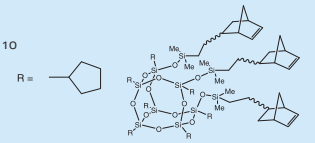
53,443-9
$C_{35}H_{63}F_3O_9Si_7$

1g $31.80; 5g $106.00

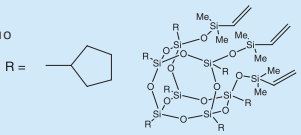
54,456-6
$C_{40}H_{75}F_3O_{12}Si_8$

1g $65.25; 5g $217.50

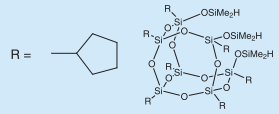
54,455-8
$C_{45}H_{75}F_{13}O_{12}Si_8$

1g $60.75; 5g $202.50

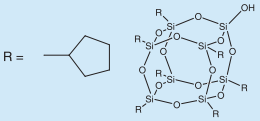
52,415-8
$C_{44}H_{80}O_{15}Si_9$

1g $64.80; 5g $216.00

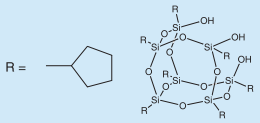
52,363-1
$C_{46}H_{82}O_{12}Si_8$

1g $58.50; 5g $195.00

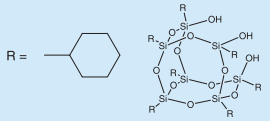
52,362-3
$C_{68}H_{120}O_{12}Si_{10}$

1g $63.00; 5g $210.00

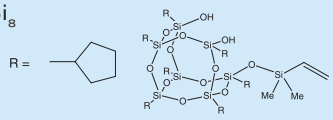
52,365-8
$C_{47}H_{90}O_{12}Si_{10}$

1g $58.50; 5g $195.00

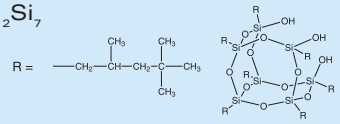
52,104-3
$C_{41}H_{84}O_{12}Si_{10}$

1g $63.00; 5g $210.00

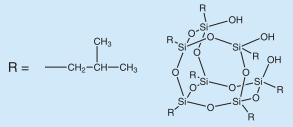
47,764-8
$C_{35}H_{64}O_{13}Si_8$

1g $62.58; 5g $208.60

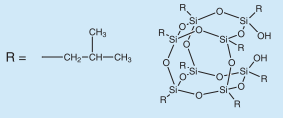
46,857-6
$C_{35}H_{66}O_{12}Si_7$

1g $36.85; 10g $259.45

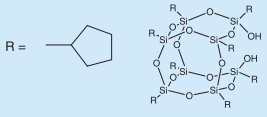
47,767-2
$C_{42}H_{80}O_{12}Si_7$

1g $59.30

54,434-5
$C_{39}H_{74}O_{12}Si_8$

1g $42.00; 5g $140.00

56,039-1
$C_{56}H_{122}O_{12}Si_7$

5g $37.30; 25g $124.30

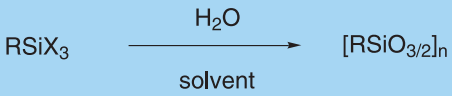
53,446-3
$C_{28}H_{66}O_{12}Si_7$

1g $25.10; 10g $83.80

53,444-7
$C_{32}H_{74}O_{13}Si_8$

1g $25.20; 10g $140.00

53,445-5
$C_{40}H_{74}O_{13}Si_8$

1g $45.00; 5g $150.00

Ready To Scale Up? For larger quantities, contact Sigma-Aldrich Fine Chemicals at 1-800-336-9719 (USA) or contact your local office

POSS™ Precursors ($RSiX_3$) and Intermediates



Scheme 4

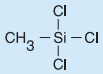
As shown in ***Schemes 1*** and ***4***, POSS™ frameworks may be prepared using trifunctional organosilicon monomers or POSS™ silanols. A selection of POSS™ precursors available from Aldrich is classified below under halide or alkoxy classes or as intermediates. Our POSS™ silanols have been listed in the previous section.

POSS™ Precursors: $RSiCl_3$

17,555-2
HCl_3Si

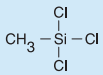
5g $16.15; 100g $28.95; 500g $46.50

M8,530-1
CH_3Cl_3Si



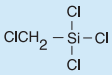
5g $9.65; 100g $10.80; 500g $26.25

44,029-9
CH_3Cl_3Si



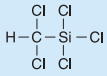
100mL $13.55; 1L $15.95

25,443-6
CH_2Cl_4Si



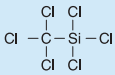
5g $15.10; 25g $56.70

44,645-9
$CHCl_5Si$



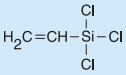
25mL $77.60

47,873-3
CCl_6Si



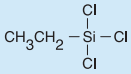
10g $29.35; 50g $109.40

10,487-6
$C_2H_3Cl_3Si$



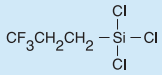
5g $12.20; 100g $14.10; 500g $51.35

44,028-0
$C_2H_5Cl_3Si$



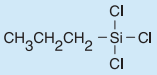
100mL $29.50; 1L $29.50

45,280-7
$C_3H_4Cl_3F_3Si$



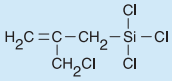
5mL $16.70; 25mL $55.65

10,483-3
$C_3H_7Cl_3Si$



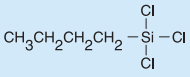
100mL $15.70; 1L $26.35

41,849-8
$C_4H_6Cl_4Si$



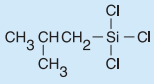
1g $11.00; 5g $36.65

10,482-5
$C_4H_9Cl_3Si$



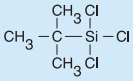
5mL $13.25; 25mL $44.95

46,114-8
$C_4H_9Cl_3Si$



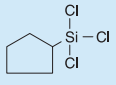
25mL $13.35; 100mL $37.90

30,861-7
$C_4H_9Cl_3Si$



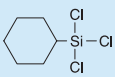
5g $21.25; 25g $69.60; 100g $190.45

44,618-1
$C_5H_9Cl_3Si$



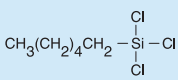
5mL $14.00; 25mL $44.55

39,106-9
$C_6H_{11}Cl_3Si$



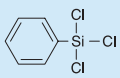
5mL $23.00; 25mL $69.00

44,696-3
$C_6H_{13}Cl_3Si$



25mL $23.95; 100mL $57.90

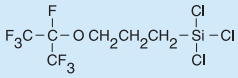
44,010-8
$C_6H_5Cl_3Si$



100mL $15.70; 1L $35.80

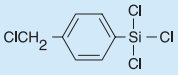
POSS™ Precursors: $RSiCl_3$ continued

38,438-0
$C_6H_6Cl_3F_7OSi$



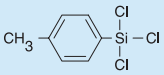
1g $13.35; 5g $38.40

44,623-8
$C_7H_6Cl_4Si$



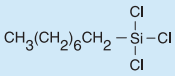
5mL $27.90; 25mL $88.90

41,935-4
$C_7H_7Cl_3Si$



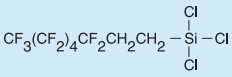
5g $16.30; 25g $54.55

23,572-5
$C_8H_{17}Cl_3Si$



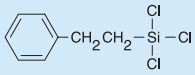
100g $31.60; 500g $110.25

44,893-1
$C_8H_4Cl_3F_{13}Si$



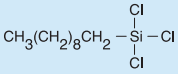
10g $37.05

42,003-4
$C_8H_9Cl_3Si$



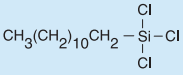
1g $11.35; 10g $63.10

44,859-1
$C_{10}H_{21}Cl_3Si$



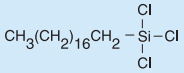
10mL $26.00; 50mL $99.00

28,056-9
$C_{12}H_{25}Cl_3Si$



25g $26.70; 100g $93.75

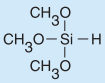
10,481-7
$C_{18}H_{37}Cl_3Si$



25g $17.10; 100g $45.35; 500g $153.60

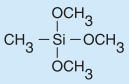
POSS™ Precursors: $RSi(OR'')_3$

28,262-6
$C_3H_{10}O_3Si$



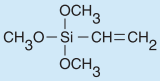
25g $69.40; 100g $200.10

24,617-4
$C_4H_{12}O_3Si$



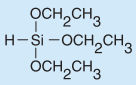
5mL $13.80; 250mL $23.80; 1L $72.50

23,576-8
$C_5H_{12}O_3Si$



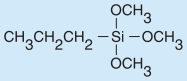
5mL $16.60; 100mL $27.15; 500mL $72.40

39,014-3
$C_6H_{16}O_3Si$



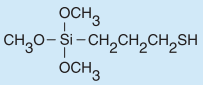
10mL $21.15; 50mL $61.25

44,020-5
$C_6H_{16}O_3Si$



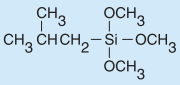
100mL $17.85; 1L $39.55

17,561-7
$C_6H_{16}O_3SSi$



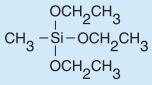
25g $15.30

44,406-5
$C_7H_{18}O_3Si$



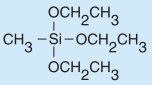
25mL $10.50; 100mL $29.70

17,557-9
$C_7H_{18}O_3Si$



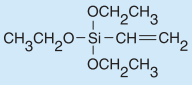
50g $22.65; 250g $29.85

33,964-4
$C_7H_{18}O_3Si$



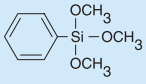
500mL $31.50

17,556-0
$C_8H_{18}O_3Si$



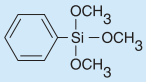
100mL $19.05; 500mL $63.20

10,474-4
$C_9H_{14}O_3Si$



50mL $13.35; 250mL $39.00

43,565-1
$C_9H_{14}O_3Si$

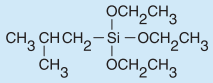


500mL $27.55; 1L $46.05

Ready To Scale Up? For larger quantities, contact Sigma-Aldrich Fine Chemicals at 1-800-336-9719 (USA) or contact your local office

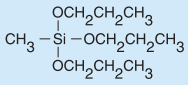
POSS™ Precursors: $RSi(OR'')_3$ continued

43,567-8
$C_{10}H_{24}O_3Si$



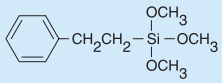
500mL $30.10; 1L $50.25

44,890-7
$C_{10}H_{24}O_3Si$



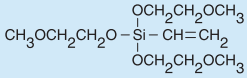
5mL $16.70; 25mL $55.75

43,834-0
$C_{11}H_{18}O_3Si$



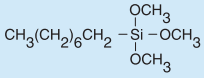
1g $19.30; 5g $64.55

17,558-7
$C_{11}H_{24}O_6Si$



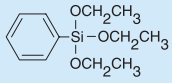
100mL $19.25

37,622-1
$C_{11}H_{26}O_3Si$



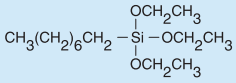
5mL $14.65; 25mL $48.60

17,560-9
$C_{12}H_{20}O_3Si$



5g $13.80; 250g $23.50; 1kg $69.65

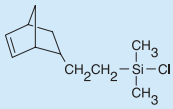
44,021-3
$C_{14}H_{32}O_3Si$



100mL $17.85; 1L $53.75

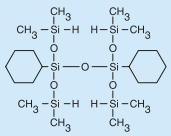
POSS™ Intermediates

54,433-7
$C_{11}H_{19}ClSi$



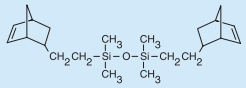
1mL $36.32; 5mL $121.08

52,000-4
$C_{20}H_{50}O_5Si_6$



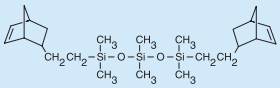
1mL $45.00; 5mL $150.00

52,361-5
$C_{22}H_{38}OSi_2$



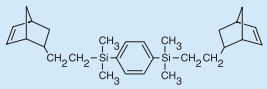
1g $25.20; 5mL $84.00

52,359-3
$C_{24}H_{44}O_2Si_3$



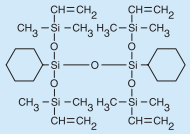
1mL $36.00; 5mL $120.00

52,360-7
$C_{28}H_{42}Si_2$



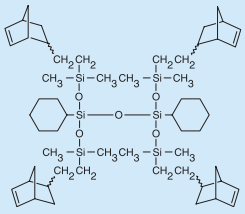
1mL $43.50; 5mL $145.00

52,001-2
$C_{28}H_{58}O_5Si_6$

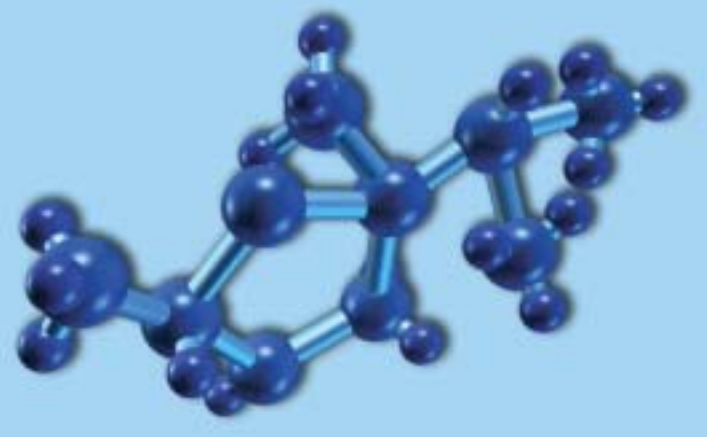


1mL $49.50; 5mL $165.00

52,737-8
$C_{56}H_{98}O_5Si_6$



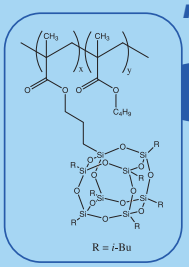
1mL $24.00; 5mL $80.00



POSS™ Polymers

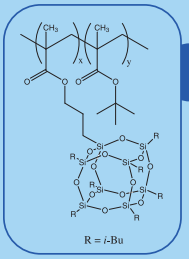
Courtesy of Hybrid Plastics, Inc., Fountain Valley, CA 92708-6117.

POSS™ monomers can be polymerized or grafted using standard techniques to yield inorganic–organic hybrid homopolymers and copolymers.[24,36-38] As illustrated in the adjacent figure, the size of the pendant POSS™ cage is comparable to the dimensions of the linear polymer, enabling POSS™ to control the motions of the chains at the molecular level. Thus, an enhancement in the physical properties is observed, while the processability and mechanical properties of the base resin are retained.[37,24,35,36] POSS™ copolymers available from Aldrich are listed below. They are typically soluble in THF and toluene. Using both solution and melt techniques, they can be processed into fibers, foams, films, and monolithic pieces.



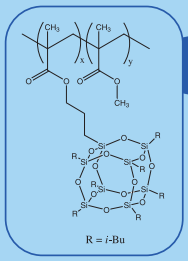
Poly[(propyl methacryl-heptaisobutyl-POSS™)-*co*-(*n*-butyl methacrylate)]

56,519-9	56,520-2	56,521-0
15 wt. % POSS™	25 wt. % POSS™	45 wt. % POSS™
5g $24.00; 25g $80.00	**5g $37.00; 20g $112.00**	**2g $36.30; 10g $110.00**



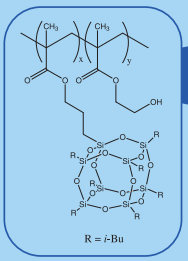
Poly[(propyl methacryl-heptaisobutyl-POSS™)-*co*-(*t*-butyl methacrylate)]

56,522-9	56,523-7	56,524-5
15 wt. % POSS™	25 wt. % POSS™	45 wt. % POSS™
2g $27.00; 10g $90.00	**2g $41.25; 10g $125.00**	**1g $33.75; 5g $112.50**



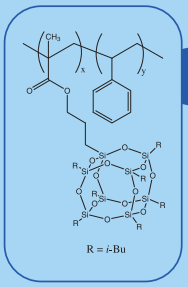
Poly[(propyl methacryl-heptaisobutyl-POSS™)-*co*-(methyl methacrylate)]

56,516-4	56,517-2	56,518-0
15 wt. % POSS™	25 wt. % POSS™	45 wt. % POSS™
5g $24.00; 25g $80.00	**5g $36.96; 20g $112.00**	**2g $36.30; 10g $110.00**



Poly[(propyl methacryl-heptaisobutyl-POSS™)-*co*-hydroxyethyl methacrylate]

56,529-6	56,531-8	56,532-6
15 wt. % POSS™	25 wt. % POSS™	45 wt. % POSS™
5g $30.00; 25g $100.00	**5g $42.30; 20g $128.00**	**2g $33.00; 10g $100.00**



Poly[(propyl methacryl-heptaisobutyl-POSS™)-*co*-styrene]

56,525-3	56,526-1	56,528-8
15 wt. % POSS™	25 wt. % POSS™	45 wt. % POSS™
5g $24.00; 25g $80.00	**5g $37.00; 20g $112.00**	**2g $36.30; 10g $110.00**

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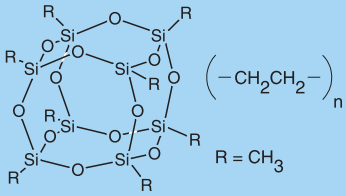
POSS™ Nanoreinforced Resin

The fully condensed silsesquioxane cages surrounded by nonreactive organic groups permit the robust, inorganic, Si-O core to be compatible with an organic matrix. Thus, they may be compounded with traditional plastics yielding true nanocomposites with molecular-level dispersion as shown to the left.[39] The TEM image provides insight into the sub-micron morphology obtained in this hybrid system. Features that appear as black spots are comprised of domains compositionally richer in POSS™ content, as contrasted with the lighter background regions compositionally consisting of the polypropylene component.

Such nanoreinforced polymers lead to significant thermomechanical property enhancements while simultaneously improving or retaining the material's other physical properties (optical clarity, mechanicals, etc.) as well as its processability. Other property enhancements such as gas permeability may also be realized.

***Blackscale = 50nm**

Courtesy of Hybrid Plastics, Inc., Fountain Valley, CA 92708-6117.



Polypropylene, isotactic

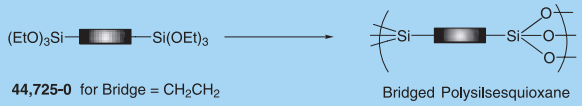
56,562-8
10 wt. % Methyl-POSS™ nanoreinforced
250g $23.80; 1kg $66.00

42,789-6
Polypropylene; unreinforced homopolymer
1kg $20.05; 3kg $38.30

Mesoporous Polysilsesquioxanes – Xerogels, Aerogels, Crystals

As discussed above, $RSiX_3$ monomers (R=alkoxy, halide) oligomerize under typical sol-gel conditions to form polyhedral oligosilsesquioxanes, or soluble, randomly linked arrays of polycyclic cages.[39] On the other hand, sol-gel polymerization of a molecular building block that contains an organic fragment attached to two or more trialkoxysilyl groups leads to bridged polysilsesquioxanes (see ***Scheme 5***).[8,9]

Scheme 5



44,725-0 for Bridge = CH_2CH_2

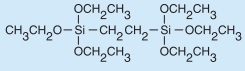
Bridged Polysilsesquioxane

These network polymers resulting from the bridged silsesquioxane monomers (such as 44,725-0) may be porous xerogels and aerogels, or nonporous polymers depending on whether the organic spacer is a rigid arylene group or a flexible alkylene group. Monolithic gels containing organic dyes have been prepared for waveguide, NLO, and laser applications.[40] The dye functionality in these materials is built into the organic bridging group, assuring no phase separation, aggregation, or loss by leaching.

More recently, the surfactant template approach[10] has been used to synthesize mesoporous polysilsesquioxanes with well-defined mesoscopic morphology; crystal-like external morphologies of hexagonal rod, spherical, and decaoctahedron shapes were reported.[11,41] New applications for such periodic mesoporous silsesquioxane hybrids include optical filters, separation membranes, and metal ion recognition sorbents.[42] Below is a list of the bridged silsesquioxane monomers available from Aldrich.

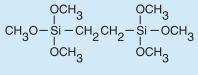
Bridged Silsesquioxane Monomers

44,725-0
$C_{14}H_{34}O_6Si_2$



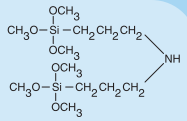
5mL $9.85; 25mL $32.15

44,724-2
$C_8H_{22}O_6Si_2$



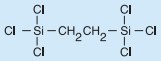
5mL $18.00; 25mL $59.90

41,335-6
$C_{12}H_{31}NO_6Si_2$



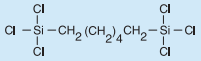
50mL $24.80; 250mL $69.40

44,704-8
$C_2H_4Cl_6Si_2$



5mL $44.35; 25mL $175.35

45,224-6
$C_6H_{12}Cl_6Si_2$



1g $8.70; 10g $30.90

The singular control over the morphology of the mesoporous polysilsesquixoane crystals is governed by the synthesis temperature and the alkyl chain length of the surfactant. Aldrich offers a wide variety of surfactants including quaternary ammonium halides, alkylamines, poly(ethylene oxides), and block copolymers. For a comprehensive list, please contact us at aldrich@sial.com or visit our website.

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