

PROCESS FOR ASSEMBLY OF POSS MONOMERS

Cross-Reference to Related Applications and Patents

This application claims priority from U.S. Provisional Patent Application Serial No. 60/659,722 Filed March 7, 2005.

Field of the Invention

This invention relates generally to a process for enhancing the properties of functionalized POSS monomers for incorporation into polymeric and biological products.

BACKGROUND OF THE INVENTION

Nanostructured chemicals are best exemplified by those based on low-cost Polyhedral Oligomeric Silsesquioxanes (POSS) and Polyhedral Oligomeric Silicates (POS). POSS systems contain hybrid (i.e. organic-inorganic) compositions in which the internal cage like framework is primarily comprised of inorganic silicon-oxygen bonds. The exterior of the nanostructure is covered by both reactive and nonreactive organic functionalities (R), which ensure compatibility and tailorability of the nanostructure with organic monomers and polymers. These and other properties and features of nanostructured chemicals are discussed in detail in U.S. Pat. Nos. 5,412,053 and U.S. Pat. No. 5,484,867, both of which are expressly incorporated herein by reference in their entirety.

Current engineering practices produce functionalized POSS molecules in high yield but certain microelectronic, medical, and biological applications require higher purity or chemical functionalities that are not readily or economically produced using the prior art. Prior art methods include the use of hydroxide base, anionic salts, and

1 protic acid catalysts in the assembly of POSS cages and their functionalization (see
2 US Patent Application Nos. 09/631,892 and 10/186,318, and US Patent Nos.
3 6,770,724; 6,660,823; 6,596,821; and 3,390,163). While these approaches are
4 known to be generally effective, they are limited in that both protic acids and
5 hydroxide bases can also catalyze the self-condensation of POSS individual cages
6 into oligomerized POSS cage containing resins (Figure 1). Such resins are not
7 desirable in microelectronics, biological or medical applications, as their structure is
8 molecularly imprecise. Furthermore, the dispersion of the POSS molecules and their
9 compatibility with polymers is thermodynamically governed by the free energy of
10 mixing equation ($\Delta G = \Delta H - T\Delta S$). The nature of the R group and ability of the
11 reactive groups on the POSS cage to react or interact with polymers and surfaces
12 greatly contributes to a favorable enthalpic (ΔH) term while the entropic term (ΔS) for
13 POSS is highly favorable when the cage size is monoscopic and the corresponding
14 distribution of oligomers is 1.0.

15 Consequently a need exists for improvement upon the prior art methods of
16 POSS cage assembly and functionalized monomers. An improved process yielding,
17 higher purity, and molecularly precise POSS systems is described.

18 SUMMARY OF THE INVENTION

19 The present invention provides an improved synthesis process for polyhedral
20 oligomeric silsesquioxanes which produces rapidly, in high yield, low resin content,
21 and solvent free, monomer products suitable for use in polymerization, grafting and
22 alloying applications. The synthesis process uses phosphazene superbases in
23 reaction with silane coupling agents of the formula R^1SiX_3 to form POSS cages
24 functionalized with silanols of the formula types $[(R^1SiO_{1.5})_7(HOSiO_{1.5})_1]_{\Sigma 8}$,

1 $[(R^1SiO_{1.5})_6(R^1HOSiO_1)_2]_{\Sigma 8}$, $[(R^1SiO_{1.5})_2(R^1HOSiO_1)_4]_{\Sigma 6}$, $[(R^1SiO_{1.5})_4(R^1HOSiO_1)_3]_{\Sigma 7}$.
 2 The synthesis process can also involve the reaction of phosphazene superbases in
 3 reaction with silane coupling agents of the type R^2SiX_3 to form polyfunctional POSS
 4 cages functionalized with R^2 groups of the formula types $[(R^2SiO_{1.5})_6]_{\Sigma 6}$,
 5 $[(R^2SiO_{1.5})_8]_{\Sigma 8}$, $[(R^2SiO_{1.5})_{10}]_{\Sigma 10}$, $[(R^2SiO_{1.5})_{12}]_{\Sigma 12}$ and larger sized cages.

6 Alternately the phosphazene superbases can be reacted with POSS silanols
 7 of the formula $[(R^1SiO_{1.5})_7(HOSiO_{1.5})_1]_{\Sigma 8}$, $[(R^1SiO_{1.5})_6(R^1HOSiO_1)_2]_{\Sigma 8}$,
 8 $[(R^1SiO_{1.5})_4(R^1HOSiO_1)_3]_{\Sigma 7}$ in the presence of a silane coupling agent of the formula
 9 $R^2R^3R^4SiX$, $R^2R^3SiX_2$, or R^2SiX_3 for sufficient time in the presence of a solvent and
 10 superbase where the elimination of HX occurs and renders a monofunctional POSS
 11 monomer of the formula $[(R^1SiO_{1.5})_8(R^2R^3R^4SiO_1)]_{\Sigma 9}$, $[(R^1SiO_{1.5})_8(R^2R^3SiO_2)]_{\Sigma 17}$,
 12 $[(R^1SiO_{1.5})_8(R^2SiO_3)]_{\Sigma 25}$, $[(R^1SiO_{1.5})_6(R^1SiO_1)_2(R^2R^3R^4SiO)_2]_{\Sigma 10}$,
 13 $[(R^1SiO_{1.5})_6(R^1SiO_1)_2(R^2R^3SiO_2)]_{\Sigma 9}$, $[(R^1SiO_{1.5})_6(R^1HOSiO_1)_1(R^2R^3SiO)]_{\Sigma 8}$,
 14 $[(R^1SiO_{1.5})_6(R^1(R^2R^3R^4SiO)SiO_1)(R^2R^3SiO)]_{\Sigma 9}$, $[(R^1SiO_{1.5})_4(R^1(R^2R^3R^4SiO)SiO_1)_3]_{\Sigma 10}$,
 15 $[(R^1SiO_{1.5})_7(R^2SiO_{1.5})_1]_{\Sigma 8}$, respectively. The resulting monomer is essentially free of
 16 impurities and has controllable properties through selection of composition, R
 17 groups, and nanostructure size and topology. Highly purified nanostructured POSS
 18 monomers are desirable as they exhibit improved filtration capability, reduced
 19 contamination and viscosity, more reliable polymerization, lower cost and waste
 20 reduction over impure systems.

21 A preferred process involves the reaction of POSS silanols of the formula
 22 $[(R^1SiO_{1.5})_7(HOSiO_{1.5})_1]_{\Sigma 8}$, $[(R^1SiO_{1.5})_6(R^1HOSiO_1)_2]_{\Sigma 8}$, $[(R^1SiO_{1.5})_4(R^1HOSiO_1)_3]_{\Sigma 7}$
 23 with a silane coupling agent of the formula, $R^2R^3R^4SiX$, $R^2R^3SiX_2$, R^2SiX_3 in the
 24 presence of a solvent and superbase.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows a comparison of the prior art and improved silation process;

FIG. 2 shows a variety of the preferred phosphazene superbases; and

FIG. 3 shows the structure of the compound synthesized in Example 5.

DEFINITION OF FORMULA REPRESENTATIONS FOR NANOSTRUCTURES

For the purposes of understanding this invention's chemical compositions the following definition for formula representations of Polyhedral Oligomeric Silsesquioxane (POSS) and Polyhedral Oligomeric Silicate (POS) nanostructures is made.

Polysilsesquioxanes are materials represented by the formula $[\text{RSiO}_{1.5}]_{\infty}$ where ∞ represents molar degree of polymerization and R = represents organic substituent (H, siloxy, cyclic or linear aliphatic or aromatic groups that may additionally contain reactive functionalities such as alcohols, esters, amines, ketones, olefins, ethers or halides or which may contain fluorinated groups). Polysilsesquioxanes may be either homoleptic or heteroleptic. Homoleptic systems contain only one type of R group while heteroleptic systems contain more than one type of R group.

POSS and POS nanostructure compositions are represented by the formula:

$[(\text{RSiO}_{1.5})_n]_{\Sigma\#}$ for homoleptic compositions

$[(\text{RSiO}_{1.5})_n(\text{R}'\text{SiO}_{1.5})_m]_{\Sigma\#}$ for heteroleptic compositions (where $\text{R} \neq \text{R}'$)

1 $[(\text{RSiO}_{1.5})_n(\text{RXSiO}_{1.0})_m]_{\Sigma\#}$ for functionalized heteroleptic compositions (where R
2 groups can be equivalent or in equivalent)

3 In all of the above R is the same as defined above and X includes but is not
4 limited to OH, Cl, Br, I, alkoxide (OR), formate (OCH), acetate (OCOR), acid
5 (OCOH), ester (OCOR), peroxide (OOR), amine (NR_2) isocyanate (NCO), and R.
6 The symbols m and n refer to the stoichiometry of the composition. The symbol Σ
7 indicates that the composition forms a nanostructure and the symbol # refers to the
8 number of silicon atoms contained within the nanostructure. The value for # is
9 usually the sum of m+n, where n ranges typically from 1 to 24 and m ranges typically
10 from 1 to 12. It should be noted that $\Sigma\#$ is not to be confused as a multiplier for
11 determining stoichiometry, as it merely describes the overall nanostructural
12 characteristics of the system (aka cage size).

13 DETAILED DESCRIPTION OF THE INVENTION

14 The present invention teaches an improved method of synthesis for POSS
15 nanostructured chemicals yielding a higher purity and lower cost product than
16 previously described.

17 The key feature of the invention is the use of phosphazene superbases to
18 catalyze the assembly of POSS cages. A range of phosphazenes are applicable and
19 include polyphosphazenes which vary in molecular weight and composition.
20 Phosphazene oligomers and molecules are preferentially utilized and in particular P
21 1 type $\text{P}(\text{NtBu})(\text{NH}_2)_3$, P2 type $(\text{H}_2\text{N})_3\text{P}=\text{N}-\text{P}(\text{NH}_2)_4$, P3 type $(\text{H}_2\text{N})_3\text{P}=\text{N}-\text{P}(\text{NH}_2)-$
22 $\text{N}=\text{P}(\text{NH}_2)_3$, P4 type $(\text{H}_2\text{N})_3\text{P}=\text{N}-\text{P}(\text{NH}_2)_3=\text{N}-\text{P}(\text{NH}_2)_3-\text{N}=\text{P}(\text{NH}_2)_3$. The basicity of
23 phosphazene superbases increase with increasing number of phosphorous atoms
24 and this provides a valuable tool in the utility of this reagent. The preferred

1 concentration of superbase relative to trisilanol is 2 mol % but a useful range
2 includes 0.1mol % to 10 mol %.

3 **General Process Variables Applicable To All Processes**

4 As is typical with chemical processes there are a number of variables that can
5 be used to control the purity, selectivity, rate and mechanism of any process.
6 Variables influencing the process include the size, polydispersity, and composition of
7 the nanostructured chemical, separation and isolation methods, and use of catalyst
8 or cocatalysts, solvents and cosolvents. Additionally, kinetic and thermodynamic
9 means of controlling the synthesis mechanism, rate, and product distribution are
10 also known tools of the trade that can impact product quality and economics.

11 **Example 1.**

12 **Synthesis of $[(\text{isobutylSiO}_{1.5})_7(\text{methacrylpropylSiO}_{1.0})_1]_{\Sigma 8}$:**

13 $[(\text{isobutylSiO}_{1.5})_4(\text{isobutyl}(\text{OH})\text{SiO}_{1.0})_3]_{\Sigma 7}$ (688 g, 0.87 mole) was dissolved in THF
14 followed by addition of methacrylpropyltrimethoxysilane (204 g, 0.87 mole) and the
15 solution was cooled to 5°C. Phosphazene superbase (FW 234.32, 15.72 mmol) was
16 then added and the mixture stirred at room temperature for 3 days. The solution was
17 then quenched with acetic acid (1.5g). Then 1 liter of methanol was added and the
18 mixture was stirred and filtered. The solid was dried to render pure white product in
19 75% yield.

20 **Example 2.**

21 **Synthesis of $[(\text{EtSiO}_{1.5})_7(\text{glycidylSiO}_{1.0})_1]_{\Sigma 8}$:**

22 $[(\text{EtSiO}_{1.5})_4(\text{Et}(\text{OH})\text{SiO}_{1.0})_3]_{\Sigma 7}$ (50 g, 84 mmole) was dissolved in methanol

1 followed by addition of 3-glycidoxypropyltrimethoxysilane (19.86 g, 84 mmole) and
2 the solution was cooled to 5°C. Phosphazene superbase (FW 234.32, 15.72 mmol)
3 was then added and the mixture stirred for 3 days at 5°C. The solution was then
4 quenched with acetic acid (87mg) filtered, and volatiles removed and dried to render
5 a solid. The solid was washed with methanol (1400 ml) and dried to render 415 g of
6 pure white product in 87% yield.

7 **Example 3.**

8 **Synthesis of $[(\text{EtSiO}_{1.5})_7(\text{ethylnorborneneSiO}_{1.0})_1]_{\Sigma 8}$:**

9 $[(\text{EtSiO}_{1.5})_4(\text{Et}(\text{OH})\text{SiO}_{1.0})_3]_{\Sigma 7}$ (12 g, 20 mmole) was dissolved in methanol
10 followed by addition of exo-norbornenylethyltrimethoxysilane (4.84 g, 20 mmole) and
11 the solution was cooled to 5°C. Phosphazene superbase was then added and the
12 mixture stirred for 2 days at 5°C. The solution was then quenched with acetic acid
13 (87mg) filtered, and volatiles removed, washed with additional methanol and dried to
14 render a white product.

15 **Example 4.**

16 **Synthesis of $[(\text{CyclohexylSiO}_{1.5})_7(\text{aminoethylaminopropylSiO}_{1.0})_1]_{\Sigma 8}$:**

17 $[(\text{CyclohexylSiO}_{1.5})_4(\text{Cyclohexyl}(\text{OH})\text{SiO}_{1.0})_3]_{\Sigma 7}$ (10 g, 10.3 mmole) was dissolved
18 in THF followed by addition of 3-(N-aminoethyl)aminopropyltrimethoxysilane (2.32 g,
19 10.27 mmole) and phosphazene superbase (FW 234.32, 15.72 mmol) was then
20 added and the mixture stirred at room temperature. The solution was then quenched
21 with acetic acid methanol was added. The volatiles were removed and product
22 dried to render a pure white solid in 62% yield.

1 **Example 5.**

2 **Synthesis of [(PhenylSiO_{1.5})₇(aminopropylSiO_{1.0})₁]_{Σ8}:**

3 [(PhenylSiO_{1.5})₄(Phenyl(OH)SiO_{1.0})₃]_{Σ7} (5.9g, 6.3mol) was dissolved in toluene
4 followed by addition of (2.0g, 11mmol) 3-aminopropyltrimethoxysilane and was then
5 stirred at room temperature for 12 hours. Acetonitrile was added and the solution
6 was filtered and product dried to render a pure white solid in 40% yield.

7 While certain representative embodiments and details have been shown for
8 purposes of illustrating the invention, it will be apparent to those skilled in the art that
9 various changes in the methods and apparatus disclosed herein may be made
10 without departing from the scope of the invention which is defined in the appended
11 claims.

12 What is claimed is:

CLAIMS

1. A method for preparing functionalized POSS monomers comprising the step of reacting a silane coupling agent having the formula RSiX_3 in the presence of a solvent and a phosphazene superbase, wherein:
R is selected from the group consisting of hydrogen, siloxy, and aliphatic, aromatic, and olefinic groups, wherein said groups may contain reactive functionalities selected from the group consisting of alcohols, esters, amines, ketones, olefins, ethers and halides and may contain fluorinated substituents;
X is selected from the group consisting of OH, Cl, Br, I, alkoxide (OR), formate, acetate (OCOR), acid (COOH), ester (OCOR), peroxide (OOR), amine (NR_2), isocyanate (NCO), and R; and
each R and each X may be the same or different.
2. The method of claim 1, wherein the superbase is selected from the group consisting of P1, P2, P3, and P4 type phosphazenes.
3. The method of claim 1, wherein a mixture of different silane coupling agents are reacted are utilized to prepare functionalized POSS monomers.
4. The method of claim 1, wherein a mixture of different superbases are utilized as homogeneous catalysts or coreagents.
5. The method of claim 1 wherein a mix of different solvents or reaction media are utilized.

6. The method of claim 1 wherein a continuous process rendering functionalized POSS monomers is utilized that uses the superbase as a heterogeneous catalyst or coreagent.
7. A method for preparing functionalized POSS monomers comprising the step of silating a POSS silanol with a silane coupling agent having the formula selected from the group consisting of RSiX_3 , R_2SiX_2 , and R_3SiX in the presence of a solvent and a phosphazene superbase, wherein:
R is selected from the group consisting of hydrogen, siloxy, and aliphatic, aromatic, and olefinic groups, wherein said groups may contain reactive functionalities selected from the group consisting of alcohols, esters, amines, ketones, olefins, ethers, and halides, and may contain fluorinated substituents;
X is selected from the group consisting of OH, Cl, Br, I, alkoxide (OR), formate, acetate (OCOR), acid (COOH), ester (OCOR), peroxide (OOR), amine (NR_2), isocyanate (NCO), and R; and
each R and each X may be the same or different.
8. The method of claim 7, wherein the superbase is selected from the group consisting of P1, P2, P3, and P4 type phosphazenes.
9. The method of claim 7, wherein a mixture of different, POSS silanols and silane coupling agents are silated.
10. The method of claim 7, wherein a mixture of different superbases are utilized as homogeneous catalysts or coreagents.

11. The method of claim 7, wherein a mix of different solvents or reaction media are utilized,
12. The method of claim 7, wherein a continuous silation process is utilized that uses the superbases as a heterogeneous catalyst or coreagent.