

Hydrosilylation of Allyl Alcohol with $[\text{HSiMe}_2\text{OSiO}_{1.5}]_8$: Octa(3-hydroxypropyldimethylsiloxy)octasilsesquioxane and Its Octamethacrylate Derivative as Potential Precursors to Hybrid Nanocomposites

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Received January 28, 2000

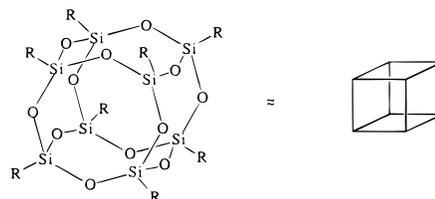
Abstract: Octakis(3-hydroxypropyldimethylsiloxy)octasilsesquioxane (OHPS) can be synthesized by direct hydrosilylation of allyl alcohol with octakis(dimethylsiloxy)octasilsesquioxane, $(\text{HSiMe}_2\text{O})\text{Si}_8\text{O}_{12}$ ($\text{Q}_8\text{M}_8^{\text{H}}$), using platinum divinyltetramethyldisiloxane $[\text{Pt}(\text{dvs})]$ as catalyst. Surprisingly, C-hydrosilylation occurs in preference to O-silylation. Hydrosilylation of trimethylsiloxy-2-propene with $\text{Q}_8\text{M}_8^{\text{H}}$, followed by desilylation also gives pure OHPS. OHPS reacts with methacryloyl chloride to give octakis(3-methacryloxypropyldimethylsiloxy)octasilsesquioxane (OMPS), a thermal and UV/vis curable precursor to organic/inorganic nanocomposites. Direct hydrosilylation of $\text{Q}_8\text{M}_8^{\text{H}}$ with 2-allyloxyethanol also proceeds primarily via C- rather than O-silylation. In contrast, compounds such as 1,3,5,7-tetramethylcyclotetrasiloxane (D_4^{H}), 1,1,3,3-tetramethyldisiloxane (TMDS) or terminal Si–H functionalized poly(dimethylsiloxane) (PDMS-H, MW = 400), give significant amounts of O-silylation along with C-silylation. Initial catalyst concentration studies suggest that the catalytic cycle requires the intermediacy of Pt cluster complexes in contrast to recent studies on the mechanism of hydrosilylation which suggest monometallic complex catalysis.

I. Introduction

Nanocomposite materials, because of the length scales involved, incorporate extensive interfacial interactions that can result in nonlinear changes in composite properties.^{1,2} These changes can be so great, that the rule-of-mixtures approximation commonly used to estimate macroscopic composite properties fails. Thus, nanocomposites offer potential access to completely new classes of materials with unique properties. Unfortunately one of the more difficult problems with nanocomposites is in developing synthetic and processing approaches that precisely define the volume and shape of the individual phases and their periodicity.² Such efforts are needed to generate nanocomposite materials that permit one to probe how small changes in nanostructure affect macroscopic properties.

For these reasons, we have sought to develop methods of preparing organic/inorganic hybrid nanocomposites based on cubic silsesquioxanes.³ Cubic silsesquioxanes, $\text{R}_8\text{Si}_8\text{O}_{12}$, consist of a rigid, crystalline silica-like core that is perfectly defined spatially (0.5–0.7 nm) and that can be linked covalently to eight R groups.⁴ By designing the functionality of the R group, it is possible to create octafunctional macromonomers that will self-

polymerize or copolymerize³ with other functionalized cubes to provide nanocomposites whose length scales and interfacial interactions are exactly defined. Note that all of the silicon atoms in cubes are at the “surface” of these reinforcing particles.



As detailed elsewhere,^{3b} we seek to develop polymerizable cubes with good-to-excellent control of the lengths and architectures of the organic segments that tether two points on two cubes. Because the structure of the organic phase between the rigid, hard particles can be varied systematically, the potential exists to carefully probe mechanical, photonic and/or electronic properties to establish structure-processing-property relationships.³ Such relationships are expected to provide fundamental principles for the selective design of nanocomposites for specific applications.

We report here novel syntheses of octahydroxy functionalized cubes that offer potential access to diverse polyester nanocomposites and related polymers.⁹ These compounds also offer potential utility for developing new ligands for inorganic and

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organometallic chemistry,^{10a,b} and as cores for hyperbranched or dendritic materials.^{10c,d} The current work emphasizes a polymethacrylate precursor to organic/inorganic nanocomposites.

II. Experimental Section

II.A. Materials. Solvents for hydrosilylation were purified under N₂ as follows: CH₂Cl₂ was distilled from P₂O₅, toluene from benzophenone/Na, THF from CaH₂. Allyl alcohol and methacryloyl chloride were distilled before use. Q₈M₈^H was synthesized following modified literature procedures.⁶ Platinum divinyltetramethyldisiloxane complex, Pt(dvs) was obtained from PCR Co. and diluted to a 2 mM solution in distilled toluene before use. Dicyclopentadiene Pt complex, Pt(dcp), was synthesized following literature procedures and used as a 2 mM solution in toluene.¹¹ Hexachloroplatinic acid, H₂PtCl₆ was obtained from Aldrich and used as a 2 mM solution in isopropyl alcohol. 1,1,3,3-Tetramethyldisiloxane (TMDS) and Si-H terminated poly(dimethylsiloxane) (PDMS-H, MW = 400) were obtained from Hüls America Inc. 1,3,5,7-tetramethylcyclotetrasiloxane (D₄^H) was obtained from Gelest Inc. Other reagents and solvents were obtained from standard vendors and used as received.

II.B. Techniques. B.1. NMR analyses. All ¹H- and ¹³C NMR analyses were done in CDCl₃ and recorded on a Varian INOVA 400 spectrometer. ¹H NMR spectra were collected at 400.0 MHz using a 6000 Hz spectral width, a relaxation delay of 3.5 s, a pulse width of 38°, 30k data points, and CHCl₃ (7.259 ppm) as internal reference. ¹³C{¹H} NMR spectra were obtained at 100.6 MHz using a 25 000 Hz spectral width, a relaxation delay of 1.5 s, a pulse width of 40°, 75k data points, and CDCl₃ (77.23 ppm) as internal reference.

All ²⁹Si NMR spectra were recorded on a Bruker 360 spectrometer operated at 71.5 MHz using a 32000 Hz spectral width, a pulse angle of 90°, a relaxation delay of 10.0 s, 32k data points, and TMS as external reference.

II.B.2. GC–Mass Spectral Analyses. Analyses were conducted on a Finnigan model 4021 quadrupole GC/mass spectrometer by electron ionization. Data were recorded and analyzed using the software package provided by Galwin.

II.B.3. Fourier Transform Infrared Spectra. Spectra were recorded on a Nicolet 5DXB FT-IR 300 spectrometer. Random cuttings of crystalline, optical-grade KBr from International Crystal Laboratories were used to prepare samples. About 600 mg of KBr was ground in a mortar with a pestle, and enough solid sample was ground with KBr to make a 1 wt % mixture for making KBr pellets. Liquid samples were cast on salt plates. After the sample was loaded, the sample chamber was purged with nitrogen for a minimum of 10 min before data collection. A minimum of 32 scans was collected for each sample at a resolution of ±4 cm⁻¹.

II.B.4. Thermal Gravimetric Analyses. Analyses were performed on a Perkin-Elmer TGA-7 thermogravimetric analyzer (Perkin-Elmer Co., Norwalk, CT). The instrument was calibrated with Alumel and

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Iron supplied by Perkin-Elmer. Measurements were performed under a continuous flow of nitrogen or synthetic air (25 mL/min), at 20 °C/min.

II.B.5. Differential Scanning Calorimetry. The calorimetry was performed on a Perkin-Elmer DSC-7 differential scanning calorimetry (Perkin-Elmer Co., Norwalk, CT). The instrument was calibrated with indium supplied by Perkin-Elmer. Measurements were performed under a continuous flow of nitrogen (25 mL/min). Samples (1–2 mg) were typically equilibrated at 30 °C, ramped to the desired temperature (~20 °C lower than its decomposition temperature), and then allowed to cool back to 30 °C at 10 °C/min. Three heating–cooling cycles were recorded for each sample unless otherwise noted.

II.B.6. Gel Permeation Chromatography. Chromatographic analyses were performed on a Waters GPC system, using a Waters 410 RI detector, Waters Styragel columns (7.8 × 300, HR 0.5, 1, 3, 4), and a PL-DCU data capture unit from Polymer Laboratory. The system was calibrated using polystyrene standards obtained from Polymer Laboratory. THF was used as the eluent, at a flow rate of 1.0 mL/min.

II.C. Synthesis of Octakis(3-hydroxypropyldimethylsiloxy)octasilsesquioxane (OHPS). II.C.1. Reaction of Q₈M₈^H with Allyl Alcohol. Q₈M₈^H (5.00 g, 4.91 mmol) was placed in a 100 mL Schlenk flask equipped with a reflux condenser and a magnetic stirrer. Toluene (25 mL) was added to dissolve the cube, followed by addition of allyl alcohol (3.34 mL, 49.1 mmol). The reaction flask was evacuated and refilled with N₂ three times. Pt(dvs) (2 mM solution, 1.2 mL) was added via a syringe. The reaction began to reflux immediately due to the exothermic hydrosilylation and was complete in ~30 min. Two layers were formed. Triphenylphosphine, PPh₃ (~10 mg), was added to deactivate the Pt(dvs) catalyst, and the mixture was stirred for ~1 h. The bottom layer containing the product, OHPS, was recovered. Residual allyl alcohol and toluene were removed first under N₂ stream, and then under vacuum. OHPS is a white solid (6.2 g, 86%), soluble in methanol, THF, acetone, CH₂Cl₂ etc. Selected characterization data: FTIR (KBr, cm⁻¹) ν O–H: 3339s; ν C–H: 2959s, 2931s, 2875m; δ CH₃: 1258m; ν Si–C: 1173m; ν Si–O: 1082s. ¹H NMR (400 MHz, CDCl₃, CHCl₃ ref) 3.76 (s, 8H, OH), 3.54 (t, 16H, CH₂–OH), 1.59 (p, 16H, CH₂–CH₂–CH₂), 0.58 (t, 16H, CH₂–Si), 0.13 (s, 48H, Si(CH₃)₂). ¹³C NMR (100 MHz, CDCl₃, CDCl₃ ref) 65.2 (CH₂–OH), 26.3 (CH₂–CH₂–CH₂), 13.6 (CH₂–Si), –0.2 (Si(CH₃)₂). ²⁹Si NMR (71.5 MHz, CH₂Cl₂, TMS ref) 13.9 (–OSi(CH₃)₂CH₂), –108.3 (SiO₄). TGA (ceramic yield in air) 51.0% (64.8% theoretical, see results and discussion). DSC: mp 84 °C. Elemental analysis found (%): C: 32.35, H: 6.98; Calculated (%): C: 32.40, H: 7.07, Si: 30.31, O: 30.22. GPC: M_n 1.72 × 10³, M_w 1.80 × 10³, PDI 1.04 (FW of OHPS 1482).

NMR data in methanol: ¹H NMR (400 MHz, CD₃OD, CD₃OD ref, taken with a fresh sample) 4.78 (s, ~2H, OHs), 3.47 (t, ~1.4H, CH₂–OH), 3.44 (t, ~0.6H, CH₂–OSi), 1.55 (m, 2H, CH₂–CH₂–CH₂), 0.59 (m, 2H, CH₂–Si), 0.13 (s, ~4H, Si(CH₃)₂), 0.05 (s, ~2H, Si(CH₃)₂). ¹H NMR (400 MHz, CD₃OD, CD₃OD ref, taken after 2 days, see Figure 8) 4.78 (s, ~2H, OHs), 3.44 (t, 2H, CH₂–OSi), 1.50 (p, 2H, CH₂–CH₂–CH₂), 0.55 (t, 2H, CH₂–Si), 0.05 (s, ~6H, Si(CH₃)₂). ¹³C NMR (100 MHz, CD₃OD, CDCl₃ ref, almost no change with time) 65.6 (CH₂–O), 27.1 (CH₂–CH₂–CH₂), 14.5 (CH₂–Si), –0.02 (Si(CH₃)₂), –2.6 (Si(CH₃)₂). ²⁹Si NMR (71.5 MHz, CD₃OD, TMS ref) 13.9 (–OSi(CH₃)₂CH₂), –100.4 (see Figure 7 in results and discussion), –108.3 (SiO₄).

A GC–mass spectrum was taken when the above ¹H NMR sample in CD₃OD was first dried, and then redissolved in CDCl₃ (m/z , %) P⁺ 116 (8.1%), P-1 115 (0.2%), P-15 101 (100%), P-17 99 (24.3%), P-28 88 (38.5%). (see Results and Discussion).

II.C.2. Octakis[(3-trimethylsiloxypropyl)dimethylsiloxy]silsesquioxane (OSPS) from Allyloxytrimethylsilane. Q₈M₈^H (5.00 g, 4.91 mmol) was placed in a 100 mL Schlenk flask equipped with a reflux condenser and a magnetic stirrer. Toluene (25 mL) was added to dissolve the cube, followed by allyloxytrimethylsilane (8.28 mL, 49.1 mmol). The reaction flask was degassed and refilled with N₂ three times. Pt(dvs) (0.1 mL, 2 mM solution) was added via a syringe. The reaction was then heated to ~65 °C/~5 h and 100 °C/4 h to completion, giving octakis[(3-trimethylsiloxypropyl)dimethylsiloxy]silsesquioxane (OSPS). Triphenylphosphine, PPh₃ (~2 mg), was added to deactivate the Pt-

(dvs) catalyst. Excess allyloxytrimethylsilane and toluene were evaporated using N_2 stream and then vacuum, to give analytically pure OSPS as a white solid (8.30 g, 82%). Selected characterization data: IR (KBr, cm^{-1}) ν C–H 2960s, 2936, 2876m; δ CH_3 : 1252s; ν Si–C: 1186m; ν Si–O: 1096s. 1H NMR (400 MHz, $CDCl_3$, $CHCl_3$ ref) 3.51 (t, 16H, CH_2 –O), 1.54 (p, 16H, CH_2 – CH_2 – CH_2), 0.55 (t, 16H, CH_2 –Si), 0.12 (s, 48H, $Si(CH_3)_2$), 0.08 (s, 72H, $Si(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$, $CDCl_3$ ref) 65.5 (CH_2 –O), 26.4 (CH_2 – CH_2 – CH_2), 13.6 (CH_2 –Si), –0.17 ($Si(CH_3)_2$), –0.22 ($Si(CH_3)_3$). ^{29}Si NMR (71.5 MHz, CH_3 –OH, TMS ref) 13.3 ($OSi(CH_3)_2CH_2$), 16.5 ($OSi(CH_3)_3$), –108.9 (SiO_4). TGA (ceramic yield in air) 46.2% (69.9% theoretical, see results and discussion). DSC: mp 35 °C. Elemental analysis found (%) C: 37.42, H: 8.06; Calculated (%) C: 37.31, H: 8.22, Si: 32.72, O: 21.75. GPC: M_n 1.99×10^3 , M_w 2.03×10^3 , PDI 1.02 (FW of OSPS 2060).

II.C.3. OHPS from OSPS. The OSPS (2 g) obtained above was combined with 10 mL of anhydrous methanol, and stirred at room temperature for 4 h. All of the trimethylsilyl groups were removed as determined by NMR analysis. OHPS was isolated by removing the entire methanol and the methoxytrimethylsilane under vacuum. The resultant white powder is identical to the OHPS obtained via the direct hydrosilylation route based on NMR, GPC, and EA.

II.D. Kinetic Studies on Direct Hydrosilylation of Allyl Alcohol with $Q_8M_8^H$. **II.D.1. Catalyst Selectivity Studies.** Three common catalysts for hydrosilylation, Pt(dvs), Pt(dcp), and H_2PtCl_6 were tested. In all reactions, concentrations of reactants and catalyst were kept constant, that is, $[Si-H] = 1.6$ M, $[allyl\ alcohol] = 2.0$ M, $[Pt] = 100$ mM. Toluene was used as solvent.

$Q_8M_8^H$ (0.500 g, 0.491 mmol) was placed in a 25 mL Schlenk flask equipped with a reflux condenser and a magnetic stirrer. Toluene (2.5 mL) was added to dissolve the cube, followed by allyl alcohol (0.334 mL, 4.91 mmol). The reaction flask was carefully degassed and refilled with N_2 three times. Pt catalyst solution (2 mM, 0.15 mL) was added. When Pt(dvs) was used, the reaction was so exothermic that it began to reflux, and NMR analysis showed that all the Si–H disappeared in ~30 min. Toluene and the excess allyl alcohol were evaporated using an N_2 stream and then vacuum. The product was a white solid (0.580 g, 77% of theoretical). NMR analysis indicates that the majority of the product results from C-silylation. GPC analysis showed a sharp peak: M_n 1.67×10^3 , M_w 1.71×10^3 , PDI 1.02 (calculated FW 1482). When Pt(dcp) and H_2PtCl_6 were used, the reactions had to be heated at 85 °C for 3 h before all the Si–H reacted, as determined by 1H NMR analysis. The resultant products were both viscous liquids. With Pt(dcp), ~86% C-silylation and ~14% O-silylation occurred based on NMR analysis, and the resultant product had a broad weight distribution: M_n 3.25×10^3 , M_w 8.49×10^3 , PDI 2.61. With H_2PtCl_6 , ~14% C-silylation and ~86% O-silylation occurred based on NMR analysis. GPC analysis: M_n 3.04×10^3 , M_w 2.59×10^4 , PDI 8.53.

II.D.2. Solvent Effects. Three additional solvents—heptane, dichloromethane, and THF were also tested. Pt(dvs) was used as the catalyst. Concentrations of $Q_8M_8^H$, allyl alcohol, and Pt(dvs) were the same as above, and the same procedure was followed. When heptane was used, the reaction proceeded in the same way as in toluene. When CH_2Cl_2 was used, the reaction had to be refluxed for 2 h to force completion. NMR analysis indicated ~81% C-silylation and ~19% O-silylation. GPC analysis gave: M_n 2.37×10^3 , M_w 4.01×10^4 , PDI 1.69. When THF was used, the reaction required 8 h of reflux to force completion. NMR analysis showed ~87% C-silylation and ~13% O-silylation. GPC analysis gave: M_n 2.10×10^3 , M_w 2.57×10^4 , PDI 1.22.

II.D.3. Pt(dvs) Concentration Studies. On the basis of the above results, Pt(dvs) was chosen as the catalyst, and toluene the solvent. Different catalyst concentrations ranging from 10 to 100 mM were tested. A typical procedure was as follows: $Q_8M_8^H$ (0.500 g, 0.491 mmol) was placed in a 25 mL Schlenk flask equipped with a reflux condenser and a magnetic stirrer. Toluene (2.5 mL) was added via a syringe to dissolve the cube, followed by allyl alcohol (0.334 mL, 4.91 mmol). The reaction flask was carefully degassed and refilled with N_2 three times. Pt(dvs) was added via a syringe {2 mM solution, amount varied from 0.15, 0.12, 0.10, 0.075, 0.030, to 0.015 mL for different reactions, corresponding to $[Pt(dvs)] = 100, 80, 67, 50, 20,$ and 10 mM}. Reaction was followed by 1H NMR until complete. When $[Pt(dvs)] \geq 50$ mM, the reaction was extremely exothermic and Si–H

groups disappeared within 30 min. The products were obtained as white solids in ~80% yield, after excess allyl alcohol and toluene were removed. GPC analyses consist of a sharp peak at ~1600 Da, and a small peak at ~3000 Da corresponding to dimers. The polydispersity indices (PDI) of these products ranged from 1.02 to 1.04. No O-silylation was detected by 1H NMR analysis. When $[Pt(dvs)] = 20$ mM, the reaction required heating to 65 °C for ≥ 12 h to go to completion. The product was a waxy solid after solvent removal. About 3% O-silylation was observed by 1H NMR analysis. Approximately two-thirds of the product was monomer at ~1600, and one-third higher-molecular weight species based on the GPC trace: M_n 2.11×10^3 , M_w 2.78×10^3 , PDI 1.32. When $[Pt] = 10$ mM, the reaction had to be refluxed for ≥ 12 h to force completion. The product is a viscous liquid. About 7% O-silylation was observed. Approximately one-third of the product was monomer at ~1600, and two-third higher-molecular weight species: M_n 1.40×10^4 , M_w 6.84×10^4 , PDI 17.2.

II.D.4. Direct Hydrosilylation of Other Unsaturated Alcohols. Two additional alcohols, propargyl alcohol and 2-allyloxyethanol were reacted with $Q_8M_8^H$ to explore the applicability of the direct hydrosilylation method. Concentrations of $Q_8M_8^H$ and alcohols were kept the same as above, and $[Pt] = 100$ mM. Toluene was used as the solvent.

II.D.5. Reaction of Propargyl Alcohol. $Q_8M_8^H$ (0.500 g, 0.491 mmol), propargyl alcohol (0.29 mL, 4.9 mmol), Pt(dvs) (0.015 mL, 2 mM), toluene (2.5 mL). The reaction required heating at 60 °C for 5 h to complete. On cooling, two layers formed. The top layer was mainly toluene, and the product recovered from the bottom layer (0.610 g, 85%) was analyzed as follows. 1H NMR (400 MHz, $CDCl_3$, $CHCl_3$ ref) 6.31 (dt, 3.6H, $CH=CHSi$, β -*cis*), 5.95 (dt, 3.6H, $CH=CHSi$, β -*cis*), 5.84 (m, 4.4H, $CH=CHSi$, β -*trans*), 5.50 (m, 4.4H, $CH=CHSi$, β -*trans*), 4.29 (m, 8.8H, *trans*- $CH=CHCH_2O$), 4.17 (dd, 7.2H, *cis*- $CH=CHCH_2O$), 2.71 (s, 8H, OH), 0.28 [s, 26H, *trans*- $CH=CH-Si(CH_3)_2$], 0.23 [s, 22H, *cis*- $CH=CH-Si(CH_3)_2$]. As shown above, $-OSi(CH_3)_2-CH=CHCH_2OH$ and $-OSi(CH_3)_2-CH=CHCH_2OSi(CH_3)_2-$ structures are not differentiable from NMR analysis. However, GPC analysis gave a relatively broad distribution with higher molecular species (M_n 2.61×10^3 , M_w 3.96×10^3 , PDI 1.52), which suggests simultaneous C- and O-silylation. Thus no further characterization was pursued.

II.D.6. Reaction of 2-Allyloxyethanol. $Q_8M_8^H$ (0.500 g, 0.491 mmol), 2-allyloxyethanol (0.52 mL, 4.9 mmol), Pt(dvs) (0.015 mL, 2 mM), toluene (2.5 mL). The reaction was completed ~30 min after Pt(dvs) was added per NMR analysis. Two layers formed on cooling, the top layer was mainly toluene, and bottom layer contained the reaction product. The bottom layer was collected, and the residual 2-allyloxyethanol and toluene were removed first under N_2 stream, and then under vacuum to provide a white solid (0.790, 87%). On the basis of the characterization data, the product was found to be octakis[2-(2-hydroxyethoxy)ethyl]dimethylsiloxyoctasilsesquioxane. 1H NMR (400 MHz, $CDCl_3$, $CHCl_3$ ref) 3.71 (t, 16H, $HO-CH_2-CH_2-O$), 3.53 (t, 16H, $HO-CH_2-CH_2-O$), 3.45 (t, 16H, $OCH_2CH_2CH_2Si$), 2.70 (s, 8H, OH), 1.66 (m, 16H, $OCH_2CH_2CH_2Si$), 0.61 (t, 16H, $OCH_2CH_2CH_2-Si$), 0.15 [s, 48H, $Si(CH_3)_2$]. ^{13}C NMR (100 MHz, $CDCl_3$, $CDCl_3$ ref) 73.9 (OCH_2CH_2OH), 72.1 ($CH_2OCH_2CH_2OH$), 65.2 (CH_2-OH), 23.2 ($CH_2-CH_2-CH_2$), 13.7 (CH_2-Si), –0.3 ($Si(CH_3)_2$). ^{29}Si NMR (71.5 MHz, CH_2Cl_2 , TMS ref) 13.6 [$OSi(CH_3)_2CH_2$], –108.5 (SiO_4). GPC analysis: M_n 1.91×10^3 , M_w 2.01×10^3 , PDI 1.05.

II.E. Direct Hydrosilylation of Allyl Alcohol with Other Si–H Compounds. Three additional Si–H compounds, tetramethylcyclohexylsiloxane (D_4^H), tetramethyldisiloxane (TMDS) and Si–H capped poly(dimethylsiloxane) (PDMS–H, MW 400) were reacted with allyl alcohol. The concentration of Si–H and the allyl alcohol were kept the same as above, with $[Pt] = 100$ mM. Toluene was used as the solvent.

II.E.1. Reaction of D_4^H . D_4^H (1 mL, 4.12 mmol), allyl alcohol (1.40 mL, 20.6 mmol), toluene (10 mL), Pt(dvs) (0.50 mL, 2 mM). Violent bubbling was observed when Pt(dvs) was added. The reaction product was a cross-linked gel after stirring at room-temperature overnight, and was not further characterized.

II.E.2. Reaction of TMDS. TMDS (1 mL, 5.65 mmol), allyl alcohol (0.96 mL, 14.1 mmol), toluene (6 mL), Pt(dvs) (0.35 mL, 2 mM).

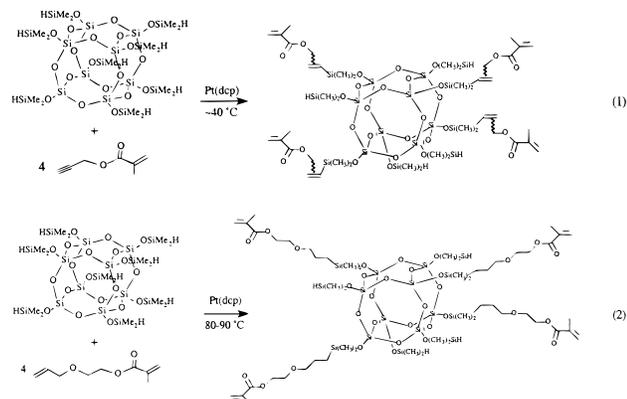
Violent bubbling was also observed after Pt(dvs) was added. The Si-H peak disappeared after ~1 h. The product was a clear, viscous liquid. NMR analysis indicated approximately ~75% C-silylation and ~25% O-silylation. GPC analysis: M_n 7.08×10^2 , M_w 7.84×10^2 , PDI 1.11.

II.E.3. Reaction of PDMS-H. PDMS-H (2 g, 5.00 mmol), allyl alcohol (0.85 mL, 12.5 mmol), toluene (6 mL), Pt(dvs) (0.35 mL, 2 mM). The reaction was exothermic, with no significant bubbling. All of the Si-H disappeared in ~30 min. NMR analysis indicated ~16% O-silylation, ~84% C-silylation. GPC analysis: M_n 1.02×10^3 , M_w 1.09×10^3 , PDI 1.07.

II.F. Synthesis of Octakis(methacryloxypropyldimethylsiloxy)octasilsesquioxane (OMPS). OHPS cube (2.57 g, 1.73 mmol) was weighed into a 50 mL Schlenk flask equipped with an addition funnel, a reflux condenser, and a magnetic stir bar. CH_2Cl_2 (20 mL) was added to dissolve the OHPS. Triethylamine (1.98 mL, 14.2 mmol) was added. The mixture was cooled in an ice bath and stirred for 15 min, then methacryloyl chloride (1.50 mL, 15.2 mmol) was added dropwise through the addition funnel. A light pink precipitate of triethylammonium chloride formed on adding the methacryloyl chloride. After all of the methacryloyl chloride was added, the reaction was further stirred at room temperature for 2 h. To isolate the methacrylate product, the reaction mixture was first filtered, and then the filtrate was transferred to a 100 mL separatory funnel and washed with DI water three times, 5% NaHCO_3 solution twice, 0.5 N NaOH twice, and last brine once. The solution was dried over Na_2SO_4 . Solvent was removed, to give OMPS as clear, yellowish, slightly viscous oil (7.2 g, 75%). Selected characterization data: IR (cm^{-1}) ν C-H: 2959s, 2930s, 2896m; ν C=O: 1719s; ν C=C: 1638w; δ CH_3 : 1254m; ν Si-C: 1164s; ν Si-O: 1088s. ^1H NMR (400 MHz, CDCl_3 , CHCl_3 ref) 6.08 [s, 8H, $\text{CH}_2=\text{C}(\text{CH}_3)(\text{C}=\text{O})$], 5.54 [s, 8H, $\text{CH}_2=\text{C}(\text{CH}_3)(\text{C}=\text{O})$], 4.08 (t, 16H, CH_2-O), 1.93 (s, 24H, $\text{CH}_2=\text{C}(\text{CH}_3)(\text{C}=\text{O})$), 1.69 (p, 16H, $\text{CH}_2-\text{CH}_2-\text{CH}_2$), 0.62 (t, 16H, CH_2-Si), 0.15 (s, 48H, $\text{Si}(\text{CH}_3)_2$). ^{13}C NMR (100 MHz, CDCl_3 , CDCl_3 ref) 167.4 (C=O), 136.6 ($\text{CH}_2=\text{CH}-$), 125.3 ($\text{CH}_2=\text{CH}-$), 67.0 (CH_2-O), 26.4 ($\text{CH}_2-\text{CH}_2-\text{CH}_2$), 18.4 ($\text{CH}_2=\text{CH}-$), 13.7 (CH_2-Si), -0.33 ($\text{Si}(\text{CH}_3)_2$). ^{29}Si NMR (71.5 MHz, CH_3-OH , TMS ref) 14.4 ($\text{OSi}(\text{CH}_3)_2\text{CH}_2$), -107.8 (SiO_4). TGA (ceramic yield in air) 45.8% (47.4% theoretical). DSC: (broad exothermal onset at 176 °C in first heating cycle, which was absent from subsequent heating cycles). Elemental analysis found (%) C: 42.29, H: 6.65; Calculated (%) C: 42.66, H: 6.76, Si: 28.41, O: 22.17. GPC analysis: M_n 2.00×10^3 , M_w 2.08×10^3 , PDI 1.06 (FW of OMPS 2027).

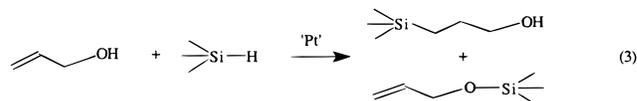
III. Results and Discussion

Our initial work on polymerizable $\text{R}_8\text{Si}_8\text{O}_{12}$ cubes targeted low viscosity, light curable, single-phase nanocomposite precursors as novel dental restoratives.³ To be compatible with current restoratives, initial efforts were made to synthesize methacrylate cubes by reacting $\text{H}_8\text{Si}_8\text{O}_{12}$ (T_8^{H}) or $\text{Q}_8\text{M}_8^{\text{H}}$ with propargyl methacrylate and 2-allyloxyethyl methacrylate, reactions 1 and 2.^{3a,c} Unfortunately, propargyl methacrylate derived macromonomers contain internal double bonds that react further with unreacted Si-H groups leading to untimely polymerization. The



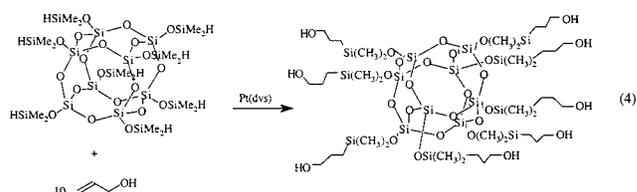
2-allyloxyethyl-methacrylate cube requires hydrosilylation temperatures of 80–90 °C, leading to premature polymerization.¹²

To avoid the problems associated with the above syntheses, we sought a simple method of introducing OH functionality via hydrosilylation. Such a route, if identified, would provide a general approach to polyester nanocomposites including the desired methacrylates. Much to our surprise, we discovered that direct hydrosilylation of allyl alcohol with $\text{Q}_8\text{M}_8^{\text{H}}$ can lead to exclusive C-silylation to give octakis(3-hydroxypropyl-dimethylsiloxy)octasilsesquioxane (OHPS). This contrasts with many literature reports wherein O-silylation competes so successfully with C-silylation that protective groups must be used to avoid O-silylation.^{13,14}



Thus, if $\text{Q}_8\text{M}_8^{\text{H}}$ is reacted with neat allyl alcohol, using conditions discussed below, then the product recovered is the octahydroxypropyl product of reaction 4. However, if low concentrations of catalyst or allyl alcohol are used then considerable O-silylation results.

To further understand the reaction process and briefly probe the catalytic cycle, simple kinetic studies were conducted. The effects of changes in reaction conditions, including types of solvents, catalyst precursors, and precursor concentrations on C- vs O-silylation were identified. The goal was first to optimize the process and then explore the scope of the reaction using different Si-H compounds and unsaturated alcohols.



III.A. Kinetic Studies of Direct Hydrosilylation of Allyl Alcohol.

The reaction kinetics were followed using ^1H NMR and GPC, to determine the percent C- vs O-silylation, and the molecular weight distributions of the products, respectively. If the reaction gives selective C- or O-silylation, the respective OHPS or octakis(allyloxy-dimethylsiloxy)octasilsesquioxane formed would be monodisperse with $\text{MW} \approx 1500$. However, if both C- and O-silylation occur with similar reaction rates, polymeric species should form as demonstrated when 4 equivalents of allyl alcohol are used, resulting in a cross-linked, transparent gel. In this case, both C- and O-silylation occur as allyl alcohol serves as a bifunctional cross-linker (Figure 1).

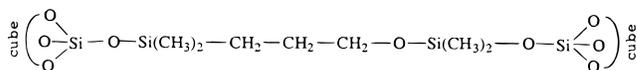


Figure 1. Cross-link produced by simultaneous C- and O-silylation of allyl alcohol.

Note that GPC can only be used to estimate the molecular weights and distributions of cubes, or their polymers, because the linear polystyrene standards have limited relevance to cubes

(12) Sellinger, A. Ph.D. Dissertation, University of Michigan, 1997.

(13) (a) Greber, V. G.; Jager, S. *Makromol. Chem.* **1962**, *55*, 96. (b) Ghose, B. N. *J. Organomet. Chem.* **1979**, *164*, 11. (c) Braun, F.; Willner, L.; Hess, M.; Kosfeld, R. *J. Organomet. Chem.* **1987**, *332*, 63. (d) Braun, F.; Willner, L.; Hess, M.; Kosfeld, R. *J. Organomet. Chem.* **1989**, *366*, 53.

(14) *Comprehensive Handbook on Hydrosilylation*; Marciniak, B., Ed.; Pergamon Press: Elmsford, NY, 1992; Chapter 3.

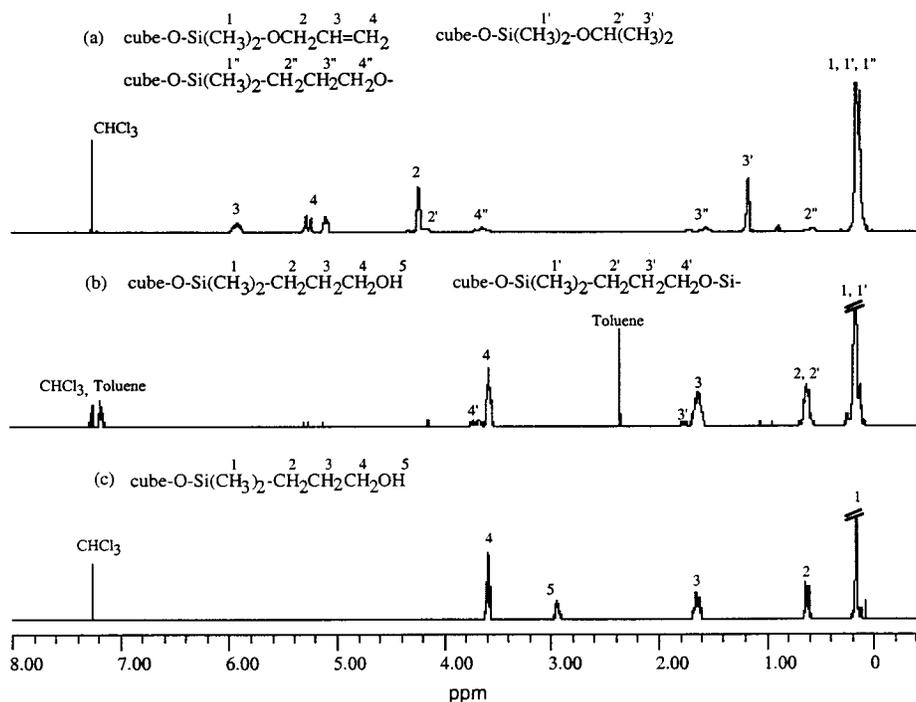


Figure 2. ^1H NMR spectra of products obtained from hydrosilylation of allyl alcohol with $Q_8M_8^H$ using (a) H_2PtCl_6 , (b) $\text{Pt}(\text{dcp})$ (a broad hump for OH at ~ 3.2 ppm does not show up in this reduced spectrum), and (c) $\text{Pt}(\text{dvs})$ as catalyst at 100 mM.

or 3-D structures.¹⁵ However, these standards provide a convenient way to estimate molecular weight, especially when comparing two similar systems.

The detailed results obtained with different catalyst precursors, solvents, Pt concentrations, and different Si-H compounds and unsaturated alcohols are presented below.

Catalyst Selectivity. The utility of three types of Pt catalyst precursors, hexachloroplatinic acid (H_2PtCl_6), platinum dicyclopentadienyl dichloride [$\text{Pt}(\text{dcp})$], and platinum divinyltetramethyldisiloxane [$\text{Pt}(\text{dvs})$] were assessed for reaction 4. The amount of added catalyst was kept at $[\text{Pt}] = 100$ mM to be consistent with studies described below. Note that for simplicity, the catalyst concentration is treated as the amount of catalyst precursor added (see experimental).

Under a set of standard reaction conditions, for reaction 4, ^1H NMR analysis indicates that $\text{Pt}(\text{dvs})$ provides the cleanest C-silylation, while $\text{Pt}(\text{dcp})$ gave $\sim 14\%$ O-silylation in addition to $\sim 86\%$ C-silylation. In contrast, H_2PtCl_6 gave $\sim 14\%$ C-silylation and $\sim 86\%$ O-silylation, with both allyl alcohol and the 2-propanol used as the catalyst solvent. Figures 2 and 3 show ^1H NMR spectra and GPC traces of the products obtained using different catalyst precursors. $\text{Pt}(\text{dvs})$ appears to be the most effective C-silylation catalyst precursor for this reaction, and was used for the remaining studies. We have not exhaustively assessed all possible catalyst precursors.

III.A.1. Solvent Effects. The influence of solvent on regioselectivity was tested, under standard conditions, using $\text{Pt}(\text{dvs})$, $[\text{Pt}] = 100$ mM. Heptane, CH_2Cl_2 , and THF were compared with toluene. Reaction 4 proceeds much the same in both heptane and toluene providing selective C-silylation. In CH_2Cl_2 and THF, 19% and 13% O-silylation were observed, respectively. Toluene was chosen for the remaining studies because it provides the cleanest C-silylation.

III.A.2. Catalyst Concentration Studies. The effects of $[\text{Pt}(\text{dvs})]$ on regioselectivity in reaction 4 were probed. Reactions

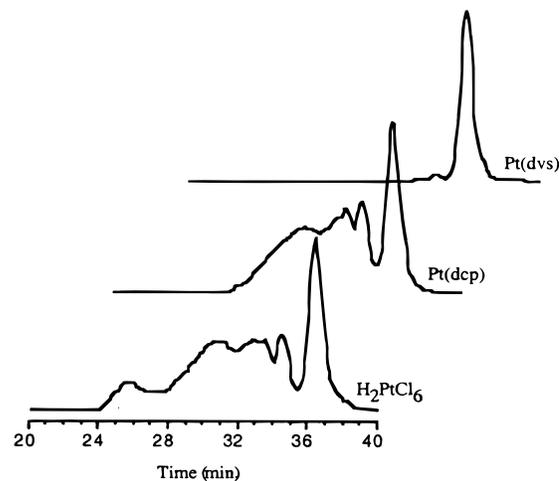


Figure 3. GPC of products obtained from hydrosilylation of allyl alcohol with $Q_8M_8^H$ using different Pt catalyst precursors at 100 mM.

were followed by NMR and GPC, as above. When $[\text{Pt}(\text{dvs})] = 10$ mM and 20 mM, the reaction required heating at reflux (110°C) for ≥ 12 h to go to completion giving either a viscous liquid or a waxy solid product. Both GPC traces show two major components, a sharp peak at ~ 1600 , and a higher-molecular weight peak with a broad distribution, indicating a mixture of different molecular weight species. For $[\text{Pt}(\text{dvs})] = 100$ mM, the reaction goes to completion in ≤ 30 min at room temperature to give a white, solid product. The GPC trace shows only a minor high molecular weight component, in addition to the sharp peak at ~ 1600 (Figure 4).

Products from the above reactions were also analyzed using NMR. At lower $[\text{Pt}(\text{dvs})]$, for example, 10 and 20 mM, about 7 and 3% O-silylation were observed, respectively. However, no $\text{CH}_2=\text{CH}-\text{CH}_2-\text{O}-\text{Si}-$ species were detectable, only $-\text{Si}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-\text{Si}-$ linkages as shown in Figure 1. This suggests that $\text{CH}_2=\text{CH}-\text{CH}_2-\text{O}-\text{Si}-$ is more susceptible to C-silylation than free allyl alcohol. At higher $\text{Pt}(\text{dvs})$

(15) Sperling, L. H. In *Introduction to Physical Polymer Science*; John Wiley & Sons: 1986; Chapter 3.

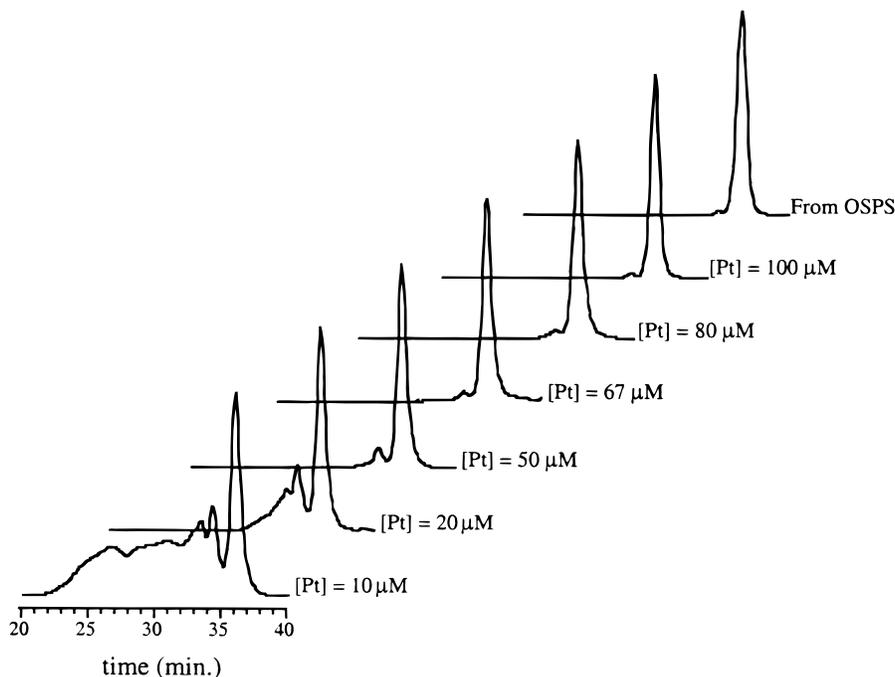
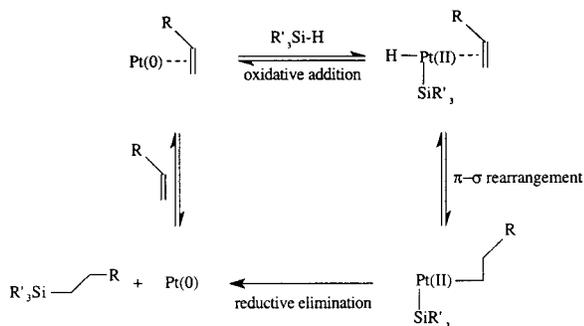


Figure 4. GPC traces of OHPS obtained from OSPS and products obtained from direct hydrosilylation of allyl alcohol using different concentrations of Pt(dvs).

Scheme 1. Chalk–Harrod Mechanism of C-Silylation



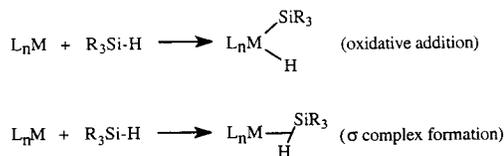
concentrations, for example, $[\text{Pt}(\text{dvs})] \geq 50 \text{ mM}$, no O-silylation is detected by NMR and the product is essentially identical to the OHPS obtained via protection–deprotection (reactions 8 and 9).

III.A.3. Comments on the Catalysis Mechanism. The above results allow us to make several observations concerning the type of catalysis mechanism that is operative for both C-silylation and O-silylation.

C-silylation has been studied extensively since the 1950s.¹⁴ The widely accepted Chalk–Harrod mechanism for alkene hydrosilylation is illustrated in Scheme 1.¹⁶ Kinetic studies on homogeneous H_2PtCl_6 catalyzed C-silylation indicate that the process is first order in [molecular Pt catalyst], and zero order in both [silane] and [alkene].¹⁷

Si–H alcoholysis resulting in O-silylation has also been studied.¹⁸ Most of the mechanistic studies suggest transition metal activation of Si–H bonds, either through oxidative addition or formation of a σ complex, which favors attack of the alcohol on Si (Scheme 2).¹⁹ Kinetic studies on $[\text{IrH}_2\text{S}_2-$

Scheme 2. Silane Activation in O-Silylation



$(\text{PPh}_3)_2\text{SbF}_6$ (S=solvent) catalyzed O-silylation also indicate that the reaction is first order in catalyst concentration, and zero order in silane and alkene.²⁰

On the basis of these observations, when the concentrations of the allyl alcohol and the cube {i.e., $[\text{Si}-\text{H}]$ } are kept constant, as above, the ratio of C- to O-silylated product should be a constant, independent of changes in [catalyst]. This contradicts the above observations, where almost no O-silylation was obtained at $[\text{Pt}(\text{dvs})] \geq 50 \text{ mM}$, and ~3 and 7% O-silylation occurred when $[\text{Pt}] = 20 \text{ mM}$ and 10 mM , respectively. Furthermore, much more forcing conditions were required at the lower catalyst concentrations. These results suggest a change in the nature of the active catalyst species.

Pt(dvs), or Karstedt's catalyst, is obtained by treating $\text{H}_2\text{-PtCl}_6$ with divinyltetramethyldisiloxane to form a Pt(0) species as suggested by the X-ray structure of $[\text{Pt}\{(\text{I}-\text{CH}_2=\text{CHMe}_2\text{-Si})_2\text{O}\}(\text{P}-t\text{-Bu}_3)]$, obtained by adding P-*t*-Bu₃ to a Pt(dvs) solution.^{21,22} The principle component of Karstedt's catalyst is suggested to be $\text{Pt}(\text{dvs})_2$ in the same report.²² However, dinuclear $\text{Pt}_2(\text{H}_2\text{C}=\text{CHSiMe}_2\text{OSiMe}_2\text{CH}=\text{CH}_2)_3$, that is, $\text{Pt}_2(\text{dvs})_3$ was isolated by removing excess divinyltetramethyldisiloxane (dvs) from a Pt(dvs) solution and characterized by X-ray crystal studies.²³ In solution however, $\text{Pt}_2(\text{dvs})_3$ is in equilibrium with $\text{Pt}(\text{dvs})_2$ (Figure 5), and the concentration of $\text{Pt}(\text{dvs})_2$ increases with increasing concentrations of dvs.²⁴

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(21) (a) Willing, D. N. U.S. Patent 3,419,593, 1968. (b) Karstedt, B. D. U.S. Patent 3775452, 1973.

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(16) (a) Harrod, J. F.; Chalk, A. J. *J. Am. Chem. Soc.* **1964**, *86*, 1776. (b) Harrod, J. F.; Chalk, A. J. *ibid.* **1965**, *87*, 16. (c) Harrod, J. F.; Chalk, A. J. *ibid.* **1966**, *88*, 3491.

(17) (a) Reikhsfel'd, V. O.; Astrakhanov, M. I. *Zh. Obshch. Khim.* **1970**, *40*(3), 699. (b) Reikhsfel'd, V.; Koroleva, G. N. *ibid.* **1966**, *36*(8), 1474.

(18) For a review see: Lukevics, E.; Dzintara, M. *J. Organomet. Chem.* **1985**, *295*, 265.

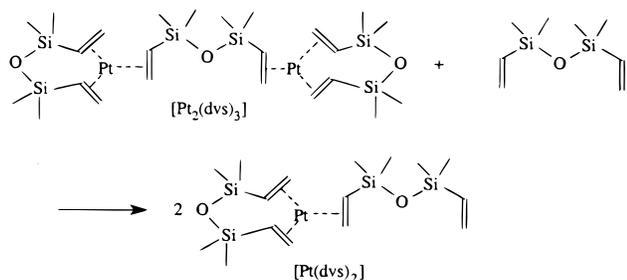


Figure 5. Equilibrium between $Pt_2(dvs)_3$ and $Pt(dvs)_2$.

The above-described studies document equilibria between complexes of different nuclearity in the $Pt(dvs)$ precursor solution. In an attempt to identify the nature of the active species in $Pt(dvs)$ catalysis systems, Lewis et al. proposed the intermediacy of colloidal platinum.²⁵ However, recent studies suggest that simple hydrosilylation involves a catalytic cycle wherein the active species is monometallic.²⁶ Hence our results appear to be quite unusual.

Our brief examination of the effects of variations in reaction conditions on products and reaction rates reveal some unusual effects that deserve further discussion vis à vis the possibility of cluster catalysis. Rosenberg and Laine²⁷ recently delineated five criteria for polynuclear metal complex catalysis including: (1) increase in turnover frequency (TF) with increases in catalyst concentration; (2) product selectivities that are different from known mononuclear catalyzed reactions; (3) enhanced catalyst reactivity with the addition of a second metal; (4) enhanced reactivity upon modification of conditions to favor metal–metal bond formation; and (5) catalytic asymmetric induction.

In the above concentration studies, when $[Pt] = 100$ and 10 mM, the reaction times were 0.5 h (RT) and ≥ 12 h (refluxing toluene), respectively. Based on these results, the turnover frequency $\{TF, [product] \cdot [catalyst]^{-1} \cdot time^{-1}\}$ at $[Pt] 100$ mM is ≥ 2.4 times that of the TF at $[Pt] 10$ mM not counting the ~ 90 °C difference in reaction temperatures. This increase in TF with increasing Pt concentration, along with the unusual regioselectivity (C- over O-silylation) which differs from known mononuclear Pt complex catalysis^{13,14} (eq 3), implies that the direct hydrosilylation of allyl alcohol in this study involves di- or polynuclear Pt complexes.

Given that higher $Pt(dvs)$ concentrations favor C-silylation under conditions that favor formation of di- or polynuclear species, it appears that di- or polynuclear Pt complexes favor C-silylation, while a mononuclear Pt catalyst leads to O-silylation. The solvent effects, while preliminary, are also in accord with di- or polynuclear Pt complex catalyzed C-silylation of allyl alcohol.

As noted above, the Lewis et al. paper suggests that C-silylation using Karstedt's catalyst proceeds via mononuclear species.²⁶ While they do observe formation of polynuclear species, they suggest that these polynuclear species represent a "resting state," not involved in the catalytic cycle. However, the considerable structural differences between our reactants and those used by Lewis et al. perhaps give rise to a special case

where cluster catalysis becomes dominant. Although on careful reading of the Lewis et al. paper, it appears that the presence of polynuclear species as intermediates and/or transition states in the catalytic cycle cannot be ruled out.

The solvent effect studies suggest that nonpolar solvents, that is, heptane or toluene, favor C-silylation, whereas polar solvents, that is, THF and CH_2Cl_2 , gave 10–20% O-silylation. Electron-donating solvents,^{20,28} for example, THF, may displace the bridging olefins of di- or polynuclear Pt complexes to produce mononuclear complexes, thus promoting O-silylation, whereas nonpolar solvents would favor C-silylation by preserving the di- or polynuclear species. The influence of CH_2Cl_2 may be understood similarly, considering the possibility that it acts as a ligand as found for MeI.²⁹

Still another important aspect of this work is the fact that C-silylation can be effected almost exclusively. Although most O-silylation catalysts catalyze C-silylation, catalysts regioselective for O-silylation in the presence of $C=C$ and $C=O$ moieties are known.^{20,30} However, efforts to develop catalysts that exhibit selective C-silylation can be expected to be frustrated, because of the strong preference for Si–O bond (bond strength ~ 120 kcal/mol) over Si–C bond formation (bond strength ~ 90 kcal/mol).³¹ For example, ion-exchange resin immobilized H_2PtCl_6 catalyzed reaction of allyl alcohol with triorganosilanes, gave a 3:2 ratio of C-:O-silylated products, the highest ever reported.^{31b} Another report describes selective C-silylation of propargyl alcohol using platinum catalysts with bulky norbornene and tri(*tert*-butyl)phosphine ligands.³² However, aside from the present study, there are no literature reports on selective C-silylation of carbon–carbon double bonds in the presence of OH groups. Note that hydrogermylation of propynol derivatives leads to a high degree of C-germylation via a π -complex transition state. This process may be selective C-germylation but insufficient details are available to verify this fact.³³

The best explanation for the above behavior is that a cluster catalyst intermediate forms wherein OH groups are shielded from reaction with silyl groups at the metal center but alkenes are not. The exact form this intermediate takes is beyond reasonable speculation based on the evidence currently available. However, the reason for its formation might be because the silsesquioxane, $Q_8M_8^H$, is polyfunctional and may induce formation of polynuclear catalytic intermediates at its "surface." A similar explanation might account for the very highly selective and extensive hydrosilylative cross-linking achieved when $Q_8M_8^H$ is reacted with $Q_8M_8^{vinyl}$.^{3(d)} If true, this change in catalytic mechanism might be classified as arising because of the presence of a nanostructured material. The unique role that $Q_8M_8^H$ appears to play may also account for the discrepancy between Lewis' recent studies²⁶ and our results.

A reviewer has suggested that the above results might be explained in terms of h^3 coordination of the allyl alcohol to

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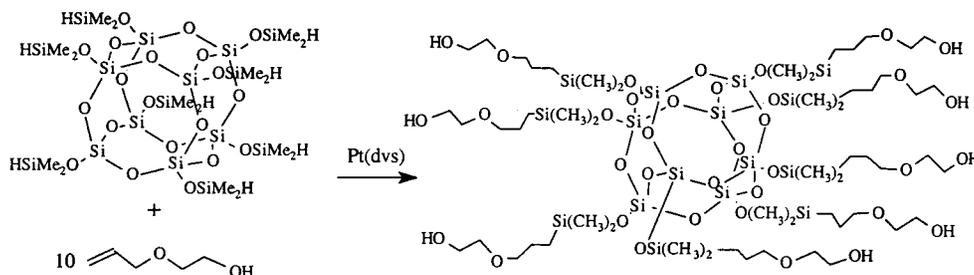


Figure 6. Hydrosilylation of $Q_8M_8^H$ with 2-allyloxyethanol.

metal combined with both steric effects and selectivity during reductive elimination, rather than invoking a bimetallic/cluster catalyst explanation. While we consider these possibilities above, the change in selectivity favoring C-silylation on going to higher catalyst concentrations does argue for the intermediacy of polynuclear species as we have discussed elsewhere.²⁷ The above results are not definitive only suggestive. Clearly, more detailed studies must be done to confirm these statements.

III.B. Direct Hydrosilylation of Other Unsaturated Alcohols and Using other Si-H Compounds. **III.B.1. Direct Hydrosilylation of Allyl Alcohol with other Si-H Compounds.** Once the hydrosilylation of allyl alcohol was optimized, we sought to extend this methodology to other Si-H compounds including D_4^H , TMDS, and PDMS-H. The reaction of D_4^H resulted in a gel, suggesting significant simultaneous O- and C-silylation. Reactions of TMDS and PDMS-H with allyl alcohol gave C- and O-silylation products as the molecular weights were higher than expected and/or exhibited a broad distribution. It appears that $Q_8M_8^H$ is a very unique substrate for this type of direct hydrosilylation—as suggested above. Again, the influence of Si-H substrates on this reaction needs further study.

III.B.2. Direct Hydrosilylation of Other Alcohols. The reactions of $Q_8M_8^H$ with propargyl alcohol and 2-allyloxyethanol were also examined. Reaction with propargyl alcohol resulted in a product with a broad molecular weight distribution, suggesting cross-linking through both C- and O-silylation. However, when 2-allyloxyethanol was used, the reaction gave exclusive C-silylation, resulting in OH functionalized cube, with a longer tether between the OH and the cube than in OHPS (Figure 6). The success of this reaction makes it possible to attach methacrylates with different spacer lengths to cubes, hence tailor the microstructure of the resultant nanocomposites after polymerization.

III.C. Characterization of OHPS. OHPS characterization data including FTIR, 1H and ^{13}C NMR, and elemental analysis (EA) are all those expected. ^{29}Si NMR in CH_2Cl_2 gives $Si(OSi)_4$ at -108.4 ppm, and $Si(OSi)_3$ at ~ 13.6 ppm, in accord with that expected based on the work of Sellinger et al.^{3(a),3(c)} However, ^{29}Si NMR data in methanol showed an unusual, small peak around -100.4 ppm, besides the corresponding peaks for $Si(OSi)_4$ and $Si(OSi)_3$ (Figure 7). This small peak was absent from both OSPS and OMPS, whichever solvent was used. Furthermore, when the desilylation of OSPS to OHPS was followed by ^{29}Si NMR in methanol, the small peak at -100.4 ppm showed up gradually along with the desilylation product. The appearance of this peak is directly related to the $CH_2CH_2-CH_2OH$ structure and also depends on the nature of the solvent.

Hasegawa and co-workers report that the $(SiO)_3SiOH$ structure formed from incomplete silylation of octaanion species $Si_8O_{20}^{8-}$ appears characteristically at -99.5 to -100.5 ppm,^{6,34} bracketing the -100.4 ppm peak seen above. This coincidence

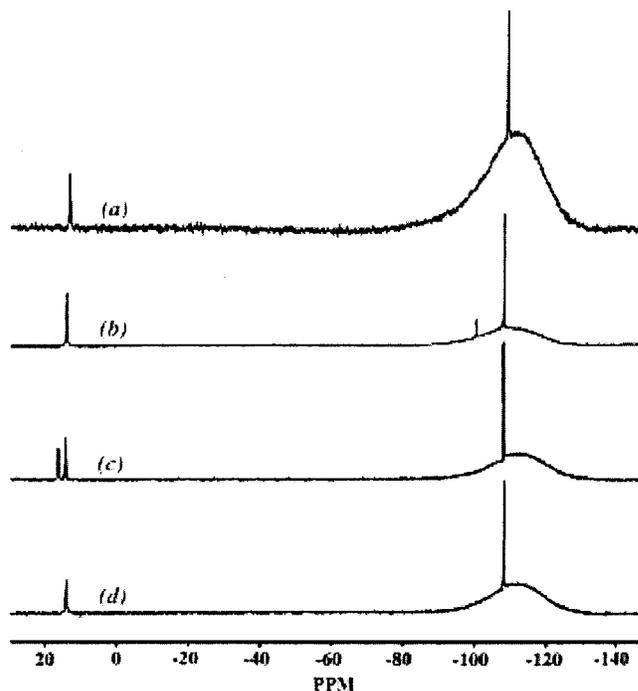
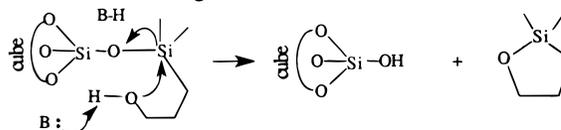


Figure 7. ^{29}Si NMR of OHPS in CH_2Cl_2 (a), OHPS in methanol (b), OSPS in methanol (c), and OMPS in methanol (d).

Scheme 3. Backbiting in OHPS



led us to tentatively attribute the peak at -100.4 ppm to $(SiO)_3SiOH$ species. This in turn suggested a back-biting process per Scheme 3.

To prove the above process occurs, we sought to detect the formation of 2,2-dimethyl-1-oxa-2-silacyclopentane in our system. The literature indicates that this cyclic compound forms via dehydration of 1,3-bis(hydroxypropyl)tetramethyldisiloxane on heating, presumably by backbiting of OH on Si (Scheme 4).³⁵ Pure 2,2-dimethyl-1-oxa-2-silacyclopentane easily polymerizes to $HO[(CH_3)_2Si(CH_2)_3O]_nH$ (Scheme 4).³⁶

The following set of experiments was designed to detect the formation of 2,2-dimethyl-1-oxa-2-silacyclopentane from OHPS. 1H NMR spectra of OHPS/ CD_3OD and OHPS/ $CDCl_3$ solutions were compared. Interestingly, while the $Si(CH_3)_2$ peak on the cube is a singlet in $CDCl_3$, it splits into two peaks in CD_3OD , a broad one at 0.12 ppm and a sharp one at 0.05 (Figure 8). The broad peak disappears after 2 days, coincident with increase of the sharp one.

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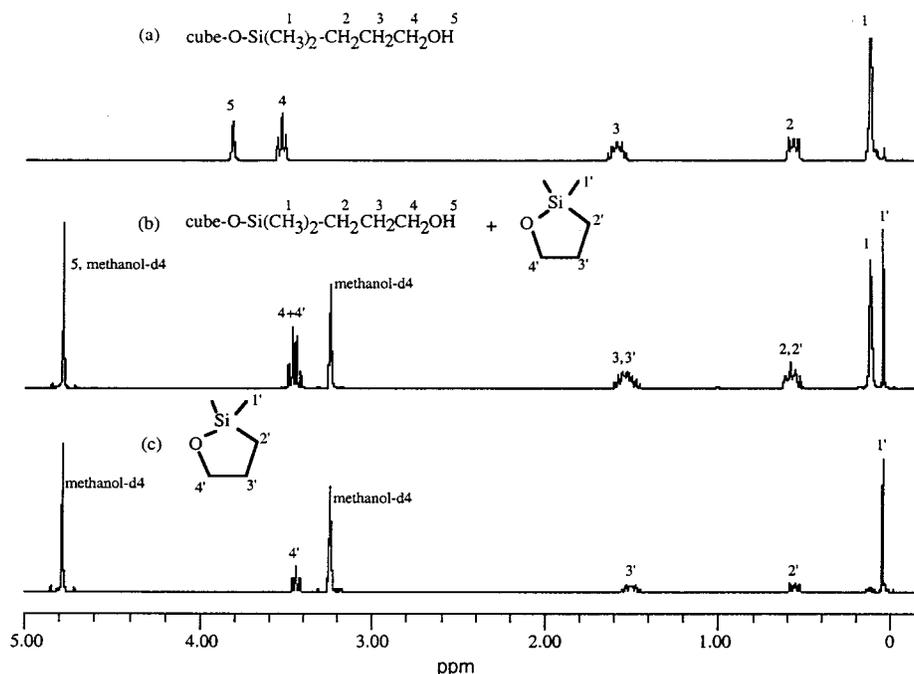
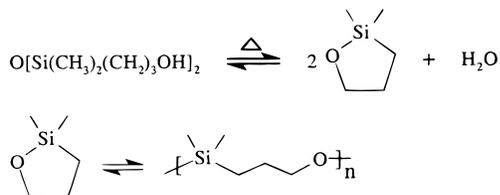
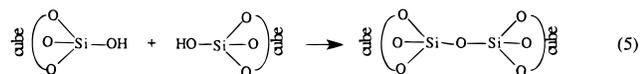


Figure 8. ^1H NMR of OHPS in CDCl_3 (a) and CD_3OD for 10 min (b) and 2 days (c).

Scheme 4. Formation and Polymerization of 2,2-Dimethyl-1-oxa-2-silacyclopentane³⁵



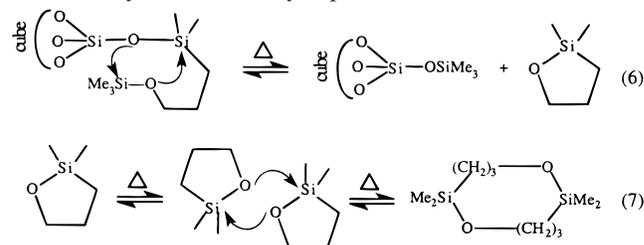
When CD_3OD was removed from the sample, the residue left was partially soluble. The soluble component was analyzed using gas chromatography-mass spectral (GC-MS) analysis. GC-MS showed one major peak beside the solvent peak, with a mass spectrum that corresponds to that reported for 2,2-dimethyl-1-oxa-2-silacyclopentane (m/z parent ion P 116 (13%), P-1 (1.7%), P-15 (100%), P-17 (16.9%), P-28 (22.4%).³⁶ Thus, the soluble part of the residue from the NMR sample was 2,2-dimethyl-1-oxa-2-silacyclopentane. The insoluble component most likely consists of polymers formed by condensation of the second product of backbiting, $\text{Si}_8\text{O}_{12}(\text{OH})_8$ (T_3OH), as shown in eq 5.



Returning to the ^1H NMR of OHPS in CD_3OD (Figure 8), it appears that the broad $\text{Si}(\text{CH}_3)_2$ peak likely results when some of the $\text{OSi}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ side chains cyclize to coincidentally generate $\text{Si}_8\text{O}_{12}(\text{OH})_x[\text{OSi}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}]_{8-x}$, while the sharp $\text{Si}(\text{CH}_3)_2$ peak is from 2,2-dimethyl-1-oxa-2-silacyclopentane. Spectrum (c) in Figure 8 correlates well with that reported for 2,2-dimethyl-1-oxa-2-silacyclopentane.^{35,36}

To sum up, the formation of 2,2-dimethyl-1-oxa-2-silacyclopentane in OHPS in methanol was firmly established. Thus the backbiting mechanism proposed in Scheme 3 most likely occurs. Likewise, the small peak at ~ 100.4 ppm in the ^{29}Si NMR (Figure 7) is most likely due to the presence of $\text{Si}(\text{OSi})_3\text{OH}$ components on cubes $\text{Si}_8\text{O}_{12}(\text{OH})_x[\text{OSi}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}]_{8-x}$, formed as a result of backbiting.

Scheme 5. Transsilylation for OSPS and 2,2-Dimethyl-1-oxa-2-silacyclopentane³⁷



While the OHPS is very stable as a dry powder, it turns into viscous oil in methanol solution after a few days, and GPC analysis indicates a significant amount of high molecular weight species. This phenomenon can also be explained by the backbiting process discussed above. As a dry powder, the OH groups on OHPS are likely immobilized by H-bonding between OHs, and thus are unable to backbite. On dissolution in methanol, H-bonding with methanol competes with that between the propanol groups and provides the propanol groups with the mobility essential for backbiting to occur.

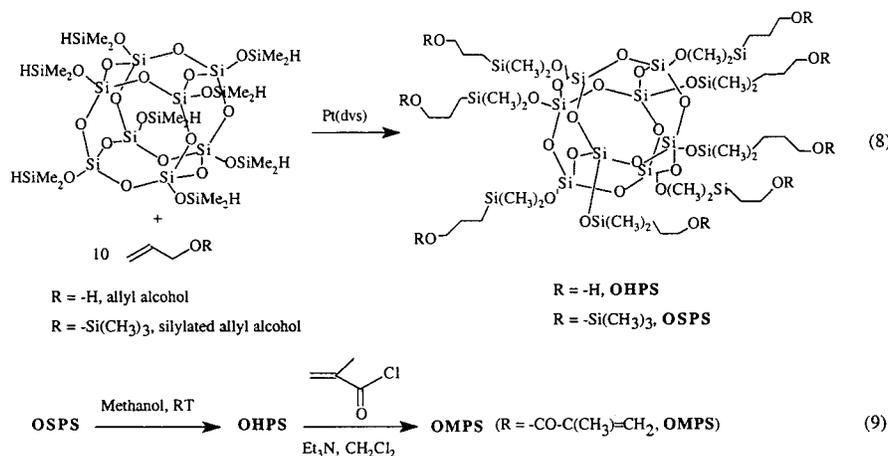
The same observation was made in ethanol. However, in aprotic solvents, such as THF, CH_3CN , or acetone, no backbiting was observed by ^1H NMR at room temperature.

OHPS melts at ~ 84 °C and decomposes (by TGA) at ~ 225 °C. The TGA ceramic yield (to SiO_2 , not shown) in air (51.0%) is much lower than expected (64.8%), probably due to a loss of some of the 2,2-dimethyl-1-oxa-2-silacyclopentane (bp 97–100 °C),³⁶ which occurs when the OH groups obtain sufficient mobility in the melt. If all the side chains were lost via backbiting, the expected ceramic yield of SiO_2 would be 43.2%.

III.D. Hydrosilylation of Protected Allyl Alcohol. When allyloxytrimethylsilane was used instead of allyl alcohol, the reaction goes exclusively via C-silylation as expected. The isolated and purified OSPS is a white solid. Deprotection by stirring in methanol gives OHPS as a white powder after workup.³⁷ Its NMR, TGA, and elemental analyses are virtually the same as those for OHPS obtained via direct hydrosilylation.

Considering the backbiting of OH groups on OHPS as shown above, methanol is not a good solvent for the desilylation of

Scheme 6



OSPS. However, backbiting is not a problem in this study, as the OHPS obtained from OSPS is virtually the same as that from the direct hydrosilylation. Furthermore, we find that almost all the OHPS in ^1H NMR sample (~ 5 mg/mL) tube converts to 2,2-dimethyl-1-oxa-2-silacyclopentane and $\text{Si}_8\text{O}_{12}(\text{OH})_8$ (Figure 8), while only a small portion in a ^{29}Si NMR sample (~ 300 mg/mL) undergoes backbiting as revealed by the small peak at -100.4 ppm (Figure 7). On the basis of these observations, the proposed backbiting in Scheme 3 is likely an equilibrium reaction. Indeed, 2,2-dimethyl-1-oxa-2-silacyclopentane is known to ring-open polymerize,^{35,36} which supports this possibility. As a result, at low concentration of OHPS (e.g., ^1H NMR sample), the equilibrium shifts toward the right, while at higher concentration (e.g., ^{29}Si NMR sample), the resultant silanolcube and 2,2-dimethyl-1-oxa-2-silacyclopentane push the reaction more toward the left, and backbiting is not very evident.

The OSPS TGA ceramic yield in air (SiO_2 , not shown), 46.2%, is lower than the expected value, 69.9%, calculated based on the assumption that all the Si is oxidized to SiO_2 . This discrepancy can be explained by the loss of Si through a transsilylation per eq 6 (Scheme 5), similar to that responsible for the transsilylation of 2,2-dimethyl-1-oxa-2-silacyclopentane (eq 7).³⁸ According to eq 6, one-third of the Si might be lost as 2,2-dimethyl-1-oxa-2-silacyclopentane, instead of being oxidized to SiO_2 . As a result, the expected ceramic yield to SiO_2 would be 46.6%. The found ceramic yield of 46.2% (by TGA) is close to the expected value, and seems to confirm the transsilylation process shown in eq 6.

III.E. OMPS Prepared from OHPS. OHPS prepared either via direct silylation or via the silylated allyl alcohol route was used to prepare OMPS (eqs 8 and 9). The final product, OMPS, was isolated as a slightly viscous liquid at room temperature (viscosity ≈ 100 centipoise).³⁹ Unlike the OHPS, OMPS is stable in solution and its GPC determined molecular weight distribution (PDI = 1.06) is close to that of OHPS (PDI = 1.04). This suggests that no significant oligomerization of methacrylates, or decomposition of the cube occurs during the preparation of OMPS.

DSC of the OMPS shows a broad exotherm with an onset at ~ 176 °C on the first heating cycle, which disappears in subsequent heating and cooling traces. This exotherm is certainly associated with the polymerization of the methacrylate groups.

Preliminary polymerization studies were conducted using (1*R*)-(–)-camphorquinone (0.1 wt %) as a photoinitiator, and (*N,N*-dimethylamino)ethyl methacrylate (0.13 wt %) as an accelerator. The liquid OMPS cured readily under blue light ($\lambda = 460$ nm) within one minute to give hard, transparent and insoluble composites. We will report the mechanical properties of nanocomposites prepared from OMPS and copolymers with other methacrylates soon (Scheme 6).⁴⁰

IV. Conclusions

(1) We report here the first example of regioselective hydrosilylation of allyl alcohol at the C=C. Hydrosilylation of allyl alcohol with $\text{Q}_8\text{M}_8^{\text{H}}$ was discovered to provide C-silylation at C=C, which provides one-step access to OHPS, and hence an efficient route to OMPS. The success of the reaction with 2-allyloxyethanol suggests a broad spectrum of OH functionalized cubes can be synthesized using this facile methodology, and thus provides access to a wide variety of macromonomers incorporating ester functionality on the periphery of octasilsesquioxane cores, such as the octamethacrylatesilsesquioxane. In another words, OHPS provides a basis for the development of polyester nanocomposite precursors.

(2) Even though the catalytic Pt species are not identified in this study, a change of nuclearity of the Pt complex is suggested. Further kinetic and mechanistic studies are needed to exploit this type of selective C- over O-silylation.

(3) Back-biting of OH on Si in OHPS and the simultaneous formation of 2,2-dimethyl-1-oxa-2-silacyclopentane were identified, which correctly explains the ^{29}Si NMR data, TGA ceramic yield of OHPS, and its instability in protic solutions.

(4) Octakis(3-methacryloxypropyldimethylsilyloxy)octasilsesquioxane (OMPS) is easily prepared directly from OHPS. Previous unwanted polymerization that accompanies hydrosilylation of allyl or propargyl methacrylates was eliminated. Preliminary polymerization studies show that OMPS readily polymerizes under UV light ($\lambda = 460$ nm) to give a cross-linked nanocomposite.

Acknowledgment. We thank NIDR for the generous support through Grant No. DE09839-03. We thank Professor John R. Wiseman and Professor M. David Curtis for helpful discussions, and Dr. Valerie A. Lee and Dr. Steven Rasmussen for help with the UV-curing study. We would like to thank the reviewers for their comments, suggestions, and proofreading.

JA000318R

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