SAND99-0995J

Dialkylenecarbonate-Bridged Polysilsesquioxanes. Hybrid Organic Sol-Gels with a Thermally Labile Bridging Group.

Douglas A. Loy*, James V. Beach, Brigitta M. Baugher, and Roger A. Assink

Catalysis and Chemical Technologies Department, Sandia National Laboratories, Albuquerque, NM 87185-1407

Kenneth J. Shea* and Joseph Tran

Department of Chemistry, University of California, Irvine, CA 92717-2025

James H. Small,

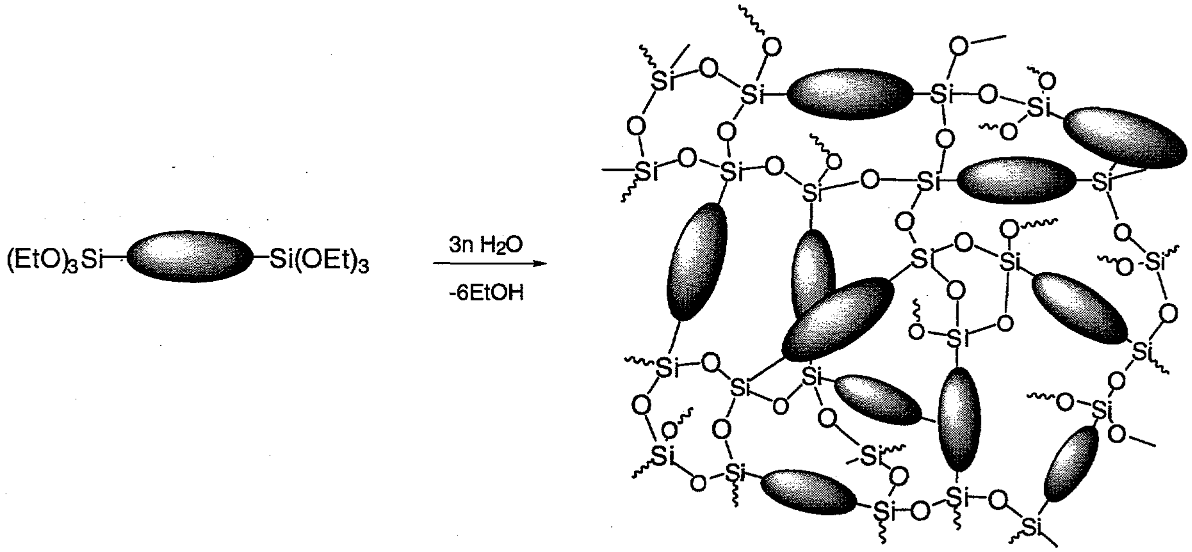
Polymers and Coatings Group, MST-7, Los Alamos National Laboratory, Los Alamos, NM 87545

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

Abstract. In this paper, we introduce a new approach for altering the properties of bridged polysilsesquioxane xerogels using *post-processing modification* of the polymeric network. The bridging organic group contains latent functionalities that can be liberated thermally, photochemically, or by chemical means after the gel has been processed to a xerogel. These modifications can produce changes in density, solubility, porosity, and or chemical properties of the material. Since every monomer possesses two latent functional groups, the technique allows for the introduction of high levels of functionality in hybrid organic-inorganic materials. Dialkylenecarbonate-bridged polysilsesquioxane gels were prepared by the sol-gel polymerization of bis(triethoxysilylpropyl)carbonate (**1**) and bis(triethoxysilylisobutyl)-carbonate (**2**). Thermal treatment of the resulting non-porous xerogels and aerogels at 300-350 °C resulted in quantitative decarboxylation of the dialkylenecarbonate bridging groups to give new hydroxyalkyl and olefinic substituted polysilsesquioxane monolithic xerogels and aerogels that can not be directly prepared through direct sol-gel polymerization of organotrialkoxysilanes.

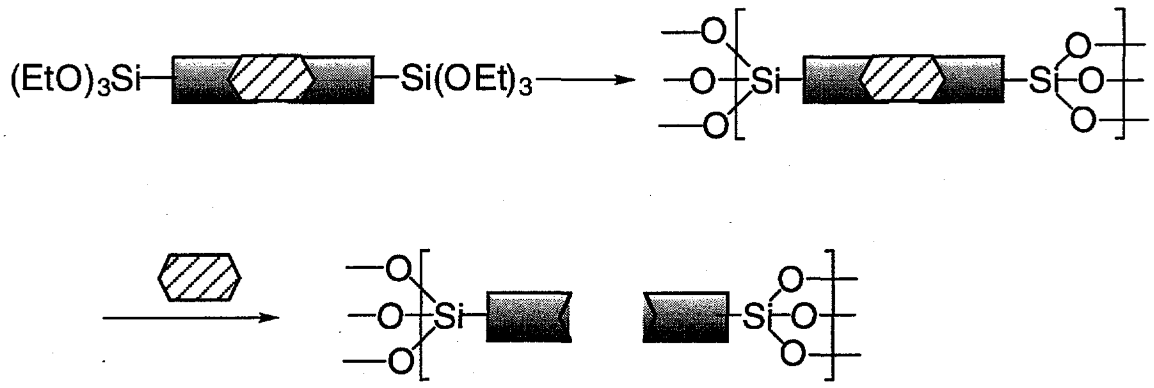
Introduction

Bridged polysilsesquioxanes are a family of hybrid organic-inorganic materials prepared by sol-gel polymerization of molecular building blocks that contain a variable organic bridging group and at least two trialkoxysilyl groups (Scheme 1).[1-9] The high level of functionality of these monomers results in their rapid gelation, even in dilute solution. Upon drying, the gels become highly condensed, solid materials (xerogels and aerogels). In contrast to silica gels[10] or silsesquioxanes with pendant organic groups, $(RSiO_{1.5})_n$,[11] the bridging organic group remains as an integral part of the network structure. Bridged polysilsesquioxane xerogels have a range of physical and mechanical properties that are strongly influenced by the organic bridging group. A considerable effort has been made to establish links between the bridging organic group and selected aspects of xerogel morphology.[1] These studies have focused on surface area and pore size distribution, two important properties of bridged polysilsesquioxanes and sol-gels in general. The studies have produced insight as to how small perturbations in the organic fragment of the molecular building block affect the polymerization chemistry and final xerogel structure.



Scheme 1. Using the organic substitutent as a bridging group between the trialkoxysilyl groups in the monomer translates into a network in which the bridging group is an integral part of the resulting polymeric scaffolding.

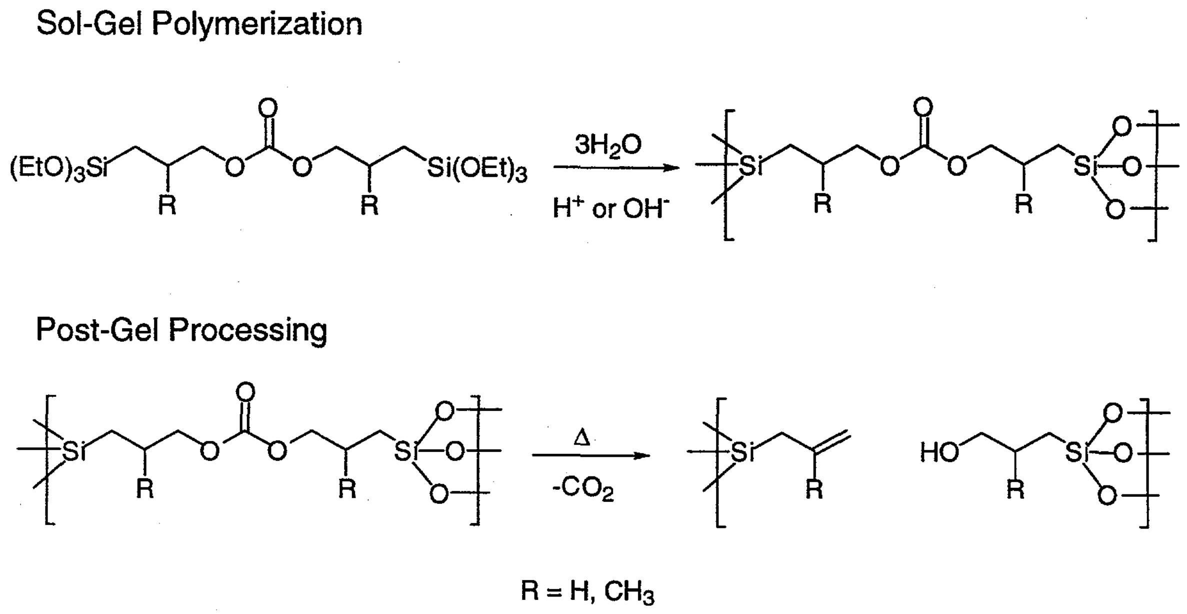
In this paper, we introduce a new approach for altering the properties of bridged polysilsesquioxane xerogels. The method involves *post-processing modification* of the polymeric network. The strategy is illustrated in Scheme 2. The bridging organic group contains latent functionality. Following polymerization and processing to a xerogel, the latent functionality can be liberated thermally, photochemically, or by chemical means. These modifications can produce changes in density, solubility, porosity, and or chemical properties of the material. Since every monomer represents two potential functional groups, the technique allows for the introduction of high levels of functionality in hybrid organic-inorganic materials. The bridging organic group in the polysilsesquioxane provides a unique handle for controlling or modifying the bulk properties of these materials. An additional advantage of this strategy is that it may be used for the synthesis of functional polysilsesquioxane xerogels that are not available by direct methods, since many alkyl or aryl trialkoxysilanes do not form gels upon sol-gel polymerization.[11]



Scheme 2. Creation of new highly functionalized polysilsesquioxanes using post processing modification.

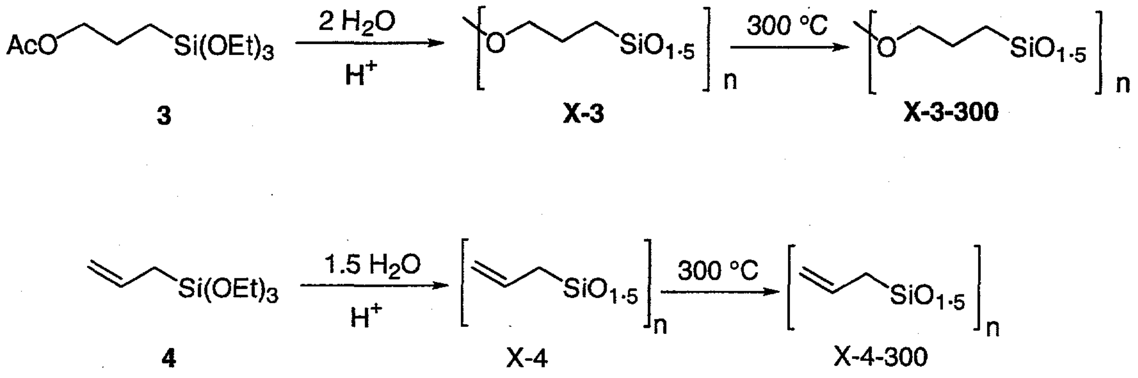
We illustrate this new concept with silsesquioxane precursors that built around dialkylene carbonate bridging groups (Scheme 3). Dialkylcarbonates with β-hydrogens undergo decarboxylation to quantitatively afford an olefin and an alcohol at temperatures between 250-350 °C.[12-14] The carbonate group is also susceptible to hydrolysis by both aqueous acids and bases.

The labile dialkylcarbonate group has found important uses in a number of technological areas including photolithography.[14]



Scheme 3. Sol-gel polymerization of monomers **1** (R = H) and **2** (R = CH_3) to give gels that are "water-processed" to afford granular xerogels or supercritically processed with carbon dioxide to give monolithic gels. Post processing, thermal modification of dialkylene-bridged polysilsesquioxanes (**X1**, R = H; **X2**, R = CH_3) results in cleavage of the bridging group with loss of carbon dioxide.

The dialkylenecarbonate bridging group was incorporated by hydrosilating diallylcarbonate to give monomer **1** and dimethallylcarbonate to give monomer **2**. Sol-gel polymerization of **1** and **2** was used to create gels that were processed to give xerogels. Post processing, thermal modification was performed on the dialkylene-bridged polysilsesquioxanes, **X1** and **X2** and its impact on the gels morphology determined. To assist in characterization of the thermolysis products, polysilsesquioxanes resins with pendant hydroxypropyl and olefinic substituents were also prepared (Scheme 4).



Scheme 4. Preparation of model polysilsesquioxane resins (gels would not form).

EXPERIMENTAL

General Methods

Ethanol was distilled from magnesium before use. Benzene was refluxed over calcium hydride and distilled before using. Chloroplatinic acid, allylacetate, allyltriethoxysilane (**4**), and triethoxysilane were used as received from Aldrich Chemical company. ^{1}H nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AM300 (300 MHz) using C_6D_6 or $CDCl_3$ as the solvent. Solid-state NMR ^{13}C and ^{29}Si CP MAS NMR spectra were obtained with a Bruker AMX 400 spectrometer using glycine and $[Si_8O_{12}](OSiMe_3)_8$ as external references, respectively. Infrared spectra were obtained on a Perkin Elmer 1750 FTIR spectrometer. Mass Spectra were obtained on a Fisons Autospec (CI, ammonia). Monomer purity was determined by GC with an HP Series II 5890 and a packed column with HP-1 (crosslinked methyl siloxane), 15 m x 0.32 mm. Thermogravimetric analyses (TGA) were performed on a Perkin-Elmer 7 apparatus under flowing nitrogen (25 cc/min). Samples were dried for thirty minutes at 150 °C, followed by a 10 °C/min ramp to 920 °C. BET surface areas[15] were determined by a Quantachrome Autosorb 6 using N_2 gas sorption analysis. Elemental analyses were performed by Galbraith Laboratories, Inc..

Synthesis of Monomers

Bis-(3-triethoxysilylpropyl)carbonate (1). Diallylcarbonate (10.50 g, 73.86 mmole) and chloroplatinic acid (0.047 g, 0.11 mmole) were added to dry benzene (50 mL). Caution, exothermic reaction. Triethoxysilane (29.11 g, 176.6 mmole) in dry benzene (20 mL) was added to the solution dropwise. After 5 days at room temperature, the product was isolated by fractional distillation. Distillate was collected at 150 °C at 10 mtorr pressure (42% yield, product 97% pure by gas chromatography). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.09 (t, 4 H, J = 7.0 Hz, $COC\underline{H}_2CH_2$), 3.81 (q, 12 H, J = 6.8 Hz, $SiOC\underline{H}_2CH_3$), 1.78 (quin, 4 H, J = 6.9 Hz, $OCH_2C\underline{H}_2CH_2Si$), 1.22 (t, 18 H, J = 6.8 Hz, $SiOCH_2C\underline{H}_3$), 0.65 (t, 4 H, J = 8.3 Hz, $SiC\underline{H}_2CH_2$). ^{13}C NMR (75 MHz, C_6D_6) δ 155.4 (C=O), 69.7 ($OCO\underline{C}H_2$), 59.5 ($SiO\underline{C}H_2CH_3$), 23.0 ($COCH_2\underline{C}H_2$), 19.5 ($SiOCH_2\underline{C}H_3$), 6.8 ($CH_2\underline{C}H_2Si$). IR (neat) υ 2975, 2928, 2888, 1746, 1588, 1442, 1391, 1366, 1353, 1320, 1256, 1198, 1167, 1104, 1079, 957, 856, 791 cm^{-1}. HRMS (CI, isobutane): Anal. Calcd for $C_{19}H_{42}O_9Si_2$ $[M]^+$: 470.2367. Found: 470.2341.

Bis(3-triethoxysilylisobutyl)carbonate (2). To bis(2-methylallylcarbonate (13.50 g, 77.3 mmole) and triethoxysilane (28.40 g, 172.3 mmole) was added dry benzene (12 mL) and chloroplatinic acid (0.055 g, 0.13 mmole). The solution was allowed to stir under argon at room temperature for 5 days. The product was isolated by fractional distillation. Distillate was collected at 161 °C at 40 mtorr pressure (55% yield, product 98% pure by gas chromatography). ^{1}H NMR (300 MHz, C_6D_6) δ 4.11 (m, 4 H, $COC\underline{H}_2CHCH_3$), 3.97 (m, 2 H, $COCH_2C\underline{H}CH_3$), 3.73 (q, 12 H, J = 7.2 Hz, $SiOC\underline{H}_2CH_3$), 2.20 (m, 2 H, $OCH_2C\underline{H}(CH_3)CH_2Si$), 1.11 (t, 18 H, J = 7.2 Hz, $SiOCH_2C\underline{H}_3$), 1.06 (d, 6 H, J = 6.8 Hz, $CHC\underline{H}_3$), 0.81 (dd, 2 H, J = 5.3, 15.2, $SiCH_2C\underline{H}$), 0.49 (dd, 4 H, J = 8.8, 15.0, $SiC\underline{H}_2CH$). ^{13}C NMR (75 MHz, C_6D_6) δ 156.0 (C=O), 74.4 ($CO_2\underline{C}H_2$), 58.4 ($SiO\underline{C}H_2CH_3$), 28.9 ($COCH_2\underline{C}H$), 19.5 ($CH\underline{C}H_3$), 18.5 ($SiOCH_2\underline{C}H_3$), 15.1

($CHCH_2Si$). HRMS (CI, isobutane): Anal. Calcd for $C_{21}H_{46}O_9Si_2$ $[M]^+$: 498.2680. Found: 498.2657

3-(Acetoxypropyl)triethoxysilane (3).[16] Allyl acetate (3.04 g, 30.3 mmole) and chloroplatinic acid (0.0205 g, 0.05 mmole) was added to dry benzene (10 mL). The solution was placed in a water bath (room temperature) and triethoxysilane (5.60 g, 34.1 mmole) was added. The reaction was kept at room temperature for 3 days. The product was purified by fractional distillation. Distillate was collected at 68 °C at 200 mtorr pressure (67% yield, 97.5 % pure by GC). ^1H NMR (300 MHz, $CDCl_3$) δ 4.02 (t, 2 H, J = 6.9 Hz, $COC\underline{H}_2CH_2$), 3.81 (q, 6 H, J = 6.5 Hz, $SiOC\underline{H}_2CH_3$), 2.03 (s, 3 H, $O{=}CC\underline{H}_3$), 1.74 (quin, 2 H, J = 6.9 Hz, $OC\underline{H}_2CH_2CH_2Si$), 1.23 (t, 9 H, J = 6.9 Hz, $SiOCH_2C\underline{H}_3$), 0.65 (t, 2 H, J = 6.9 Hz, $SiC\underline{H}_2CH_2$). ^{13}C NMR (75 MHz, C_6D_6) δ 170.5 ($O{=}\underline{C}CH_3$), 66.4 ($CH_3CO_2\underline{C}H_2$), 58.5 ($SiO\underline{C}H_2CH_3$), 22.8 ($CO\underline{C}H_2CH_2$), 20.8 ($O{=}C\underline{C}H_3$), 18.5 ($SiOCH_2\underline{C}H_3$), 7.1 ($CH_2\underline{C}H_2Si$). IR (neat) υ 2976, 2928, 2888, 1742, 1442, 1413, 1390, 1366, 1294, 1240, 1197, 1168, 1104, 1082, 958, 893, 791, 775 cm^{-1}.

1,7-Bis(triethoxysilyl)-4-oxaheptane (5).

To a solution of diallyl ether (12.1 g, 123 mmol) and triethoxysilane (44.5 g, 271 mmol) in benzene (100 mL) was added chloroplatinic acid (110 mg, 2.7×10^{-4} mol) and the solution stirred overnight at room temperature. Solvent and excess triethoxysilane were removed *in vacuo* and the remaining brown oil distilled (2X, 112°C at 59 μmHg) to afford **2** as a clear colorless oil (25.6 g, 58%). Purity was determined to be 96% by gas chromatography. ^1H NMR (300 MHz, $CDCl_3$) δ 3.70 (q, 12H, J = 6.96 Hz, $OC\underline{H}_2CH_3$), 3.27 (t, 4H, J = 6.78 Hz, $SiCH_2CH_2C\underline{H}_2O$), 1.57 (m, 4H, $SiCH_2C\underline{H}_2CH_2O$), 1.11 (t, 18H, J=8.71 Hz, $OCH_2C\underline{H}_3$), 0.54 (m, 4H, $SiC\underline{H}_2CH_2CH_2O$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 72.76 ($SiCH_2CH_2\underline{C}H_2O$), 58.08 ($O\underline{C}H_2CH_3$), 22.86 ($SiCH_2\underline{C}H_2CH_2O$), 18.06 ($OCH_2\underline{C}H_2$), 6.30 ($Si\underline{C}H_2CH_2CH_2O$); ^{29}Si NMR (99 MHz, $CDCl_3$) δ

-45.44; FTIR (NaCl) υ 2974, 2927, 2885, 1389, 1169, 1107, 1084, 957, 775, 667, cm^{-1}; LRMS (CI$^+$, NH_3) m/z 427 (20), 382 (28), 381 (100), 205 (47), 180 (32), 175 (46); HRMS (CI$^+$, NH_3) calcd. for $C_{18}H_{42}O_7Si_2$: (M+1) 427.2547, found: (M+1) 427.2537.

Sol-Gel Polymerizations

All polysilsesquioxane gels were made from 0.4 M solutions of monomers **1** or **2** in dry ethanol (distilled from magnesium turnings) with six equivalents H_2O and 10.8 mol% catalyst (HCl or NaOH). A typical formulation is as follows. A monomer solution was made of **1** or **2** (2.0 mmole) in dry ethanol (1.0 mL). A catalyst solution was made by adding 1.0 M HCl (aqueous) or 1.0 M NaOH (aqueous) (0.215 g, 12 mmole H_2O) to dry ethanol (1.0 mL). The catalyst and monomer solutions were combined and the total volume of the solution was brought to 5.00 mL by the addition of dry ethanol. Gelation time was determined by the time it took for the combined solutions to cease to flow. Gels were allowed to age for 2 weeks before processing. Xerogels were made by crushing the wet gel under distilled water. The crushed gels were washed with 200 mL of distilled water followed by 100 mL of diethyl ether. The resulting powders were dried under vacuum at 100 °C for 12 h. Aerogels were made be submitting the wet gels to supercritical CO_2 extraction. Polymers are denoted (*vide infra*) as **X** (xerogel) or **A** (aerogel), then the monomer number **1-5**, the type of catalyst used in the gels' preparation (**H** for aqueous HCl; **OH** for aqueous NaOH) and the thermolysis temperature (**300**) where appropriate.

Thermolyses

A sample of dry gel (approximately 200 mg) was placed in a ceramic boat. The boat was placed into a pyrolysis tube. The tube was purged with a steady stream of argon for 15 minutes. The tube was then placed in a pyrolysis oven at 275-350 °C for 2 hours under a positive pressure of argon. The gel was allowed to cool to room temperature before exposing it to the atmosphere and weighing.

X-1-H. Monomer **1** (0.94 g, 2.00 mmole) was added to dry ethanol (1.0 mL). To dry ethanol (1.0 mL) was added 1.0 M HCl (aqueous) (0.215 g, 12 mmole H_2O). The catalyst and monomer solutions were combined and the total volume of the solution was brought to 5.00 mL by the addition of dry ethanol. After 2 weeks the gel was crushed under distilled water, washed with 200 mL of water and 100 mL of diethyl ether. The resulting white powder was dried under vacuum at 100 °C for 12 hours (mass of dry gel = 0.507 g). ^{13}C CP MAS-NMR (50.20 MHz) δ 156.0 ($\underline{C}$=O), 69.8 (OCO$\underline{C}$H$_2$), 23.0 (COCH$_2\underline{C}$H$_2$), 9.4 (CH$_2\underline{C}$H$_2$Si). ^{29}Si CP MAS-NMR (39.74 MHz) δ -47.8 (T^1) -58.1 (T^2), -65.3 (T^3). IR (KBr) υ 3450 (br), 2944, 1751, 1412, 1283, 1204, 1130, 1037, 859, 792, 696 cm^{-1}. Elemental analysis calcd. for $C_7H_{12}O_6Si_2$: : C 33.9%, H 4.9%, Si 22.6%, found: C 32.3%, H 4.8%, Si 23.0%.

X-1-H-275. Ground gel (0.138 g) was heated at 275 °C for 1.75 hours affording a white powder with no visible discoloration (0.106g, 80.6%). IR (KBr) υ 3450 (br), 2942, 1752, 1261, 1203, 1087, 1044, 928, 779 cm^{-1}.

A-1-H. Monomer **1** (0.95 g, 2.01 mmole) was added to dry ethanol (1.0 mL). To dry ethanol (1.0 mL) was added 1.0 M HCl (aqueous) (0.214 g, 12 mmole H_2O). The catalyst and monomer solutions were combined and the total volume of the solution was brought to 5.00 mL by the addition of dry ethanol. After 2 weeks the transparent wet monolith was dried by supercritical CO_2 extraction. The monolith lost much of its transparency upon drying (mass of dry gel = 0.511 g, density = 0.64 g/mL).

X-1-OH. Monomer **1** (0.95 g, 2.01 mmole) was added to dry ethanol (1.0 mL). To dry ethanol (1.0 mL) was added 1.0 M NaOH (aqueous) (0.212 g, 12 mmole H_2O). The catalyst and monomer solutions were combined and the total volume of the solution was brought to 5.00 mL by the addition of dry ethanol. After 2 weeks the gel was crushed under distilled water, washed with 200 mL of water and 100 mL of diethyl ether. The resulting white powder was dried under vacuum at 100 °C for 12 hours (mass of dry gel = 0.491 g). ^{13}C CP MAS-NMR (50.20 MHz) δ 156.0 ($\underline{C}$=O), 69.9 (OCO$\underline{C}$H$_2$), 23.2 (COCH$_2\underline{C}$H$_2$), 9.3 (CH$_2\underline{C}$H$_2$Si). ^{29}Si CP MAS-NMR (39.74 MHz) δ -57.8 (T^2), -69.7 (T^3). IR (KBr) υ 3450 (br), 2944, 1751, 1412, 1283, 1204, 1130, 1037, 859, 792, 696 cm^{-1}. Elemental analysis calcd. for $C_7H_{12}O_6Si_2$: C 33.9, H 4.9, Si 22.6. Found: C 32.2%, H 4.8%, Si 22.4%.

X-1-OH-275. Ground gel (g)was heated at 275 °C for 1.75 hours (g, %). ^{13}C CP MAS-NMR (50.20 MHz) δ 156 (small, $\underline{C}$=O), 132 (small, $CH_2{=}\underline{C}HCH_2$), 115 (small, $\underline{C}H_2{=}CHCH_2$) 65.2 ($RO\underline{C}H_2CH_2CH_2Si$), 26.6 ($ROCH_2\underline{C}H_2CH_2Si$), 9.2 ($CH_2\underline{C}H_2Si$). IR (KBr) υ 3450 (br), 2942, 1752, 1261, 1203, 1087, 1044, 928, 779 cm^{-1}. Elemental analysis calcd. $C_3H_6O_2Si$: C 35.3, H 5.9, Si 27.5, found: C 32.3%, H 5.6%, Si 27.4%.

X-1-OH-350. Ground gel (0.110 g) was heated at 350 °C for 2 hours (0.107g, %). ^{13}C CP MAS-NMR (50.20 MHz) δ 65.2 ($RO\underline{C}H_2CH_2CH_2Si$), 26.3 ($ROCH_2\underline{C}H_2CH_2Si$), 9.0 ($CH_2\underline{C}H_2Si$). IR (KBr) υ 2940, 1412, 1274, 1087, 930, 885, 785 cm^{-1}. Elemental analysis calcd. $C_3H_6O_2Si$: C 35.3, H 5.9, Si 27.5, found: C 23.3%, H 3.6%, Si 28.4%.

X-1-TMSOMe ^{13}C CP MAS-NMR (50.20 MHz) δ 65.2 ($RO\underline{C}H_2CH_2CH_2Si$), 26.3 ($ROCH_2\underline{C}H_2CH_2Si$), 9.0 ($CH_2\underline{C}H_2Si$). IR (KBr) υ 2940, 1412, 1274, 1087, 930, 885, 785 cm^{-1}. Elemental analysis calcd. $C_3H_6O_2Si$: C 35.3, H 5.9, Si 27.5, found: C 37.3%, H 7.6%, Si 22.6%.

A-1-OH. Monomer **1** (0.948 g, 2.01 mmole) was added to dry ethanol (1.0 mL). To dry ethanol (1.0 mL) was added 1.0 M NaOH (aqueous) (0.217 g, 12 mmole H_2O). The catalyst and monomer solutions were combined and the total volume of the solution was brought to 5.00 mL by the addition of dry ethanol. After 2 weeks, the opaque white monolith was dried by supercritical CO_2 extraction (mass of dry gel = 0.546 g, density = 0.71g/mL).

X-2-H. Monomer **2** (1.008 g, 2.02 mmole) was added to dry ethanol (1.0 mL). To dry ethanol (1.0 mL) was added 1.0 M HCl (aqueous) (0.216 g, 12 mmole H_2O). The catalyst and monomer solutions were combined and the total volume of the solution was brought to 5.00 mL by the addition of dry ethanol. After 2 weeks, the gel was crushed under distilled water, washed with

200 mL of water and 100 mL of diethyl ether. The resulting white powder was dried under vacuum at 100 °C for 12 hours (mass of dry gel = 0.609 g). ^{13}C CP MAS-NMR (50.20 MHz) δ 156.0 ($\underline{C}$=O), 74.7 ($OCO\underline{C}H_2$), 29.1 ($COCH_2\underline{C}H$), 18.8 ($CH_2\underline{C}H_2Si$ + $CH_2CH\underline{C}H_3$). ^{29}Si CP MAS-NMR (39.74 MHz) δ -48.5 (T^1) -59.8 (T^2), -65.8 (T^3). IR (KBr) υ 3483 (br), 2971, 1752, 1467, 1409, 1380, 1259, 1091, 972, 915, 791, 741, 594 cm^{-1}. Elemental analysis calcd. for $C_9H_{16}O_6Si_2$: C 39.1%, H 5.8%, Si 20.3%. Found: C 39.2%, H 6.3%, Si 18.1%.

X-2-H-400. Ground gel (g)was heated at 375 °C for 1.75 hours (g, %). ^{13}C CP MAS-NMR (50.20 MHz) δ 156 (small, $\underline{C}$=O), 150 (small), 131 (small), 70.9 ($RO\underline{C}H_2CHCH_3CH_2Si$), 32.0 ($ROCH_2\underline{C}HCH_3CH_2Si$), 19.4 ($ROCH_2CH\underline{C}H_3\underline{C}H_2Si$). IR (KBr) υ 2961, 2926, 2876, 1751, 1459, 1406, 1282, 1228, 1191, 1062, 1027, 862, 840, 786, 740 cm^{-1}. Elemental analysis calcd. for $C_3H_6O_2Si$: C 35.3%, H 5.9%, Si 27.5%. Found: C 34.5%, H 6.1%, Si 26.2%.

A-2-H. Monomer **2** (0.995 g, 1.99 mmole) was added to dry ethanol (1.0 mL). To dry ethanol (1.0 mL) was added 1.0 M HCl (aqueous) (0.215 g, 12 mmole H_2O). The catalyst and monomer solutions were combined and the total volume of the solution was brought to 5.00 mL by the addition of dry ethanol. After 2 weeks the wet monolith was dried by supercritical CO_2 extraction (mass of dry gel = 0.572 g, density = 0.88 g/mL).

X-2-OH. Monomer 2 (0.999 g, 2.00 mmole) was added to dry ethanol (1.0 mL). To dry ethanol (1.0 mL) was added 1.0 M NaOH (aqueous) (0.213 g, 12 mmole H_2O). The catalyst and monomer solutions were combined and the total volume of the solution was brought to 5.00 mL by the addition of dry ethanol. After 2 weeks the gel was crushed under distilled water, washed with 200 mL of water and 100 mL of diethyl ether. The resulting white powder was dried under vacuum at 100 °C for 12 hours (mass of dry gel = 0.589 g). ^{13}C CP MAS-NMR (50.20 MHz) δ 156.0 ($\underline{C}$=O), 74.4 ($OCO\underline{C}H_2$), 29.2 ($COCH_2\underline{C}H$), 18.8 ($CH_2\underline{C}H_2Si$ + $CH_2CH\underline{C}H_3$). ^{29}Si CP MAS-NMR (39.74 MHz) δ -45.2 (T^1) -58.9 (T^2), -67.1 (T^3). IR (KBr) υ 3483 (br), 2971, 1752, 1467, 1409, 1380, 1259, 1091, 972, 915, 791, 741, 594 cm^{-1}. Elemental analysis calcd. for $C_9H_{16}O_6Si_2$: C 39.1%, H 5.8%, Si 20.3%. Found: C 39.6%, H 6.5%, Si 19.2%.

X-2-OH-400. Ground gel (0.181 g)was heated at 400 °C for 1.75 hours (0.139g, 76%). ^{13}C CP MAS-NMR (50.20 MHz) δ 156 (small, $\underline{C}$=O), 150 (small), 131 (small), 70.9 ($RO\underline{C}H_2CHCH_3CH_2Si$), 32.0 ($ROCH_2\underline{C}HCH_3CH_2Si$), 19.4 ($ROCH_2CH\underline{C}H_3\underline{C}H_2Si$). ^{29}Si CP MAS-NMR (39.74 MHz) δ -34.2, –41.4 (T^0), -59.9 (T^2), -64.1 (T^3), 100.2 (Q). IR (KBr) υ 2961, 2926, 2876, 1751, 1459, 1406, 1282, 1228, 1191, 1062, 1027, 862, 840, 786, 740 cm^{-1}.

A-2-OH. Monomer **2** (1.00 g, 2.00 mmole) was added to dry ethanol (1.0 mL). To dry ethanol (1.0 mL) was added 1.0 M NaOH (aqueous) (0.218 g, 12 mmole H2O). The catalyst and monomer solutions were combined and the total volume of the solution was brought to 5.00 mL by the addition of dry ethanol. After 2 weeks the wet monolith was dried by supercritical CO_2 extraction (mass of dry gel = 0.63 g, density = 0.80 g/mL).

X-3-H. Monomer **3** (1.06 g, 4.01 mmole) was added to dry ethanol (1.0 mL). To dry ethanol (1.0 mL) was added 1.0 M HCl (aqueous) (0.216 g, 12 mmole H_2O). The catalyst and monomer solutions were combined and the total volume of the solution was brought to 5.00 mL by the addition of dry ethanol. After 3 weeks, no gel had formed. The solution was concentrated to a viscous oil upon which gelation soon occurred. After 3 days aging, the transparent gel was crushed and washed with 200 mL of distilled water followed by 100 mL of diethyl ether. The resulting white powder was dried under vacuum at 65 °C for 12 hours (mass of dry gel = 0.36 g, some losses occurred during transfer). ^{13}C CP MAS-NMR (100.62 MHz) δ 63.0 ($HO\underline{C}H_2CH_2CH_2Si$), 25.8 ($HOCH_2\underline{C}H_2CH_2Si$), 8.0 ($HOCH_2CH_2\underline{C}H_2Si$). ^{29}Si CP MAS-NMR (39.74 MHz) δ -44.7 (T^0), -51.2 (T^1), -58.8 (T^2), -66.8(T^3). IR (KBr) υ 3361, 2938, 2883, 1741, 1719, 1413, 1257, 1196, 1142, 1054, 889, 862, 787, 697 cm^{-1}.

Elemental analysis calcd. for $C_3H_7O_{2.5}Si$: C 32.4, H 6.4, Si 25.3. Found: C 33.5, H 6.8, Si 22.6.

X-3-H-300. Ground gel (0.609 g)was heated at 300 °C for 1 hour (0.559 g, 92%). ^{13}C CP MAS-NMR (100.63 MHz) δ 64.3 (HO$\underline{C}$H$_2$CH$_2$CH$_2$Si), 25.9 (HOCH$_2\underline{C}$H$_2$CH$_2$Si), 8.8 (HOCH$_2$CH$_2\underline{C}$H$_2$Si). ^{29}Si CP MAS-NMR (39.74 MHz) δ –45.0 (T^0), -51.5 (T^1) –59.1 (T^2), -66.8 (T^3). IR (KBr) υ 3399 (br), 2939, 1741, 1720, 1651, 1413, 1257, 1196, 1137, 1053, 928, 886, 862, 786 cm^{-1}. Elemental analysis calcd. for $C_3H_7O_{2.5}Si$: C 32.4%, H 6.4%, Si 25.3%. Found: C 34.3%, H 6.8%, Si 24.9%.

X-3-OH. Monomer **3** (1.055 g, 4.00 mmole) was added to dry ethanol (1.0 mL). To dry ethanol (1.0 mL) was added 1.0 M NaOH (aqueous) (0.214 g, 12 mmole H_2O). The catalyst and monomer solutions were combined and the total volume of the solution was brought to 5.00 mL by the addition of dry ethanol. After 3 weeks, no gel had formed. The solution was concentrated to a viscous oil. After 4 months, no gelation was seen and the solution discarded.

X-4-H. Monomer **4** (25.0 g, 0.122 mole) was added to dry ethanol (25 mL). To dry ethanol (25 mL) was added 1.0 M HCl (aqueous) (13.2 mL, 12 mmole H_2O). The catalyst and monomer solutions were combined and the total volume of the solution was brought to 100 mL by the addition of dry ethanol. After 3 weeks, no gel had formed. The solution was concentrated to a viscous oil upon which gelation soon occurred. After 3 days aging, the transparent gel was crushed and washed with 200 mL of distilled water followed by 100 mL of diethyl ether. The resulting white powder was dried under vacuum at 65 °C for 12 hours (8.09 g, 74%). ^{13}C CP MAS-NMR (100.62 MHz) δ 131.7 (CH$_2$=$\underline{C}$HCH$_2$), 115.2 ($\underline{C}$H$_2$=CHCH$_2$), 19.7 (CH$_2$=CH$\underline{C}$H$_2$Si). ^{29}Si CP MAS-NMR (39.74 MHz) δ -61.4 (T^2), -69.3 (T^3). IR(KBr) υ 3569, 3081, 3004, 2978, 2929, 1636, 1421, 1393, 1184, 1127, 1044, 931, 902, 787, 761 cm^{-1}. Elemental analysis calcd. for $C_3H_5O_{1.5}Si$: C 38.7, H 5.4, Si 30.2. Found: C 38.5, H 5.9, Si 29.8.

X-4-H-300. Ground gel (0.458 g)was heated at 300 °C for 1 hour (0.424 g, 93%). ^{13}C CP MAS-NMR (100.62 MHz) δ 131.6 (CH$_2$=$\underline{C}$HCH$_2$), 114.7 ($\underline{C}$H$_2$=CHCH$_2$), 28.0 (broad shoulder), 19.6 ($CH_2=CH\underline{C}H_2Si$). ^{29}Si CP MAS-NMR (39.74 MHz) δ -47.8 (T^1) -58.1 (T^2), -65.3 (T^3). IR (KBr) υ 3426 (br), 3080, 2977, 2927, 1636, 1421, 1127, 931, 902, 761 cm^{-1}. Elemental analysis calcd. for $C_3H_5O_{1.5}Si$: C 38.7%, H 5.4%, Si 30.2%. Found: C 33.4%, H 5.6%, Si 29.4%.

X-3-co-4-H. Monomer **3** (1.001 g, 3.78 mmole) and allyltriethoxysilane (**4**) (0.770 g, 3.77 mmole) was added to dry ethanol (1.0 mL). To dry ethanol (1.0 mL) was added 1.0 M HCl (aqueous) (0.218 g, 12 mmole H_2O). The catalyst and monomer solutions were combined and the total volume of the solution was brought to 5.00 mL by the addition of dry ethanol. After 5 days, no gel had formed. The solution was concentrated to a viscous oil upon which gelation occurred in a few minutes. After 10 days aging, the transparent gel was crushed and washed with 100 mL of distilled water followed by 100 mL of diethyl ether. The resulting white powder was dried under vacuum at 65 °C for 12 hours (0.704 g). ^{13}C CP MAS-NMR (100.62 MHz) δ 132.3 ($CH_2=\underline{C}HCH_2Si$), 115.4 ($\underline{C}H_2=CHCH_2Si$), 64.3 ($HO\underline{C}H_2CH_2$), 24.9 ($HOCH_2\underline{C}H_2$), 20.8 ($CH_2=CH\underline{C}H_2Si$), 9.1 ($CH_2\underline{C}H_2Si$). ^{29}Si CP MAS-NMR (39.74 MHz) δ -57.9, -66.9, -71.8. IR (KBr) υ 3567, 3397, 3080, 2941, 2887, 1636, 1127, 1034, 931, 901, 862 cm^{-1}. Elemental analysis calcd. for $C_3H_6O_2Si$: C 35.3%, H 5.9%, Si 27.5%. Found: C 36.7%, H 6.6%, Si 26.4%.

X-3-co-4-300. Ground gel (0.690 g)was heated at 300 °C for 1 hour (0.540 g, 71%). ^{13}C CP MAS-NMR (100.62 MHz) 132.1 ($CH_2=CHCH_2Si$), 115.1 ($CH_2=CHCH_2Si$), 64.6 (HOCH2CH2), 30.0 (broad shoulder than extends downfield to 50 ppm) 25.8 ($HOCH_2CH_2$), 22.0, 20.0 ($CH_2=CHCH_2Si$), 8.9 (CH_2CH_2Si). ^{29}Si CP MAS-NMR (39.74 MHz) -65.2 (T^3), 101.0 (Q^3). IR (KBr) υ 3087, 2941, 1748, 1636, 1025, 783 cm^{-1}. Elemental analysis calcd. for $C_3H_6O_2Si$: C 35.3%, H 5.9%, Si 27.5%. Found: C 33.6%, H 5.9%, Si 28.0%.

X-5-H To a solution of 1,7-Bis(triethoxysilyl)-4-oxaheptane 5 (1.71 g, 4.03 mmol) and ethanol

(3.50 mL) in a 10.00 mL volumetric flask was added aqueous 1 N HCl (0.432 mL, 6 equiv H_2O) in ethanol (3.50 mL) and the solution diluted to the mark with ethanol. The solution was shaken vigorously to insure homogeneity, poured into a polyethylene bottle, capped and sealed. The solution gelled overnight (15 h). The gel was aged for 2 weeks, fragmented, water processed, air-dried for 2 days, ground, and dried under dynamic vacuum at 100°C to afford a white powder (0.80 g, 98%). ^{13}C CP MAS NMR (100.62 MHz) δ 74.0 ($SiCH_2CH_2\underline{C}H_2O$), 59.2 ($O\underline{C}H_2CH_3$), 24.7 ($SiCH_2\underline{C}H_2CH_2O$), 19.5 ($OCH_2\underline{C}H_3$), 10.0 ($Si\underline{C}H_2CH_2CH_2O$); ^{29}Si CP MAS NMR (39.73 MHz) δ -49.3 (T^1), -58.1 (T^2), -66.2 (T^3); IR (KBr) ν 3425, 2939, 2877, 1196, 1103, 906, 775, 694 cm^{-1}; Elemental analysis calcd. for $C_6H_{12}Si_2O_4$: C 35.3%, H 5.9%, O 31.3%, Si 27.5%. Found: C 32.6%, H 6.6%, O 33.4%, Si 27.4%.

RESULTS AND DISCUSSION

1. Gel Formation

Formation of dialkylenecarbonate bridged polymeric gels was the first requirement for this study. Monomers **1** and **2** were prepared by hydrosilation of diallylcarbonate and 1,5-dimethylallylcarbonate, respectively. Sol-gel polymerizations of **1** and **2** (0.4 M in ethanol) were carried out under conditions similar to those used preparing other hydrocarbon-bridged polysilsesquioxanes.[17] Under acidic conditions, **1** gelled within 15 minutes at a monomer concentration of 0.4 M. Monomer **2** required about 20 hours to gel under the same conditions. Both monomers yielded optically transparent monolithic gels that acquired only a slight blue tint (from light scattering) after two weeks of aging.[4] Under basic conditions, both monomers gelled in one hour. In contrast to the acid-catalyzed gels, the base-catalyzed gels were opaque white. As with many organotrialkoxysilanes,[11] hydrolysis and condensation of 3-acetoxypropyltriethoxysilane **3** and/or allyltriethoxysilane **4** failed to form gels under acidic or basic conditions at these concentrations even without solvent other than ethanol generated by the hydrolysis reaction. Only by distilling off condensation products while the sol-gel polymerization was taking place was it possible to obtain solid resins to use as model polymers.

After aging, all of the dialkylenecarbonate-bridged gels showed a significant amount of shrinkage (syneresis) facilitating their removal from the containers in which they were prepared. The gels were then either crushed under water and vacuum dried to form xerogel powders or were dried as monoliths with supercritical carbon dioxide extraction to form aerogels. The transparent aerogels prepared under acidic conditions became translucent upon drying. Aerogels were hard and slightly elastic making the materials difficult to crush. Both aerogels and xerogels were insoluble in organic and aqueous solvents. Surface area analysis by nitrogen sorption porosimetry revealed that all of the carbonate polysilsesquioxanes gels, whether water processed and dried or supercritically dried, were *non-porous* indicating that the polymeric networks were sufficiently compliant to permit collapse of pores during drying. These results are not unexpected considering the non-porous xerogels obtained with long chain alkylene-bridged polysilsesquioxanes.[18]

2. Spectroscopic Characterization

Infrared and solid-state ^{13}C and ^{29}Si NMR spectroscopies were used to determine if the bridging groups survived the sol-gel conditions without hydrolysis of the carbonate functionalities or cleavage of the silicon-carbon bonds. Figure 1 shows a representative solid-state ^{29}Si NMR spectra of one of the carbonate gels. As with most sol-gels prepared from tetra- or trialkoxysilanes,[19] the base-catalyzed gels show more complete condensation than acid-catalyzed gels. The chemical shifts of the peaks are consistent with polysilsesquioxanes prepared from monomers **1** and **2**; there is no evidence of Q resonances that would come with cleavage of the silicon-carbon bonds and formation of silica.

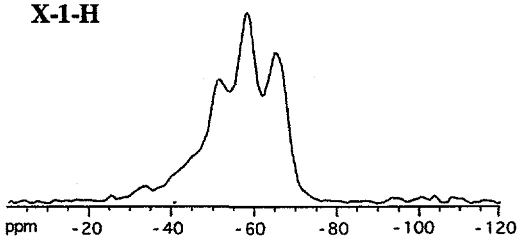


Figure 1. ^{29}Si CP MAS NMR spectrum of dipropylene-carbonate bridged polysilsesquioxane (X-1-H).

Solid state ^{13}C NMR spectroscopy of gels prepared from **1** and **2** under basic conditions have well resolved resonances for all unique carbons. Gels prepared from **1** have a peak due to the carbonate carbonyl at $\delta_C = 156.0$, and three peaks due the α, β, and γ carbons of the propylene groups at $\delta_C = 69.9$, 23.2, and 9.3, respectively (Figure 2a).

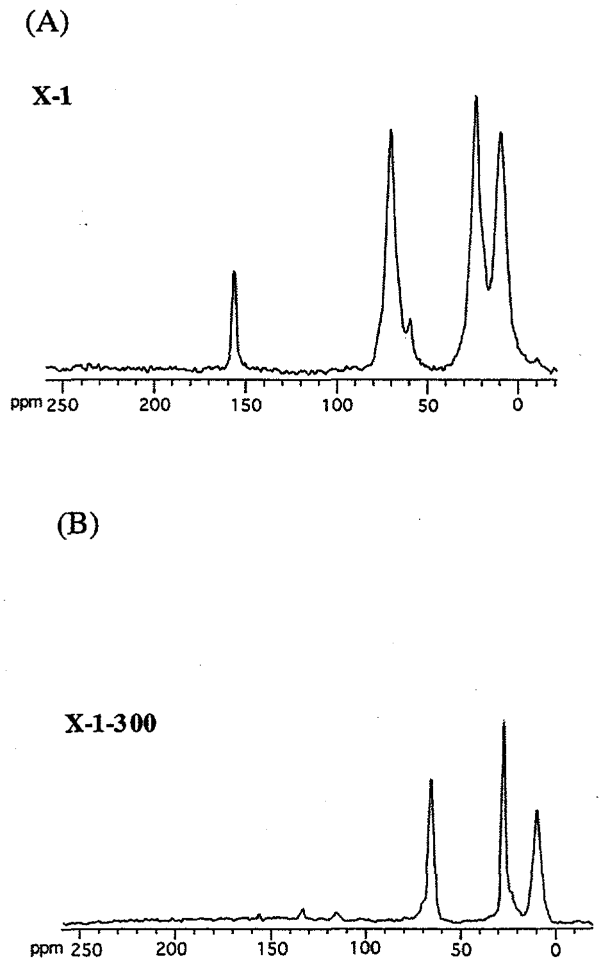


Figure 2. ^{13}C CP MAS NMR spectra of dipropylenecarbonate-bridged polysilsesquioxane before (A) and after (B) pyrolysis at 300 °C for 1 hour.

Gels prepared from **2** have a carbonyl resonance at $\delta_C = 155.9$ and three peaks from the isobutylene groups at $\delta_C = 74.7$, 29.1 and 18.8 (Figure 3a). Interestingly, while the gels prepared from **2** show no sign of hydrolysis of the carbonate under sol-gel conditions, **1** underwent some hydrolytic decarboxylation with base-catalyzed sol-gel polymerizations, but not under acidic conditions. This was ascertained through the appearance of new peaks at $\delta_C = 64.7$ ($SiCH_2CH_2\underline{C}H_2O$) and $\delta_C = 26.5$ ($SiCH_2\underline{C}H_2CH_2O$) from hydroxypropylsilsesquioxane functionalities that were consistent with those observed for poly(hydroxypropylsilsesquioxane) prepared directly from the acid-catalyzed polymerization of 3-acetoxypropyltriethoxysilane (**3**).

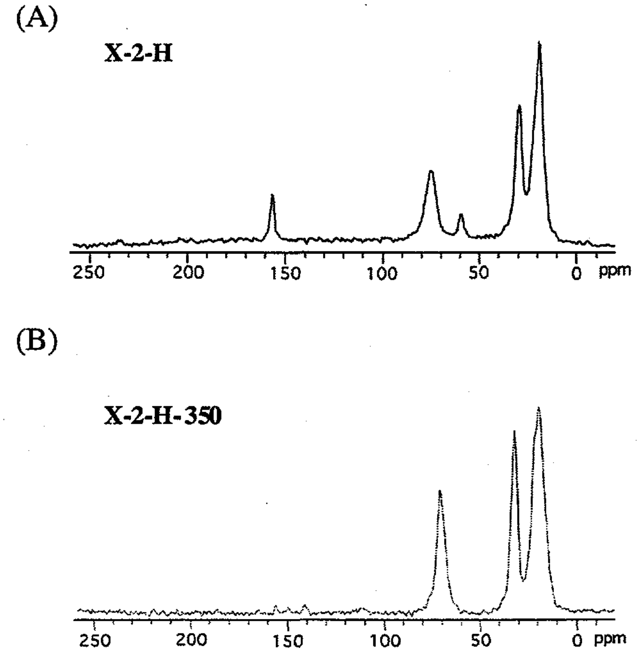


Figure 3. ^{13}C CP MAS NMR spectra of diisobutylenecarbonate-bridged polysilsesquioxane before (A) and after (B) pyrolysis at 340 °C for 1 hour.

The ^{13}C CP MAS NMR of this material exhibited three peaks at δ_C = 64.3 ($SiCH_2CH_2\underline{C}H_2O$), 26.1 ($SiCH_2\underline{C}H_2CH_2O$) and 9.1 ($Si\underline{C}H_2CH_2CH_2O$). Gels **X-1-H**, **X-2-H** and **X-2-OH** all show a small peak at δ_C = 59 which can be assigned to the alpha carbon of unhydrolyzed ethoxy groups. Gel **X-1-OH** does not have the δ_C = 59 signal but shows two small peaks at δ_C = 65 and 26. These peaks are the result of a small amount of hydrolysis of the carbonate functionality. The IR spectrum (Figure 4, top) of the dry gels show the expected strong carbonyl stretch at 1750 cm^{-1}. Also present in the spectrum of all (unsilylated) gels is a broad OH stretch that can be attributed to uncondensed silanols.[20]

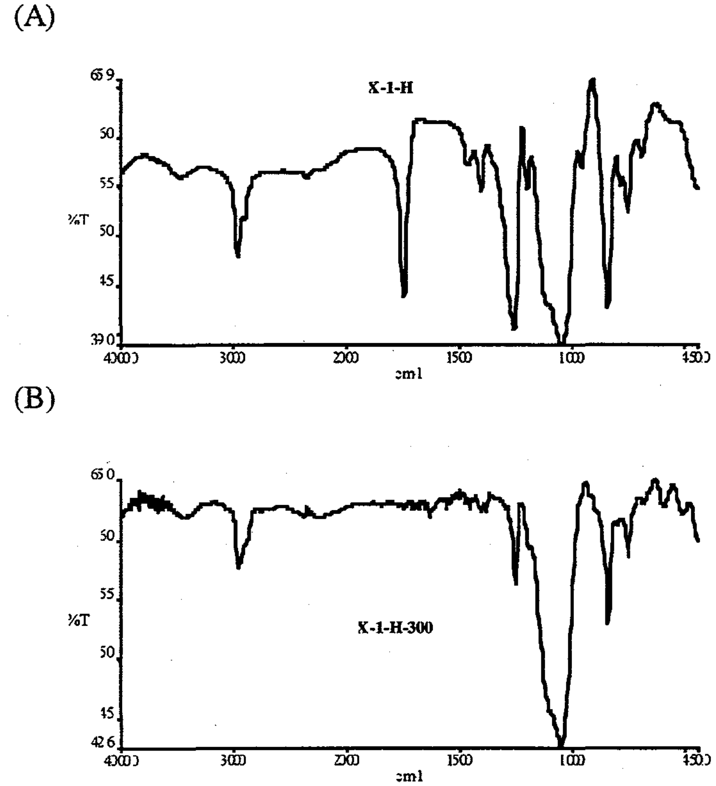


Figure 4. Infrared spectra of dipropylenecarbonate-bridged polysilsesquioxane before (A) and after (B) pyrolysis at 300 °C for 1 hour.

3. Thermally-Induced Decarboxylations

In order to carry out post-gelation processing, samples of the dipropylene carbonate and diisobutylene carbonate-bridged polysilsesquioxanes were heated to determine if and when thermal decarboxylation would occur. Uncatalyzed thermally induced decarboxylation of polymers containing dialkylene carbonate groups have been reported at temperatures ranging from 250-350°C.[21] The structural consequences of the thermal treatments were determined by solid state ^{13}C and ^{29}Si NMR. The physical changes were determined by porosimetry, scanning electron microscopy, and volumetric studies on monolithic gels. First, thermal gravimetric analysis (TGA) was used to establish the onset temperature for the rearrangement and loss of carbon dioxide. The TGA of both dipropylene carbonate and isobutylene carbonate-bridged gels show two distinct transitions (Figure 5). The onset for decarboxylation occurred between near 300 °C for the dipropylene carbonate bridged gels and near 340 °C for the isobutylenecarbonate-bridged gels. The mass loss at the initial transition ranges from 20-24%. This range is close to the expected mass loss due to decarboxylation.

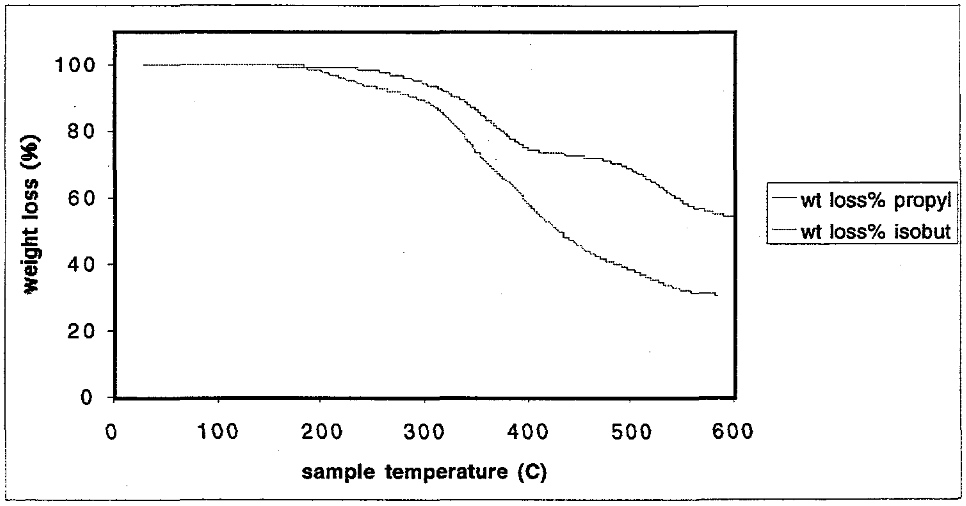


Figure 5. Thermal gravimetric analysis for dipropylenecarbonate- and diisobutylenecarbonate-bridged polysilsesquioxane gels.

Theoretically, a fully-condensed gel of monomer **1** that completely decarboxylated would lose 18.6% of its mass and a gel of monomer **2** would lose 16.6% of its mass. Since these gels are not completely condensed, the observation of a mass loss greater than 19% might be attributed in part to the loss of water and ethanol from further condensation events. This is supported by the observation that a few of the dipropylenecarbonate bridged materials began losing mass at 275 °C with evolution of ethanol detected by TGA-mass spectrometry. Analogous mass losses beginning at 275 °C, but none between 300-350 °C, were also observed for polysilsesquioxanes prepared from monomer **3** and **4** that bear no carbonate functionality. The second transition at 500 °C in the dialkylene carbonate bridged materials is accompanied by mass loss consistent with the degradation of the remaining organic functionalities in the gels.

Thermolysis of bulk samples of the carbonate-bridged polysilsesquioxanes yielded materials that were surprisingly similar in appearance to their precursors. While there was approximately 40 % shrinkage associated with the thermolyses of monolithic gels, there was rarely any change in the roughness of the surface features even under examination with scanning electron microscopy. Treatment of a similar monolithic gel of a hexylene-bridged polysilsesquioxane at 300 °C resulted in no measurable shrinkage. In addition, decarboxylated gels were determined by nitrogen sorption porosimetry to be non-porous. This loss of volume in the dialkylenecarbonate-bridged gels, coupled with the observation that thermally treated gels are still nonporous, suggest that the network is collapsing in response to the loss of carbon dioxide.

Spectroscopic analysis of the thermally treated gels shows clear evidence of the decarboxylation of the carbonate bridge. Both solid-state ^{13}C NMR (Figures 2b & 3b) and IR (Figure 4b) spectra show loss of the carbonyl carbon after thermal treatment. These spectroscopic studies showed that the onset of decarboxylation occurred at 300 °C, but that residual carbonate remained even after 2 hours at this temperature. At 320 °C or above both dipropylene and diisobutylene carbonate bridged materials quantitatively decarboxylated after 1 hour. As the observed mass loss is very close to the theoretical mass loss due to decarboxylation and as the IR and ^{13}C NMR spectra show small carbonyl signals, most of the observed mass loss can be attributed to the loss of CO_2 rather than the loss of water and ethanol. Absent in these ^{13}C CP MAS NMR spectra are any olefinic and allylic methylene resonances one would expect from the thermal decarboxylation. Instead, three large peaks were observed indicating that products with simpler and only saturated aliphatic organic constituents was present. The heat treated isobutylene- carbonate bridged materials also showed three large peaks, but with a slight shoulder on the downfield side of the peak at 18 ppm. Solid-state ^{29}Si NMR of the gels treated at 300 °C show only slight spectral changes in the size of the three silicon resoances. Thermolysis at 400 °C, however, gave rise to peaks at –34 and –100 ppm, indicating that some kind of disproportionation reaction occurred to give rise to both siloxane (D) and silica (Q) species.

4. Model Polysilsesquioxanes

In order to clarify the characterization of the thermolysis products (*vide supra*), several polysilsesquioxanes were prepared as models. Allyl- and hydroxypropyl-substituted polysilsesquioxanes and copolymers were prepared and characterized by solid state ^{13}C NMR before and after thermolysis at 300 °C for 1 hour. 3-Acetoxypropyltriethoxysilane (**3**) was polymerized under acidic conditions to give a 3-“hydroxypropylsilsesquioxane” polymer (Scheme 4). Clearly, the hydroxyl group can potentially condense with silanols to give an alkoxide linkage. If this “esterification” reaction were a favorable process, then the monomer would effectively be tetrafunctional. However, the poor gelation of **3** to suggests that contributions from this linkage may be minor. Allyltriethoxysilane (**4**) was polymerized to give an allylsilsesquioxane polymer to provide the model for the other half of the thermolyzed carbonate. A 1:1 copolymer (**X-3-co-4**) of **3** and **4** was also prepared as a model for the expected product of the thermal decarboxylation of the dipropylenecarbonate gels prepared from **1**. If the thermal decarboxylation of a gel prepared from **1** were to generate allylic and hydroxypropyl substituents, one would expect a spectrum similar to that of **X-3-co-4** with two olefinic resonances at $\delta_C = 132.3$ and 115.4, the allylic methylene at $\delta_C = 20.7$, and the hydroxypropyl resonances at $\delta_C =$ 64.3, 26.0, and 9.1 (Figure 6a). Instead, the spectra of the decarboxylated dipropylenecarbonate bridged materials were virtually identical to that of **X-3** (Figure 7a-b) with three resonances at $\delta_C = 65.2$, 26.3, and 9.0. These results suggest that either hydrolytic decarboxylation to two hydroxypropyl groups, similar to the minor side reaction observed with sol-gel polymerization of **1**, had occurred or that the allyl group was undergoing degradation at the thermolysis temperature. Thermolysis of the copolymer **X-3-co-4** at 300 °C for 1 hour, gave materials in which the olefinic resonances due to the allylic group had diminished in intensity, but were still resolvable (Figure 6b). However, there was a broad shoulder, not observed in the thermolyzed dialkylene-carbonates, extending downfield from the peak at $\delta = 26$.

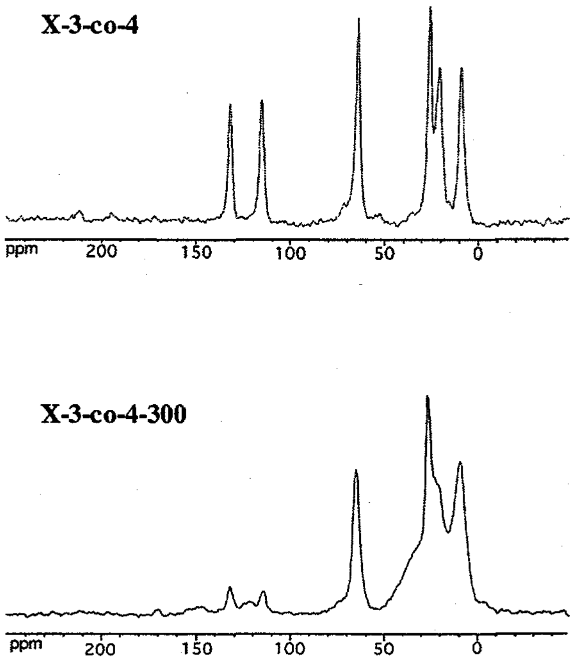


Figure 6. ^{13}C CP MAS NMR spectra of poly(allyl-co-hydroxypropylsilsesquioxane) before (A) and after (B) heating at 300 °C.

An alternative explanation of the symmetrical post-thermolyses spectra is the formation of propyl or diisobutyl ether-bridged polysilsesquioxanes at 300°C from the allyl or methallyl and hydroxypropyl or hydroxyisobutyl groups. This hypothesis was discounted by examination of the ^{13}C NMR spectrum of authentic dipropyl ether-bridged polysilsesquioxane (**X-5**) prepared from the polymerization of 1,7-bis(triethoxysilyl)-4-oxa-heptane (**5**). The three bridging carbons in the dipropylene ether bridged material are significantly different (δ_C = 74.0, 24.7, and 10.0) from those observed in the thermolysis products obtained from the carbonate-bridged gels.

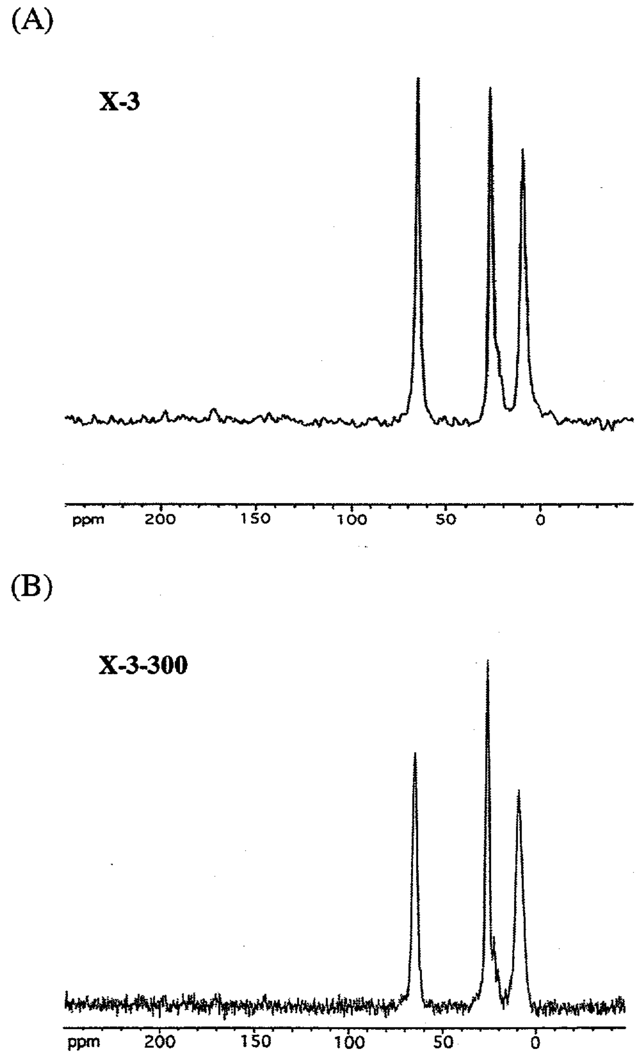
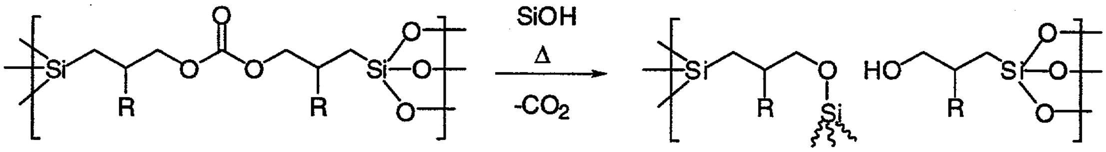


Figure 7. ^{13}C CP MAS NMR spectra of polyhydroxypropylsilsesquioxane before (A) and after (B) heating at 300 °C.

5. Silation/Thermolysis Experiments

One possible explanation of degradation of the allylic substituents was that residual silanols in the silsesquioxanes at elevated temperatures were causing hydrolysis of the carbonate (Scheme 5). From the presence of fairly large T^2 resonances in the solid state ^{29}Si NMR and little or no residual ethoxides in the solid state ^{13}C NMR spectra, there are substantial numbers of silanols present in these materials. In order to test this hypothesis, we silylated carbonate-bridged xerogels and aerogels to protect any residual silanols before thermolysis.



Scheme 5. Hydrolytic decarboxylation with residual silanols. Some condensation of the resulting alcohols with silanols would be expected at 300 °C.

However, due to the low surface area of the dry gels, most of the silanols proved to be inaccessible to silation with chlorotrimethylsilane/ hexamethyldisilazane (TMSCl/HMDS), hexamethyldisilazane (HMDS), trimethylsilylimidazole, methoxytrimethylsilane or trimethylsilylacetamide. Therefore, gels were silated before drying. More of the silanols were accessible to the silylating agents in the wet gels and fairly good protection was achieved, though some residual silanols were detectable by ^{29}Si CP MAS NMR and infrared spectroscopy. Solid state ^{13}C NMR spectra of the silylated polysilsesquioxanes were identical to the unsilylated, save the addition of a single resonance at 2 ppm due to the trimethylsilyl (TMS) groups (Figure 8a). Thermolysis of the dipropylcarbonate-bridged gels silated with TMSCl/HMDS or MeOTMS at 300 °C afforded gels with strikingly different ^{13}C CP MAS NMR spectra (Figure 8b) from those observed with the thermolyzed, unsilylated gels (Figure 2b & 3b). The spectra were nearly identical to that of the copolymer of allyltriethoxysilane and acetoxypropyltriethoxysilane (**X-3-**

co-4) after pyrolysis at 300 °C (Figure 6b), save the presence of a peak at $\delta_C = 1.5$ due to the TMS groups in the gel. Olefinc resonances due to allylic groups were clearly visible at $\delta_C = 131$ and 115 along with the broad shoulder on the peak at $\delta_C = 26$ that appears to be due to thermal degradation of the allylic functionality. Thermal gravimetric analysis also revealed that the onset for mass loss of the silylated dipropylenelcarbonate-bridged polysilsesquioxanes was 340-360 °C, 40-60 °C higher than the unsilylated dipropylenecarbonate bridged materials. It is not possible to tell with this data whether the increase is due to reduction in the loss of water or residual ethanol from the silylated material or due to changes in the decarboxylation mechanism.

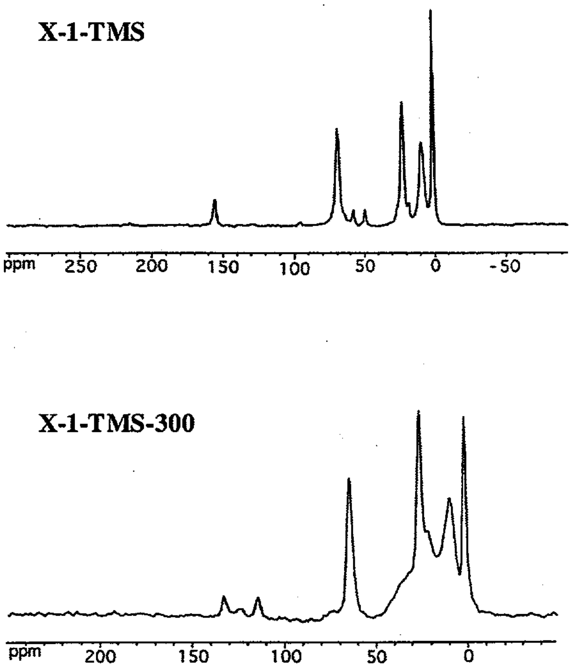


Figure 8. ^{13}C CP MAS NMR spectra of the silylated dipropylenecarbonate-bridged polysilsesquioxane before (A) and after (B) heating at 300 °C.

CONCLUSION

Thermal post-processing of dialkylene carbonate-bridged polysilsesquioxane xerogels was successfully used to decarboxylate and cleave the organic bridging groups. Thermal gravimetric analysis revealed that the onset of decarboxylation occurred between 300 °C for dipropylenecarbonate bridged materials and near 340 °C for the diisobutylene-bridged materials. Infrared and solid state ^{13}C NMR confirmed the loss of most of the carbonate functionality. Similarly, TGA-MS provided evidence for loss of carbon dioxide associated with the mass losses. Interestingly, this disruption of the network architecture caused some shrinkage of monolithic gels with no cracking or disintegration. Furthermore, the molecular structure of the thermally treated gels was affected by the presence (or absence) of residual silanols. If the gels were not silylated with trimethylsilyl groups thermolysis gave only hydroxyalkyl substituted polysilsesquioxanes with spectroscopic evidence of hydrolytic cleavage of the carbonate. Silylated gels gave a mixture of hydroxyalkyl and allyl substituents as would be expected for the thermal decarboxylation. Future efforts will focus on designing bridging groups with more labile functionality to permit lower temperature processing and to broaden the range of latent functional groups.

Acknowledgments

We would like to thank Lisa Ciszek and Edward Russick for their help with TGA analysis and supercritical CO_2 extractions (respectively). Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

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