

**DIALKYLENECARBONATE-BRIDGED POLYSILSESQUOXANES.
HYBRID ORGANIC-INORGANIC SOL-GELS WITH A THERMALLY
LABILE BRIDGING GROUP**

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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. Dialkylencarbonate-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 dialkylencarbonate 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 [1-5]. 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 or silsesquioxanes with pendant organic groups, $(RSiO_{1.5})_n$, the bridging organic group remains as an integral part of the network structure. 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.

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 1**. The bridging organic group contains latent functionality. Following polymerization and processing to a xerogel, the latent functionality can

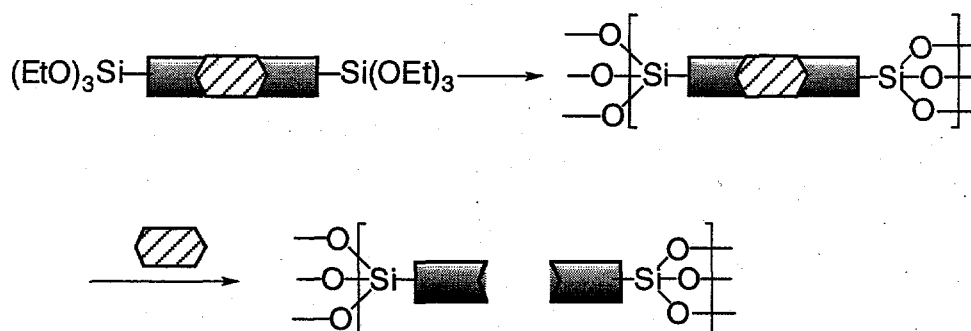
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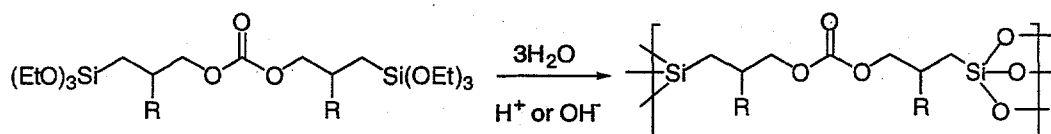
be liberated thermally, photochemically, or by chemical means. These modifications can produce changes in density, solubility, porosity, and or chemical properties of the material. Since every monomer is a potential functional group, the technique allows for the introduction of high levels of functionality in hybrid organic-inorganic 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 [6].



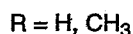
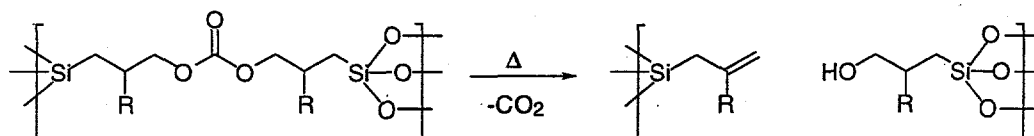
Scheme 1. Creation of new highly functionalized polysilsesquioxanes using post processing modification.

We illustrate this new concept with silsesquioxane precursors that are built around dialkylene carbonate bridging groups (**Scheme 2**). Dialkylcarbonates with β -hydrogens undergo decarboxylation to quantitatively afford an olefin and an alcohol at temperatures between 250–350 °C [9,10]. The carbonate group is also susceptible to hydrolysis by both aqueous acids and bases.

Sol-Gel Polymerization



Post-Gel Processing



Scheme 2. Sol-gel polymerization of monomers **1** ($\text{R} = \text{H}$) and **2** ($\text{R} = \text{CH}_3$) 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**, $\text{R} = \text{H}$; **X2**, $\text{R} = \text{CH}_3$) should result in cleavage of the bridging group with loss of carbon dioxide.

The dialkylencarbonate 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, polysilsesquioxane resins with pendant hydroxypropyl and olefinic substituents were prepared.

EXPERIMENTAL

General Methods

Solid-state ^{13}C NMR and ^{29}Si CP MAS NMR spectra were obtained with a Bruker AMX 400 spectrometer using glycine and $[\text{Si}_8\text{O}_{12}](\text{OSiMe}_3)_8$ external references. Thermogravimetric analyses (TGA) were performed on a Perkin-Elmer 7 apparatus under flowing nitrogen (25 cc/min). BET surface areas were determined by a Quantachrome Autosorb 6 using N_2 gas sorption analysis.

Sol-Gel Polymerizations

Monomers **1** and **2** were prepared by the chloroplatinic acid-catalyzed hydrosilylation of diallylcarbonate and dimethallylcarbonate, respectively. Both compounds gave spectral data consistent with their indicated structures. 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 by submitting the wet gels to supercritical CO_2 extraction.

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.

RESULTS AND DISCUSSION

1. Gel Formation

Formation of dialkylencarbonate bridged polymeric gels was the first requirement for this study. Sol-gel polymerizations of **1** and **2** (0.4 M in ethanol) were carried out under conditions similar to those used to prepare other hydrocarbon-bridged polysilsesquioxanes. The

monomers formed gels within 24 hours: transparent when prepared under acidic conditions, opaque, white when prepared under basic conditions. Polymeric resins were obtained from the polymerizations of the allyl and hydroxypropyl silsesquioxanes by distilling off condensation products while the sol-gel polymerization was taking place. The gels were then either crushed in water and vacuum dried to form xerogel powders or were dried as monoliths with supercritical carbon dioxide extraction to form aerogels. 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 xerogels and aerogels were non-porous indicating that the polymeric networks in the gels were sufficiently compliant to permit collapse of pores during drying [18].

2. Spectroscopic Characterization

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. The chemical shifts of the peaks in the solid state ^{29}Si NMR spectra 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. 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 $\delta_{\text{C}} = 156.0$, and three peaks due to the α , β , and γ carbons of the propylene groups at $\delta_{\text{C}} = 69.9$, 23.2, and 9.3, respectively (Figure 1A).

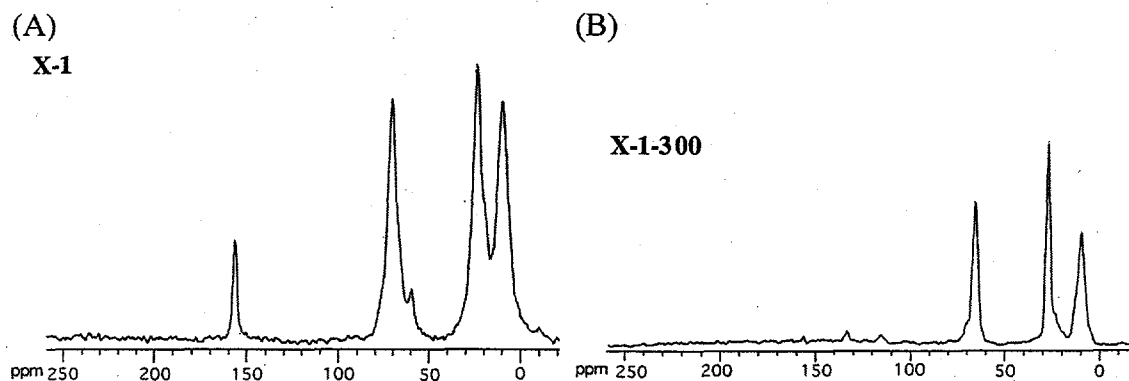


Figure 1. ^{13}C CP MAS NMR spectra of dipropylencarbonate-bridged polysilsesquioxane before (A) and after (B) pyrolysis at 300 °C for 1 hour.

3. Thermally-Induced Decarboxylations

Thermal gravimetric analysis (TGA; Figure 2) was used to establish the onset temperature for the rearrangement and loss of carbon dioxide. The onset for decarboxylation occurred near 300 °C for the dipropylene carbonate bridged gels and near 340 °C for the isobutylencarbonate-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. 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 shrinkage associated with the thermolyses, there was rarely any change in the roughness of the surface features even under examination with scanning electron microscopy. In addition, decarboxylated gels were determined by nitrogen sorption porosimetry to be non-porous. Thermal treatment of dry, monolithic gels resulted in a 40% loss in volume (no cracking was observed). Treatment of a similar monolithic gel of a hexylene-bridged polysilsesquioxane at 300 °C resulted in no measurable shrinkage.

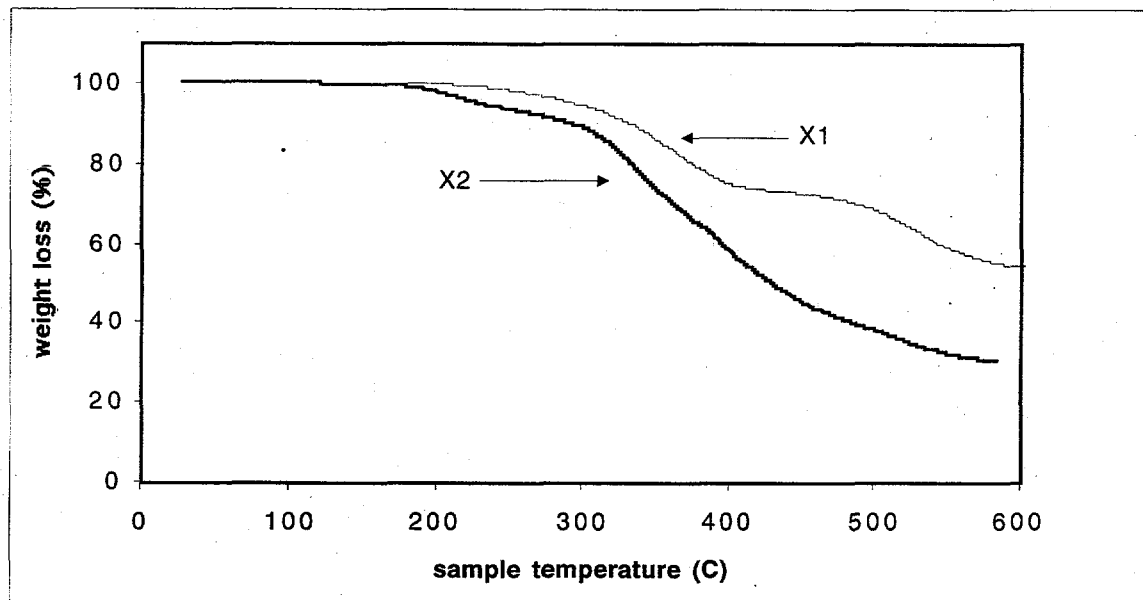


Figure 2. Thermal gravimetric analysis for dipropylencarbonate- (X-1) and diisobutylencarbonate (X-2)-bridged polysilsesquioxane gels.

Spectroscopic analysis of the thermally treated gels shows clear evidence of the decarboxylation of the carbonate bridge. Solid-state ^{13}C NMR spectra (**Figure 1B**) show loss of the carbonyl carbon after thermal treatment. At 320 °C or above both dipropylene and diisobutylene carbonate bridged materials quantitatively decarboxylated after 1 hour. 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 with chemical shifts indicative of a hydroxypropyl-substituted polysilsesquioxane. The heat-treated isobutylene- carbonate bridged materials similarly showed three large peaks, but with a slight shoulder on the downfield side of the peak at 18 ppm.

4. Silylation/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. 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. In order to insure silylation, the wet gels were treated with chlorotrimethylsilane or methoxytrimethyl silane. Solid state ^{13}C NMR spectra of the silylated polysilsesquioxanes were identical to the unsilylated

except for the addition of a single resonance at 9 ppm due to the trimethylsilyl (TMS) groups. Thermolysis of the silylated dipropylcarbonate-bridged gels at 300 °C afforded gels with strikingly different ¹³C CP MAS NMR spectra from those observed with the thermolyzed, unsilylated gels. The spectra were nearly identical to that of the copolymer of allyltriethoxysilane and acetoxypolytriethoxysilane after pyrolysis at 300 °C, except for the presence of a peak at $\delta_c = 1.5$ due to the TMS groups in the gel. Olefinic 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.

CONCLUSION

Thermal post-processing of dialkylene carbonate-bridged polysilsesquioxane xerogels was successfully used to decarboxylate and cleave the organic bridging group. Thermal gravimetric analysis revealed that the onset of decarboxylation occurred between 300 °C for dipropylcarbonate bridged materials and near 340 °C for the diisobutylene-bridged materials. Solid state ¹³C NMR confirmed the loss of the carbonate functionality. 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.

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