

CONTROLLING POROSITY IN BRIDGED POLYSILSESQUIOXANES THROUGH ELIMINATION REACTIONS

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ABSTRACT

The retro Diels-Alder reaction was used to modify porosity in hydrocarbon-bridged polysilsesquioxane gels. Microporous polysilsesquioxanes incorporating a thermally labile Diels-Alder adduct as the hydrocarbon bridging group were prepared by sol-gel polymerization of *trans*-2,3-bis(triethoxysilyl)norbornene. Upon heating the 2,3-norbornenylene-bridged polymers at temperatures above 250°C, the norbornenylene-bridging group underwent a retro Diels-Alder reaction losing cyclopentadiene and leaving behind a ethenylene-bridged polysilsesquioxane. Less than theoretical quantities of cyclopentadiene were volatilized indicating that some of the diene was either reacting with the silanol and olefinic rich material or undergoing oligomerization. Both scanning electron microscopy and nitrogen sorption porosimetry revealed net coarsening of pores (and reduction of surface area) in the materials with thermolysis.

INTRODUCTION

Hydrocarbon-bridged polysilsesquioxanes are a class of hybrid organic-inorganic materials prepared by sol-gel polymerization of bridged monomers, $(\text{EtO})_3\text{Si-R-Si}(\text{OEt})_3$, in which siloxane bonds and organic bridging groups are both integral structural components of a highly crosslinked network polymer [1]. Air drying affords micro- and mesoporous xerogels [1-4] in which the surface area and pore sizes can be controlled to some extent through the choice of the bridging group [4,5]. Alternatively, porosity can be created in non-porous gels or modified in porous gels by using the bridging organic functionality as a pore template. Previous efforts have used hydrolysis [2,6] or thermal [7] and low temperature plasma oxidations [8] to completely remove the hydrocarbon groups without any selectivity affording only inorganic silica gels as the final product.

We have prepared and characterized the first polysilsesquioxane utilizing a Diels-Alder adduct as the organic bridging group in a new approach to altering the porosity in a gel: partial decomposition of the 2,3-norbornenylene-bridging group through a *retro* Diels-Alder reaction (Figure 1). Volatile cyclopentadiene is evolved, leaving a 1,2-ethenylene-bridged polysilsesquioxane.

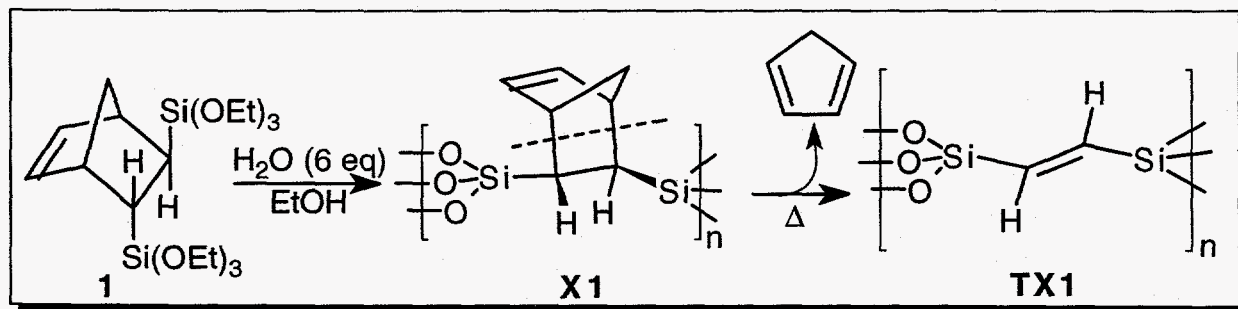


Figure 1. Preparation and retro Diels-Alder reaction of norbornenylene-bridged xerogels.

EXPERIMENTAL SECTION

The norbornenylene-bridged monomer (1) was prepared in several steps: (E)-1,2-bis(trichlorosilyl)ethene was reacted with cyclopentadiene to give *trans*-2,3-bis(trichlorosilyl)-5-

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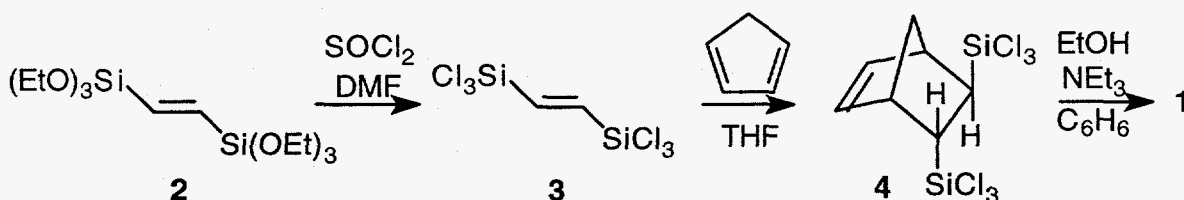
norbornene (94% yield), which was subsequently esterified with ethanol in 71% yield. Gels were prepared in ethanol (0.1-0.4 M) using 1.0 M NaOH (10.8 mol %) as catalyst/water source (6 eq. H₂O) and processed with water as described previously [3].

Norbornenylene-Bridged Polysilsesquioxanes: Solutions of **1** and aqueous NaOH (6 eq. H₂O) in ethanol were prepared and transferred to tightly stoppered glass bottles. Cloudy solutions were formed which set to form opaque gels (Table I). ¹³C CP-MAS NMR (50.2 MHz) δ 187 (ssb), 180 (ssb), 137.4, 132.8, 90 (ssb), 83 (ssb), 58.4 (CH₂CH₃), 49.1, 44.8, 25.8, 18.0 (CH₂CH₃).

Thermal Treatment of Xerogels. Weighed samples were placed in a ceramic boat and inserted into a quartz tube containing an in-line trap for collection of volatiles. The apparatus was evacuated (60 μ) and sealed from the vacuum source. The trap was cooled with liquid nitrogen as the tube was heated in a tube furnace. Xerogel X1A (0.398 g) was heated at 300°C for 3 h to give thermally treated xerogel TX1A as a light yellow powder (0.290 g, 73%). ¹³C CP-MAS NMR (50.2 MHz) δ 146, 135, 132, 59, 45, 43, 26, 18; ²⁹Si CP-MAS NMR (39.6 MHz) δ -63.7, -72.1. Anal. Calcd for C₂H₂Si₂O₃: C, 18.4; H, 1.5. Found: C, 23.69; H, 3.91. Xerogel X1B (0.398 g) was heated at 250°C for 3 h to give thermally treated xerogel TX1B as a white powder (0.327 g, 82%). ¹³C CP-MAS NMR (50.2 MHz) δ 146, 140, 138, 132, 59, 49, 44, 26, 18; ²⁹Si CP-MAS NMR (39.6 MHz) δ -63.2, -73.6. Anal. Calcd for C₂H₂Si₂O₃: C, 18.4; H, 1.5. Found: C, 27.98; H, 4.52. ¹H NMR(acetone-d₆) analysis of the volatiles from the thermolyses revealed the presence of cyclopentadiene, ethanol, and water.

RESULTS

Monomer **1** is the formal Diels-Alder adduct of (E)-bis(triethoxysilyl)ethene (**2**) and cyclopentadiene. The reaction of **2**, synthesized according to the method of Marciniak, *et al.*, [9] and cyclopentadiene or dicyclopentadiene in a high pressure reactor failed to give **1**, presumably due to the steric hinderance from the triethoxysilyl groups. To generate a more reactive dienophile, **2** was chlorinated using thionyl chloride and DMF catalyst [10], giving (E)-1,2-bis(trichlorosilyl)ethene (**3**) [11-14] in 36% yield. In contrast to **2**, dienophile **3** reacted exothermically with cyclopentadiene in solution (THF or benzene) to quantitatively give the expected Diels-Alder adduct, 2,3-bis(trichlorosilyl)norbornene (**4**). Esterification of **4** with ethanol in the presence of triethylamine readily gave the desired norbornenylene-bridged monomer **1** in good yield (71%).



Polymerization and Characterization. Sol-gel polymerization of bridged triethoxysilane monomers involves the hydrolysis of ethoxysilyl groups to silanols, followed by intermolecular condensation reactions to form siloxane linkages in a network polymer [1]. Examination of gel times for **1** gives some indication of the impact of the sterically bulky norbornenylene-bridging group upon intermolecular siloxane bond formation. Polymerization of ethenylene-bridged monomer **2** (0.4 M in ethanol) proceeds to give gels under basic conditions within a few minutes [15]. Solutions (0.4 M) of norbornenylene-bridged monomer **1** with NaOH (10.8 mol %) took six days to form opaque gels. Since **2** has olefinic (sp²) carbons rather than the saturated (sp³) carbons of **1**, its polymerization rate would be expected to be enhanced under basic conditions compared with alkyl (sp³) substituted triethoxysilanes. However, 1,6-bis(triethoxysilyl)hexane, a monomer with an alkyl (sp³) substituent attached to the triethoxysilyl groups, formed gels within 1 hour under identical conditions. Under acidic conditions, where alkyl substituents should enhance condensation rates, no gels were obtained from **1**, even after several months at 1 M monomer

concentration [16] Under identical conditions, **2** formed gels within 6 days [15] and 1,6-bis(triethoxysilyl)hexane formed gels within 12 hours.

Upon processing and drying, xerogels from both **1** and **2** were obtained as insoluble, white powders. The clear colorless solutions obtained from the acid-catalyzed sol-gel polymerization of **1** gave solid residues with removal of solvent *in vacuo*. After drying, white powders were obtained that were soluble in organic solvents indicating that the materials were either oligomers or mostly linear polymers.

Table I. Conditions, Gel Times, and Surface Area Measurements for the Sol-Gel Polymerization of **1** under Base Catalysis.

Xerogel	Conc. (M)	Gel time	Yield (%)	BET Surface Area (m ² /g)	t-Method Micropore Area (m ² /g)	Mesopore Area (m ² /g)	Ave. Pore Diam. (Å)
X1A	0.4	6 d	79	419	316	103	25.3
X1B	0.4	6 d	88	434	329	105	24.6
X1C	0.2	13 d	100	422	311	111	25.2
X1D	0.1	197 d	106				

Nitrogen sorption porosimetry revealed all the xerogels to be porous (**Table I**). Norbornenylene-bridged xerogels **X1A-C** had higher micropore areas and smaller average pore diameters than those prepared from **2**, which were completely mesoporous. Based on plots of the incremental pore volume from the adsorption isotherm versus pore size [4], most of the pore volume in norbornenylene-bridged xerogels **X1A-B** resulted from microporosity (pore diameter <20Å). The soluble materials prepared from **1** under acidic conditions were non-porous.

Cross Polarized-Magic Angle Spinning (CP-MAS) ¹³C NMR of the xerogels revealed that the hydrocarbon bridges remained intact throughout the polymerization and processing. The norbornenylene-bridged xerogels **X1A-C** gave resonances due to both the hydrocarbon bridge as well as residual ethoxy groups, a consequence of the slow rate of hydrolysis at the sterically hindered silicon atoms. In the ²⁹Si CP-MAS NMR, **X1A-C** gave broad resonances which could not be deconvoluted to quantify Tⁿ distribution (Tⁿ describes a trifunctional silicon containing n siloxane bonds) and calculate the degree of condensation, however the signals were centered in the T² region for alkylene-bridged systems (δ -58.8) [17]. The soluble oligomers gave several peaks in the ²⁹Si NMR spectra (acetone-d₆) indicative of partial hydrolysis and condensation: δ -50.0 (T¹), -51.6 (T¹), -54.9 (T¹), -58.6 (T²), -65.0 (T³). No Qⁿ resonances due to silica were observed for any of the gels, indicating no Si-C hydrolysis had occurred.

Thermolysis. Gels made from norbornenylene-bridged monomer **1** provide an interesting opportunity for chemical modification *after* polymerization due to the thermal reversibility of the [4 + 2] Diels-Alder cycloaddition reaction. Ideally, an ethenylene-bridge would remain in the polysilsesquioxane network and volatile cyclopentadiene (b.p. 40°C) would be eliminated. Complete elimination of cyclopentadiene from a fully condensed norbornenylene-bridged gel would result in a 34% mass loss.

Thermogravimetric Analysis (TGA) was used to establish the onset temperature of the retro Diels-Alder reaction. Under flowing nitrogen (25 cc/min) at a moderate heating rate (10°C/min), the norbornenylene-bridged gels started losing mass at 160°C with a second onset of mass loss at 360°C. At a slower heating rate (1°C/min), the mass loss onset temperatures were lowered (140 and 330°C, respectively), indicating that diffusion may play a role in the rate of mass loss. The identity of the volatiles during the thermolysis of norbornenylene-bridged gels was established by TGA-MS (heating rate = 60°C/min). Below 340°C, only molecular ions due to water and ethanol from further condensation reactions were observed. Above 340°C, the molecular ion for cyclopentadiene (m/z = 67, [M+H]⁺) was detected.

Larger scale themolyses (0.4 g) were run in a tube furnace (300 and 250°C) to allow analysis and quantitation of the pyrolysate and volatiles. Judging from the change in mass, residual

norbornene groups remained in the thermally treated gels **TX1A** and **TX1B** (mass loss = 27 and 18%, respectively); a somewhat larger mass loss was expected since the precursor gels **X1A-B** should also undergo further hydrolysis and condensation. ^1H NMR analysis of the volatiles collected with a cold trap (-197°C) during the thermolyses confirmed that water and ethanol, as well as cyclopentadiene, were evolved. Thermolysis of ethenylene-bridged gels under identical conditions resulted in virtually no mass loss and only traces of volatiles were produced. By TGA ($10^\circ\text{C}/\text{min}$), untreated ethenylene-bridged gels heated to 900°C under nitrogen gave a ceramic yield of 96%.

^{13}C CP-MAS NMR spectra of the thermally treated gels (**TX1A** and **TX1B**) along with the unheated norbornenylene-bridged (**X1A**) and ethenylene-bridged xerogels are shown in **Figure 2**. The spectra reveal the decomposition of the norbornenylene group and the emergence of the new ethenylene-bridged structure. The sample heated at 250°C (**TX1B**) exhibited the resonance (δ 146) from the ethenylene carbons and reduced contributions from norbornenylene sp^3 (δ 49.5, 44.8, 26.2) and sp^2 (δ 137.5, 132.7) carbons relative to the ethoxide signals (δ 58.4, 18.0). Greater conversion to the ethenylene-bridged material at 300°C (**TX1A**) was evidenced by an even greater contribution from ethenylene carbons. However, even after 3 hours at 300°C , attenuated peaks from the norbornenylene group still remained in the gel.

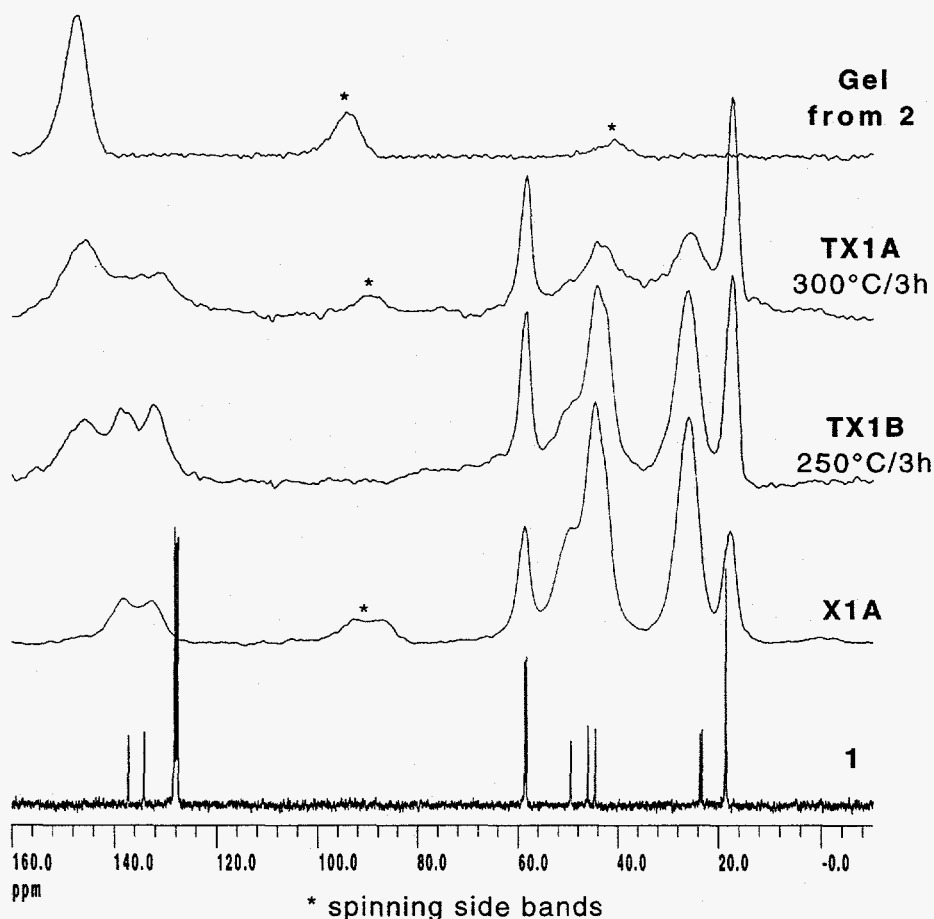


Figure 2. Evolution of ^{13}C CP-MAS NMR Spectra of Norbornenylene-Bridged Gels with Thermal Treatment and Comparison with an Ethenylene-Bridged Gel.

The ^{29}Si CP-MAS NMR spectra also revealed the conversion of the norbornenylene bridge to an ethenylene-bridging group (**Figure 3**). **TX1B** displayed a new shoulder upfield of the norbornenylene-silsesquioxane T^2 at δ -58.8. After thermolysis at 300°C , the shoulder had become a distinct resonance at δ -72, indicative of T^2 silicon in an ethenylene-bridged polysilsesquioxane. The T^2 silicon is consistent with the assignment of the silicon peak in the

untreated norbornylene-bridged polymers as T^2 suggesting that the degree of condensation was relatively unperturbed by the thermolysis.

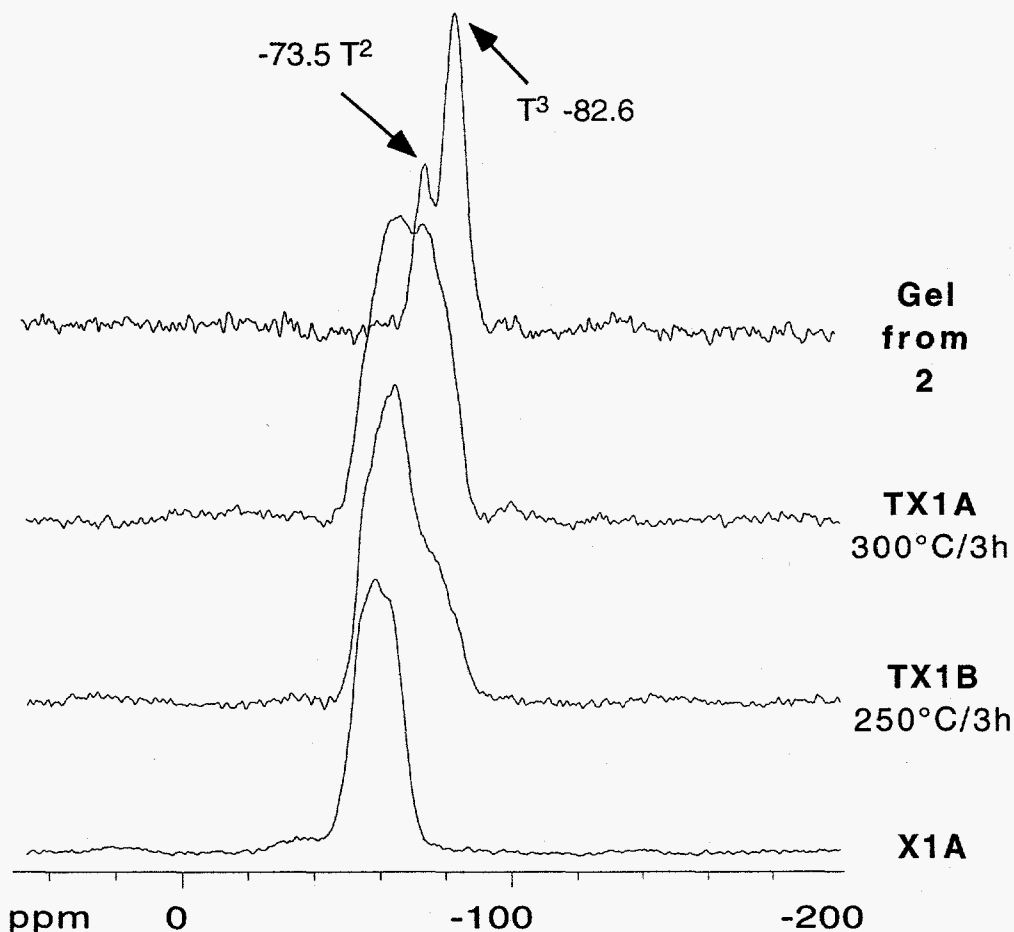


Figure 3. Evolution of ^{29}Si CP-MAS NMR Spectra of Norbornenylene-Bridged Gels with Thermal Treatment and Comparison with an Ethenylene-Bridged Gel.

After thermolysis, the composition [18] of TX1A and TX1B reflected the loss of hydrocarbon from the polymer, moving considerably closer to the theoretical composition for the ethenylene-bridged polysilsesquioxane (C, 18.4%; H, 1.5%). Incomplete conversion to the ethenylene-bridged material may be due to either oligomerization of cyclopentadiene, irreversible (radical) reactions with the ethenylene-bridging groups, or reactions with silanols. In our hands, thermal polymerization (300 °C) of neat cyclopentadiene was possible in a ethenylene-bridged polysilsesquioxane gel, resulting in a white carbon-rich polymer. Acidic silanol groups in the gels may assist or catalyze polymerization of some of the volatilized cyclopentadiene during the thermolysis of X1A as well, however, no resonances in the ^{13}C CP-MAS NMR for polymeric cyclopentadiene were identified possibly as a consequence of overlapping signals.

TX1A and TX1B still retained high surface areas (282 and 321 m^2/g , respectively), however, some microporosity and mesoporosity was lost. In contrast, the thermal treatment of ethenylene-bridged gels at 250 or 300 °C resulted in *no change* in surface area or pore size distribution. The change in porosity for the norbornenylene-bridged gels, therefore, was a direct result of the elimination of cyclopentadiene as well as from further condensation. Scanning electron micrographs of a norbornenylene-bridged polysilsesquioxane before and after treatment at 300 °C confirmed the coarsening of the pores for the thermally treated norbornenylene-bridged gels.

CONCLUSIONS

Norbornenylene-bridged polysilsesquioxanes were prepared as the first representatives of sol-gel processed materials that can be structurally modified utilizing the retro Diels Alder reaction. These materials were successfully prepared as gels under alkaline conditions, but under acidic conditions, only soluble oligomers were isolated. The retro Diels Alder reaction was realized with thermolysis of these materials at temperatures over 250 °C. However, complete conversion to an ethenylene-bridged polysilsesquioxane was never observed, even after continued treatment at 300 °C, suggesting that the cyclopentadiene may have undergone side reactions that prevented its egress from the porous material. Thermolysis was accompanied by an apparent sintering of the materials. Significant loss of microporosity was observed by nitrogen sorption porosimetry.

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18. Due to the formation of carbides, elemental analyses were generally low in carbon, even with higher analysis temperature and the addition of combustion aid.

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