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STRUCTURAL MODIFICATION OF SOL-GEL MATERIALS THROUGH RETRO DIELS-ALDER REACTION

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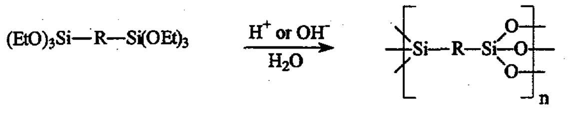
Introduction

Hydrolysis and condensation of organically bridged bis-triethoxysilanes, $(EtO)_3Si\text{-}R\text{-}Si(OEt)_3$, results in the formation of three dimensional organic/inorganic hybrid networks (Equation 1).[1] Properties of these materials, including porosity, are dependent on the nature of the bridging group, R. Flexible groups (alkylene-spacers longer than five carbons in length) polymerize under acidic conditions to give non-porous materials.[2] Rigid groups (such as arylene-, alkynylene-, or alkenylene) form non-porous, microporous, and macroporous gels.[3] In many cases the pore size distributions are quite narrow.



(1)

One of the motivations for preparing hybrid organic-inorganic materials is to extend the range of properties available with sol-gel systems by incorporating organic groups into the inorganic network.[4] For example, organically modified silica gels are either prepared by co-polymerizing an organoalkoxysilane with a silica precursor or surface silylating the inorganic gel. This can serve to increase hydrophobicity or to introduce some reactive organic functionality. However, the type and orientation of these organic functionalities is difficult to control. Furthermore, many organoalkoxysilanes can act to inhibit or even prevent gelation, limiting the final density of organic functionalities. We have devised a new route for preparing highly functionalized pores in hybrid materials using bridging groups that are thermally converted into the desired functionalities after the gel has been obtained.[5]

In this paper, we present the preparation and characterization of bridged polysilsesquioxanes with Diels-Alder adducts as the bridging groups from the sol-gel polymerization of monomers **2** and **4**. The bridging groups are constructed such that the retro Diels-Alder reaction releases the dienes and leaves the dienophiles as integral parts of the network polymers. In the rigid architecture of a xerogel, this loss of organic functionality should liberate sufficient space to modify the overall porosity. Furthermore, the new porosity will be functionalized with the dienophilic olefin bridging group. We also demonstrate that by changing the type of Diels-Alder adduct used as the bridging group, we can change the temperature at which the retro-Diels-Alder reaction will occur (Fig. 1).

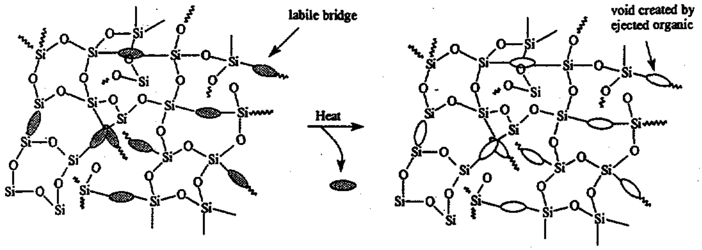


Figure 1. Template effect of partially removable bridging group.

Experimental

(E)-2,3-bis(triethoxysilyl)norbornene.[2,6] An excess of cyclopentadiene (5.4 g, 0.082 mol) and trans-2,3-bis(triethoxysilyl)ethene were placed in a Carrius tube, freeze-pump-thaw degassed and sealed. The tube was heated at 100 °C for 48 hours. The volatiles were removed under vacuum and the product distilled at 103 °C/220 mtorr. Yield, 5.0 g (62 %). ^1H NMR (C_6D_6): $\delta = 6.04$ (m, 1H), 5.94 (m, 1H), 3.77 (m, 12H), 3.02 (m, 1H), 2.91 (m, 1H), 1.37 (m, 1H), 1.24 (m, 1H), 1.18 (m, 19H), 0.68 (m, 1H). ^{13}C NMR (C_6D_6): δ =137, 134, 58.5, 58.1, 49.0, 45.4, 43.9, 22.9, 22.5, 18.2, 18.1.

(E)-bis(trichlorosilyl)ethene.[6,7] (E)-bis(triethoxysilyl)ethene (22 g, 0.062 mol) was added dropwise to an excess of thionyl chloride (89 g, 0.75 mol) containing a catalytic amount of pyridinium chloride (1.8 g, 0.016 mol) at room temperature. The mixture was then refluxed for 24 hours. and the excess thionyl chloride removed by distillation. The product was isolated by bulb to bulb vacuum distillation at approximately 60°C. ^1H NMR indicated full conversion of the ethoxysilane to the chlorosilane.

(E)-2,3-bis(trichlorosilyl)oxonorbornene. An excess of furan (13 g, 0.19 mol) and (E)-bis(trichlorosilyl)ethene were placed in a Carrius tube, freeze-pump-thaw degassed and sealed. The tube was heated at 75°C for 24 hours. The volatiles were removed under vacuum and the temperature sensitive product used without further purification. Yield, 6.7 g (77 %). ^1H NMR (C_6D_6): $\delta = 6.1$ (dd, 1H), 5.9 (dd, 1H), 4.9 (m, 1H), 4.8 (m, 1H), 2.0 (dd, 1H), 1.3 (m, 1H). ^{13}C NMR (C_6D_6): $\delta = 137$, 133, 81.2, 80.0, 36.1, 35.8.

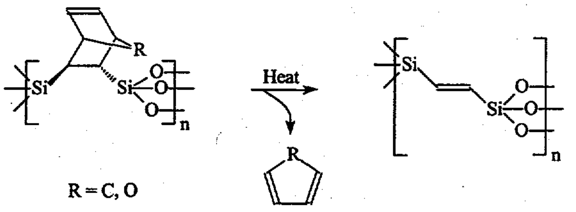
Polymerization of (E)-2,3-bis(triethoxysilyl)norbornene. In a typical reaction, 1N HCl or NaOH was mixed with ethanol or THF and the solution added to the monomer. The monomer concentration was maintained at 0.4 M and the water/monomer ratio at 6/1 equivalents. Gels were crushed, washed with water, ether and dried.

Polymerization of (E)-2,3-bis(trichlorosilyl)oxonorbornene. Water (6 equiv) was added to a stirred solution of the monomer (1.5 g) in THF (10 mL) at 0 °C. The precipitated polymer was washed with THF and dried under vacuum.

Results and Discussion

The polysilsesquioxane networks were designed with Diels-Alder adduct bridging groups in order to permit thermal modification of the polymeric architecture with the retro Diels-Alder reaction. The Diels-Alder adducts selected for this study were norbornene and oxonorbornene with silsesquioxane groups attached at the 2- and 3- positions. The expected product in both cases is the ethenylene-bridged polysilsesquioxane and the free diene. Note that during loss of organics, no bridging groups are cleaved (Equation 2).

The norbornenylene-bridged monomer used in this study ((E)-2,3-bis(triethoxysilyl)norbornene, **2**) was prepared by the Diels-Alder reaction of cyclopentadiene with (E)-bis(triethoxysilyl)ethene, **1** (Scheme 1). The (Z) isomer was not used since it can form both the endo and exo diastereomers which, if not separated, could exhibit different gelation rates resulting in non-homogeneous gels. The endo and exo isomers formed from the (E) isomer are enantiomeric and, therefore, have identical physical and chemical properties. Retro DA reaction of the polymer formed from **2** was expected to cause ejection of cyclopentadiene, leaving the ethenylene-bridged polymer intact (Equation 2).



(2)

Sol -gel polymerization of **2** under basic conditions successfully yielded gels, but under acidic conditions, only soluble oligomers formed. Thermogravimetric analysis of the polymeric xerogels indicated that the retro DA loss of cyclopentadiene occured at temperatures greater than 250 °C. Solid state ^{13}C NMR revealed the olefinic resonances from the ethenylene-bridged polysilsesquioxane arising from the retro Diels-Alder reaction. However, there were also significant contributions from saturated carbons consistent with degradation/polymerization of the norbornenyl groups and cyclopentadiene. Nitrogen sorption porosimetry of the thermolyzed polymer indicated a *significant loss* of microporosity. This coupled with the discovery

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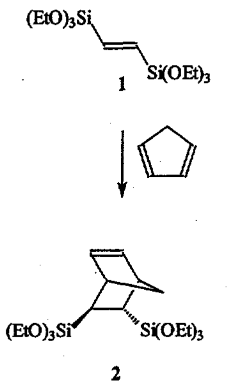
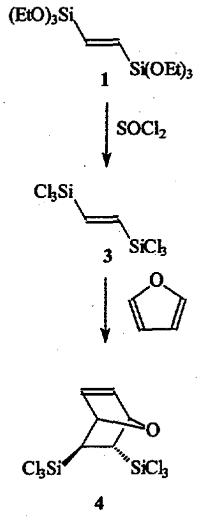
by thermal gravimetric analyses and solid state ^{13}C NMR that the retro Diels-Alder reactions were not complete, indicated that the reaction conditions were too extreme.[6]



Scheme 1. Preparation of (E)-2,3-bis(triethoxysilyl)norbornene, **2**.

Oxonorbornenyl DA adducts are known to release furan at relatively low temperatures, often below 100 °C.[8,9] Therefore incorporation of the oxo-norbornenylene functionality into the bridging group in polysilsesquioxane gels reduces the likelihood of side reactions or decomposition. Attempts to prepare the oxonorbornenylene monomer from the Diels-Alder reaction of 1,2-bis(triethoxysilyl)ethene and furan did not proceed requiring the use of the more electron deficient 1,2-bis(trichlorosilyl)ethene dienophile (Scheme 2).



Scheme 2. Synthesis of (E)-2,3-bis(trichlorosilyl)oxonorbornene, **4**.

Thermogravimetric analysis of a polymeric material prepared from **4** indicated that the retro DA reaction, releasing furan, occurred at approximately 90 °C. The data also showed that the loss was quantitative providing the means to prepare ethenylene-bridged polysilsesquioxanes through the retro DA without degradation of the porosity or functionality.

Conclusions

Norbornenylene and oxonorbornenylene bridged polysilsesquioxanes, designed to undergo retro DA at elevated temperature, were prepared. The norbornenylene system underwent retro DA at temperatures greater than 250 °C. However, the retro step was not quantitative, suggesting that the reaction was not complete or that the ejected cyclopentadiene was undergoing side reactions. The oxonorbornenylene system underwent retro DA at temperatures less than 100 °C and the ejection of furan appears to be quantitative. Efforts are presently underway to evaluate the changes in porosity of the hybrid material and to see if the forward Diels-Alder reaction can be run with the xerogels and if there is molecular recognition through a template effect.

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