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Bridged Polysilsesquioxane Xerogels: A Molecular Based Approach for the Preparation of Porous Hybrid Organic-Inorganic Materials.

James H. Small and Kenneth J. Shea*
Department of Chemistry
University of California-Irvine
Irvine, CA 92717-2025

and

Douglas A. Loy
Properties of Organic Materials Department
Sandia National Laboratories
Albuquerque, NM 87185-0367

Introduction

Hybrid organic-inorganic materials represent one of the most rapidly expanding areas of materials chemistry.[1] These novel composites incorporate the flexibility and ease of manufacturing commonly found in organic polymers as well as the structural rigidity and high thermal stability typical of inorganic oxide networks.

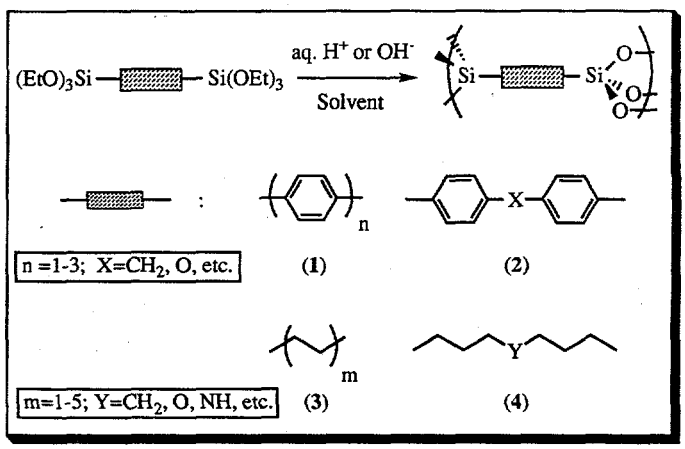
There have been three primary approaches for the preparation of hybrid organic-inorganic materials. The first approach involves the formation of an organic-inorganic polymer blend. This can be readily achieved by simply mixing the organic and inorganic components together mechanically. A common problem associated with this method is the formation of phase separation between the organic and inorganic components which oftentimes results in a drastic alteration of the bulk properties of the resulting hybrid material. Alternatively, recent investigations have examined the in situ formation of an inorganic oxide network in the presence of an organic polymer to yield a homogeneous organic-inorganic polymer blend.[2] This route has successfully reduced the amount of phase separation present within the hybrid material.

The second approach utilized for the preparation of hybrid organic-inorganic materials involves the synthesis of a multicomponent block copolymer composed of a difunctional organic polymer and a di-, tri-, or tetrafunctional inorganic oxide.[3] As with the mechanically mixed polymer blends, careful choice of the organic component must be considered due to the potential formation of a phase separated hybrid material.

The third approach used for the preparation of hybrid organic-inorganic materials involves the synthesis of a difunctional monomer combining both organic and inorganic functionalities. Subsequent polymerization affords a hybrid material whereby both organic and inorganic domains are intimately mixed at the molecular level (~1-10 Å). Because the organic and inorganic domains are dispersed at the molecular level the problems associated with phase separation do not occur. An example of this type of approach is seen in the preparation of T-resins[4] or polyhedral silsesquioxanes[5], two families of materials prepared from organotrialkoxysilanes. However, due to the relatively low amount of functionality present within the monomeric precursor (i.e. trifunctional), these materials are often prepared as a copolymer with tetraethoxysilane. This produces a hybrid material with increased amounts of inorganic functionality thereby altering the bulk properties of the material. In summary, this methodology offers the potential for the preparation of a wide variety of materials with differing morphologies.

For the past ten years the Shea group has been interested in the synthesis and characterization of bridged polysilsesquioxanes, a new family of hybrid organic-inorganic materials which contain both organic and inorganic components within the same monomeric building block (Scheme 1).[6] This has been achieved by incorporating a bridging organic moiety between two triethoxysilyl functionalities. Sol-gel polymerization of the bridged molecular-level "building block" produces a hybrid organic-inorganic polysilsesquioxane material. In analogy to the preparation of T-resins, this approach results in a *homogeneous* dispersion of the organic and inorganic components at the molecular level. Yet, in contrast to the preparation of T-resins, bridged polysilsesquioxanes may be prepared as homopolymers at much lower concentrations (as low as 0.04 M). This allows for the preparation of hybrid materials with increased amounts of organic functionality. Most importantly, alteration of the bridging organic component offers an incredible potential for the synthesis of a vast array of hybrid composite materials. Bridged polysilsesquioxanes may find applications as chromatographic and catalyst supports, ion-exchange resins, optical matrices, or as pre-ceramic materials.

We wish to report here an overview of the synthesis and characterization of bridged polysilsesquioxane xerogels. The primary focus will be on the molecular-level approach for the preparation of porous hybrid organic-inorganic composites. Specifically, the effect of alteration of the bridging organic component, and its effect on the resulting hybrid material, will be addressed.

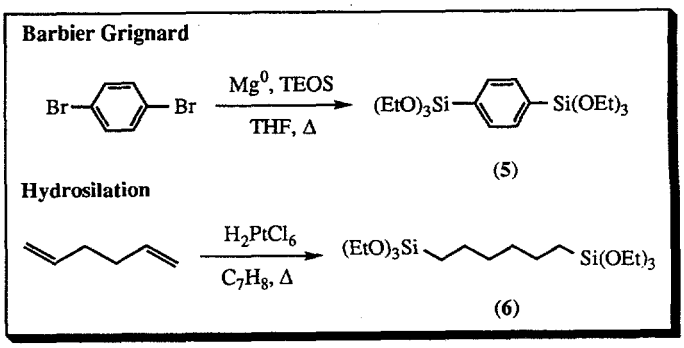


Scheme 1. Families of bridged polysilsesquioxanes.

Experimental

Monomer Synthesis

Arylene- (**1**) and heteroarylene-bridged (**2**) families of bis(triethoxy)silane monomers were prepared utilizing Barbier Grignard conditions from the corresponding arylene dibromide. In contrast, the alkylene- (**3**) and heteroalkylene-bridged (**4**) families of bis(triethoxy)silane monomers were prepared by hydrosilation of the corresponding α,ω-diene. Examples are given below for the synthesis of 1,4-bis(triethoxysilyl) benzene (**5**) and 1,6-bis(triethoxysilyl) hexane (**6**) (Scheme 2). Purity of all monomers was verified by ^{1}H, ^{13}C, and ^{29}Si NMR, IR, MS, and gas chromatography.



Scheme 2. Syntheses of arylene-(**5**) and alkylene-bridged (**6**) bis(triethoxy)silane monomers.

Polymer Synthesis

Bridged polysilsesquioxane xerogels were prepared by the sol-gel process under acid or base catalyzed conditions. The sol-gel process offers a convenient and efficient method for the polymerization of alkoxysilanes under extremely mild conditions.[7] In general, the xerogels were prepared as follows: an amount of monomer corresponding to a 0.4 or 0.2 M solution was weighed in the appropriate volumetric flask. To this was added solvent to ~1 mL below the mark. Note: ethanol was used as solvent for the alkylene- and heteroalkylene-bridged monomers while tetrahydrofuran was used for the arylene- and heteroarylene-bridged monomers. The correct amount of catalyst corresponding to 6 equivalents of water was then added and the solution diluted to the mark with additional solvent. The solution was shaken vigorously to insure homogeneity, poured into a polyethylene bottle, capped and sealed. Gellation normally occurs within 1-12 hours. However, depending upon reaction conditions, gellation may require days or even weeks to occur. The gel is then aged for 1 week and processed. The materials were processed by either "solvent series" or "water" processing conditions, air-dried for 2-3 days, ground, and dried under dynamic vacuum (< 1 mTorr, ~12 h) at 100°C to afford the corresponding amorphous polysilsesquioxane xerogel in approximately quantitative yield.

Polymer Characterization

The polysilsesquioxane xerogels were characterized by ^{13}C and ^{29}Si solid state NMR, IR, thermal analysis (DSC and TGA), adsorption porosimetry (N_2 and Ar), SEM, and elemental analysis. A brief summary of the results of a few of these techniques will be presented in this paper.

Results and Discussion

Solid State NMR

Due to the insoluble nature of bridged polysilsesquioxane xerogels, ^{13}C and ^{29}Si cross-polarization magic angle spinning (CP MAS) and Bloch decay (MAS) experiments were conducted to analyze the degree of condensation (^{29}Si) as well as the retention and stability of the bridging organic component (^{13}C and ^{29}Si). The polysilsesquioxane xerogels exhibit moderate to high degrees of condensation (~55-89%) indicative of highly cross-linked materials. An example of this is shown in the ^{29}Si CP MAS solid state NMR spectra of a base catalyzed 1,7-bis(propyl-ether) polysilsesquioxane xerogel where the predominant resonance is the completely condensed silicon species containing three siloxane linkages (T^3) (Figure 1). Examination of *all* of the polysilsesquioxane families reveals a general trend whereby higher degrees of flexibility, as found in the alkylene- and heteroalkylene-bridged materials, correspond to higher degrees of condensation. In a similar manner, the heteroarylene-bridged polysilsesquioxane xerogels also exhibit higher degrees of condensation as compared to the more rigid arylene-bridged materials. ^{13}C Solid state NMR experiments verify the retention of the bridging organic component indicative of stability of the silicon-carbon bond under sol-gel processing conditions.

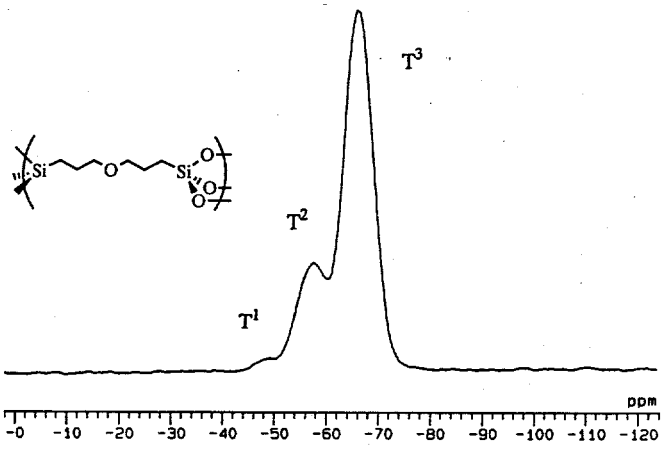


Figure 1. ^{29}Si CP MAS NMR spectra of a 1,7-bis(propyl-ether) polysilsesquioxane xerogel.

Surface Area and Porosity

The bridged polysilsesquioxane xerogels were analyzed for surface area and porosity by nitrogen and argon sorption porosimetry. These materials exhibit high surface areas (up to ~1300 m^2/g) and porosity primarily confined to the micropore (< 20 Å) and low mesopore domains (< 100 Å). Nitrogen gas sorption porosimetry was used to establish surface areas by the Brunauer-Emmett-Teller method (BET)[8]. Pore size distributions were determined by the Barrett-Joyner-Halenda method (BJH).[9] The more rigid organic spacers (i.e. arylene- and heteroarylene-bridge) result in microporous materials regardless of spacer length. In contrast, flexible organic spacers (i.e. alkylene- and heteroalkylene-bridge) result in low meso-/microporous materials with a relatively narrow pore size distribution. In addition, base catalyzed xerogels were seen to exhibit significantly greater surface areas for both the rigid and flexible spacers. However, this phenomenon is most profound for the flexible systems. The polymeric nature of the acid catalyzed polysilsesquioxane material during sol-gel processing conditions has been well documented. Subsequent drying of this material results in a large degree of pore collapse within the material producing a low volume xerogel with reduced surface area. Based upon these results, structural rigidity of the organic bridging component appears to be a key element in the preparation of high surface area hybrid organic-inorganic composite materials.

Analysis of the adsorption-desorption isotherm by the BJH method reveals that bridged polysilsesquioxane xerogels exhibit extremely narrow pore size distributions.[10] Shown below is the nitrogen average pore size distribution for a 1,7-bis(propyl-ether) bridged polysilsesquioxane xerogel (Figure 2).

Thermal Analysis

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) experiments conducted on the polysilsesquioxane xerogels indicate thermal stability up to 600°C. The flexible organic spacers (i.e. alkylene- and heteroalkylene-bridge) exhibit an onset of decomposition at ~400-500°C while the more rigid organic spacers (i.e. arylene- and heteroarylene-bridge) exhibit an onset of decomposition at 500-600°C.

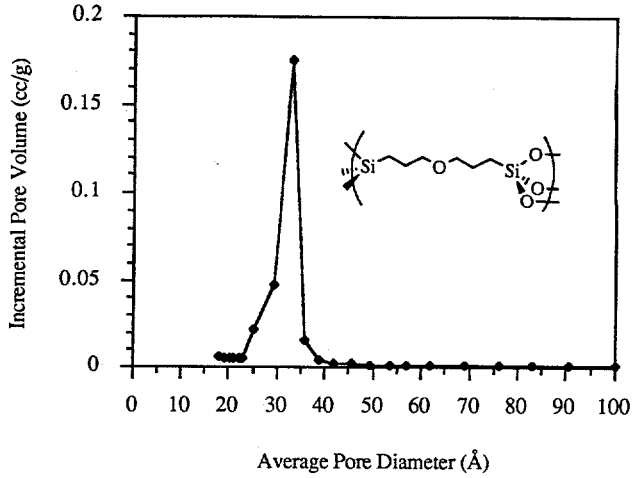


Figure 2. Nitrogen BJH desorption average pore diameter plot of a 1,7-bis(propyl-ether) bridged polysilsesquioxane.

Conclusion

Bridged polysilsesquioxanes represent an interesting family of hybrid organic-inorganic composite materials. It has been shown that manipulation of the organic bridging component offers the potential for the synthesis of a variety of materials with a range of surface areas and porosities. In addition, incorporation of a heteroatom within the bridging organic component allows for further chemical transformation of the polysilsesquioxane material.

Acknowledgments

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