LA-UR- 04-5681

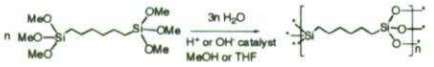
Approved for public release;
distribution is unlimited.

Title:	Influence of Aging Time on Porosity, Morphology & Structure of Hexylene-Bridged Polysilsesquioxane Gels
Author(s):	Douglas A. Loy, Kimberly A. DeFriend, and James H. Small
Submitted to:	228th American Chemical Society National Meeting

Los Alamos
NATIONAL LABORATORY

Introduction

Hexylene-bridged polysilsesquioxanes are hybrid organic-inorganic materials prepared by the sol-gel polymerization of 1,6-bis(trimethoxysilyl)hexane monomer **1**.



Previous studies showed that high surface area xerogels could be prepared from **2** with base catalyzed polymerizations while non-porous xerogels could be prepared with acidic catalysts. However, these xerogels were obtained from gels that had been aged for two weeks. The object of this study was to ascertain the influences of aging time (3, 7, 14, 28, 42, and 56 days) on the properties of the resulting xerogels.

Experimental

Monomers **1** was obtained from Gelest and was checked for purity using gas chromatography, and distilled to purify. Sol-gel polymerizations were carried out by mixing a solution of monomer in anhydrous alcohol or THF with a solution of water in alcohol or THF and catalyst in anhydrous alcohol or THF. "Standard" polymerization conditions were 0.4 M monomer concentration reacting with 6 equivalents (2.4 M) water with aqueous hydrochloric acid (0.043M) for the acid-catalyzed polymerizations and aqueous sodium hydroxide (0.043M) for the base-catalyzed polymerizations. Gels were aged for 2 weeks before crushing, washing with water and drying at 100 °C under vacuum for 24 hours. All polymerizations were carried out at least in triplicate.

Results

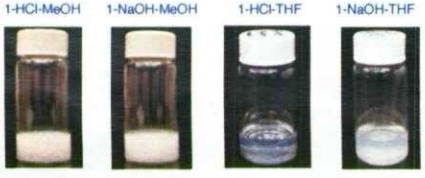
Hexylene-bridged polysilsesquioxanes formed quickly under acidic conditions in THF and under basic conditions in methanol. Slowest gelation was observed in THF, likely due to the immiscibility of the aqueous base with THF. In all cases, gels were obtained within 52 hours.

Chart 1. Gelation times for Monomers **1** (0.4 M) & six equivalents of water.

		Gel Times (Min)	
Monomer	Solvent	HCl	NaOH
1	MeOH	420	45
1	THF	7	3120.

The gels prepared in methanol were white and opaque (Figure 1). Those prepared in THF were translucent. With drying, the gels became white, brittle glassy xerogels that are insoluble in organic solvents and water. The xerogels prepared from **1** in THF with acid were non-porous. The remaining xerogels were porous.

Figure 1. Appearance of Gels prepared from **1** (0.4M) with six equivalents of water.



Porosity

Surface Areas (BET) and mean pore diameters (BJH) for hexylene-bridged polysilsesquioxanes of the xerogels were measured and plotted to show changes with aging (Charts 2-7). The surface area results for xerogels prepared in methanol with acid are shown in Charts 2 & 3.

Chart 2. Changes in nitrogen sorption (BET) surface areas for xerogels prepared from gels prepared in methanol with HCl then aged for periods ranging from 3 days to 8 weeks.

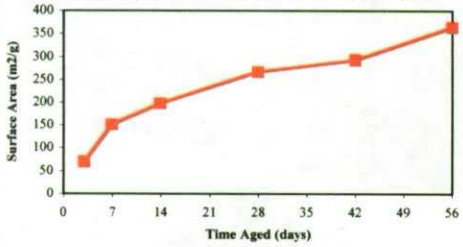
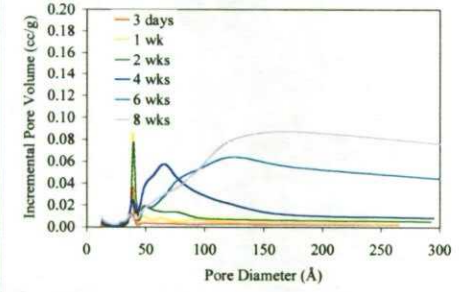


Chart 3. Changes in pore size distributions plots for xerogels prepared from gels prepared in methanol with HCl then aged for periods ranging from 3 days to 8 weeks.



The surface area in the acid catalyzed xerogels was shown to steadily increase with the amount of time provided for the gels to age. Examination of the pore size distribution plots (Chart 3) indicate that the original porosity was almost entirely from a narrow distribution of mesopores 38 Å in diameter. The increase in surface area came from the steady development of larger pores (coarsening) over time.

In contrast, the xerogels prepared from **1** in methanol with base showed an initial, dramatic increase in surface area with aging time of the gels, followed by a precipitous decline (Chart 4).

Chart 4. Changes in nitrogen sorption (BET) surface areas for xerogels prepared from gels prepared in methanol with NaOH then aged for periods ranging from 3 days to 8 weeks.

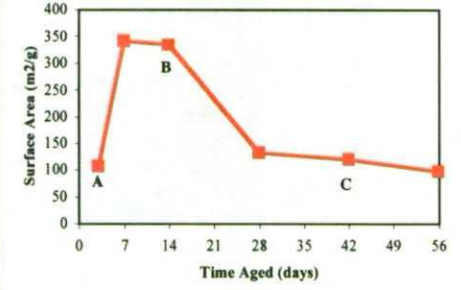
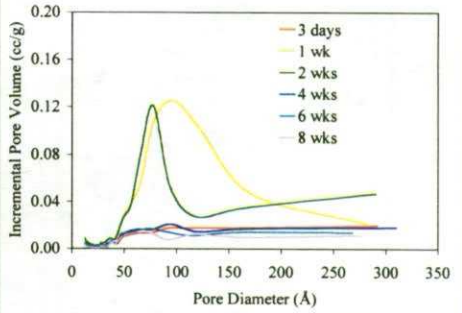


Chart 5. Changes in pore size distributions plots for xerogels prepared from gels prepared in methanol with NaOH then aged for periods ranging from 3 days to 8 weeks.



Examination of the pore size distributions revealed that the xerogels were generally mesoporous, but that the increase in surface area exhibited by the xerogels made from gels aged 1 & 2 weeks corresponded to a sharp increase in medium sized pores. The origin of this reproducible effect has not yet been determined.

Chart 6. Changes in nitrogen sorption (BET) surface areas for xerogels prepared from gels prepared in THF with NaOH then aged for periods ranging from 3 days to 8 weeks.

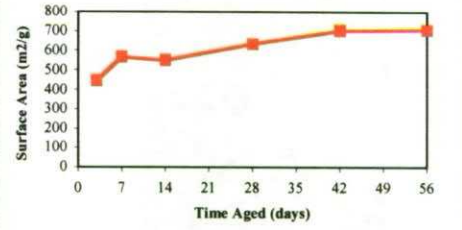
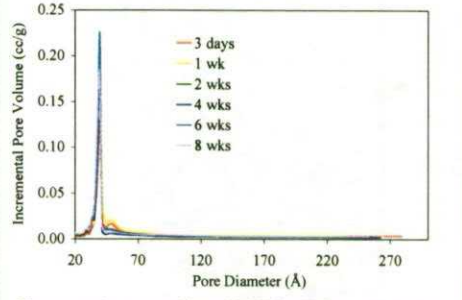


Chart 7. Changes in pore size distributions plots for xerogels prepared from gels prepared in THF with NaOH then aged for periods ranging from 3 days to 8 weeks.



The xerogels prepared from **1** in THF with base showed the least significant relationship to the amount of time the gels were aged before drying. There was only a slight increase in surface area (Chart 6) with aging time and the pore size distribution plots (Chart 7) show that the narrow distribution of mesopores did not significantly shift with aging. In fact, much of the increase in surface area may be attributed to the appearance and growth of a shoulder on the main peak in the pore size distribution as the gels were aged for longer times.

Figure 2. SEM image of hexylene-bridged xerogel prepared in methanol with NaOH & aged for 3 days.

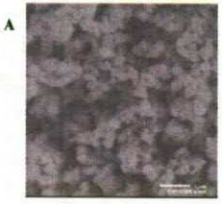


Figure 3. SEM image of hexylene-bridged xerogel prepared in methanol with NaOH & aged for 2 weeks.

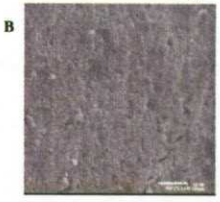
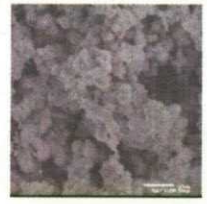


Figure 4. SEM image of hexylene-bridged xerogel prepared in methanol with NaOH & aged for 6 weeks.



The SEM images of the xerogels above correspond to the surface area and pore volume data in charts 4 & 5. Figure 3 shows that the majority of the pores are smaller compared to Figures 2 & 4, where the pores appear larger in size. The smaller pore sizes found in Figure 3 allows for the high surface area (Chart 4). The appearance of the smaller pores in Figure 3, also correlates to the pore volume data (Chart 5), where there is a sharp increase in the medium sized pores, suggesting that the majority of the pores are smaller rather than larger in size.

Conclusions

The choice of solvent and catalyst, along with aging times has a profound effect on the morphology and optical transmittance of the xerogels. The xerogels synthesized in methanol consistently produced opaque gels, while those synthesized in THF were consistently translucent, regardless of catalyst. The combination of solvent and catalyst varied the morphology of the gels. Those gels synthesized in methanol and HCl showed a steady increase in pore volume and surface area over increased aging times, however by changing the catalyst to NaOH, there is a steady increase in pore volume and surface area up to aging time of 2 weeks and then the values begin to decrease. This phenomenon is still under investigation. The gels synthesized in THF with NaOH posses a consistent pore size and surface area, with a slight increase in both at extended aging times. With this knowledge, tailoring the synthesis of the xerogels to obtain desired properties can be realized.

Los Alamos National Laboratory, is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-36.