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POROSITY IN HEXYLENE-BRIDGED POLYSILSESQUIOXANES. EFFECTS OF MONOMER CONCENTRATION

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ABSTRACT

Hexylene-bridged polysilsesquioxanes can be prepared as mesoporous or non-porous xerogels simply by switching from basic to acidic polymerization conditions. In this study, we looked at the effect of monomer concentration on porosity of hexylene-bridged xerogels prepared under acidic and basic conditions. 1, 6-Hexylene-bridged polysilsesquioxanes were prepared by sol-gel polymerizations of 1, 6-bis(triethoxysilyl)hexane **1** with concentrations between 0.1 to 1.2 M in ethanol. Gelation times ranged from seconds for 1.2 M concentration to months for 0.2 M. The gels were processed into xerogels by an aqueous work-up and the dry gels characterized by scanning electron microscopy (SEM), solid state ^{13}C and ^{29}Si CP MAS NMR spectroscopy, and gas sorption porosimetry.

INTRODUCTION

Alklylene-bridged polysilsesquioxanes are a novel class of hybrid organic-inorganic materials prepared by sol-gel polymerization of α, ω-bis(triethoxysilyl)alkanes (1, 2). It was discovered that the porosity of the alkylene-bridged xerogels was dependent on both the length of the alkylene-bridging group and the pH of the polymerization reaction. For example, Figure 1 shows porosity of alkylene-bridged polysilsesquioxane xerogels prepared with HCl or NaOH as catalyst as a function of alkylene-group length. With both acidic and basic catalysts, the xerogels with ethylene-bridging groups were mesoporous (20 Å < mean pore diameter< 500 Å) with high surface areas. Under basic conditions, the surface areas decreased gradually with increasing alkylene-bridge length until the pores were completely collapsed in the decylene-bridged polysilsesquioxanes. Collapse of porosity occured at bridging groups shorter than six carbons long with acid catalyzed gels. Evidence for collapse of porosity during drying comes from studies of alkylene-bridged polysilsesquioxane aerogels that remain porous even with long bridging groups (3). The collapse of porosity is thought to be caused by a combination of flexibility in the network polymer and the hydrophobicity of the network polymers.

While the cause of the porosity collapse in alkylene-bridged polysilsesquioxanes is still the subject of speculation, the phenomena can be viewed as a means for engineering the porosity in these polymers. For example, hexylene-bridged polysilsesquioxane xerogels can be prepared as non-porous materials under acidic conditions, and as highly porous xerogels under basic conditions. In order to utilize these materials it is necessary to determine the effect of solvent, type of alkoxide, catalyst, and type and concentration of monomer on the properties of the resulting xerogels. In the present study, the effect of monomer concentration for 1, 6-bis(triethoxysilyl)hexane **1** on xerogel structure was determined under acidic and basic conditions. Sol-gel polymerizations in ethanol with acid (10.8 mol% HCl) or base (10.8 mol% NaOH) catalysts were carried out with monomer concentrations ranging between 0.1-1.2 M. The gels were processed into xerogels by an aqueous work-up and the dry gels characterized by SEM, solid state ^{13}C and ^{29}Si NMR spectroscopy, and nitrogen sorption porosimetry.

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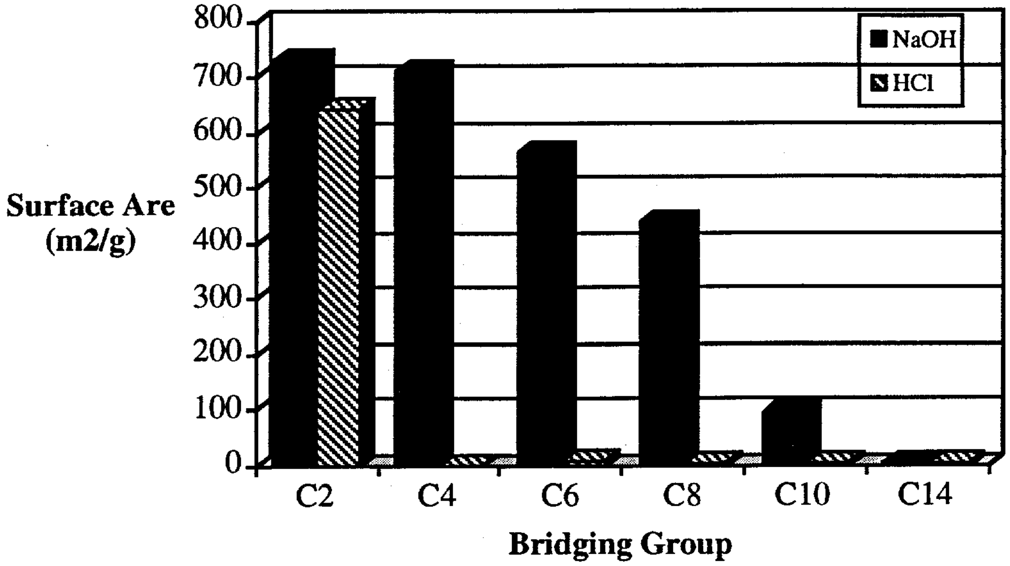


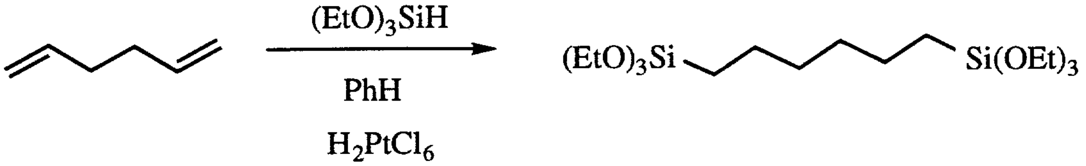
Figure 1. Surface areas of alkylene-bridged polysilsesquioxanes with alkylene groups ranging from ethylene-(C_2) to tetradecylene-(C_{14}) prepared under acidic and basic conditions.

EXPERIMENTAL

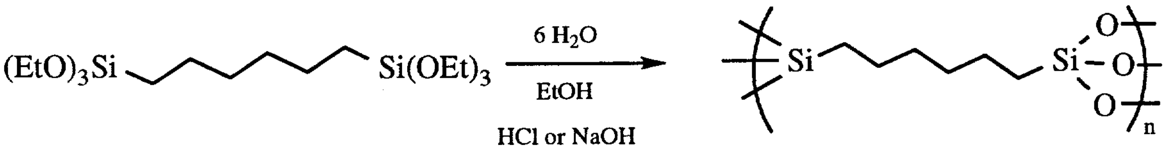
General

1, 5-Hexadiene and triethoxysilane were obtained from Aldrich Chemical Co. and used as received. Chloroplatinic acid was obtained from Kodak. Benzene (Fisher) was distilled from calcium hydride before use. Absolute ethanol was distilled from magnesium turnings. Aqueous HCl (1N) and NaOH (1N) solutions were obtained from Aldrich and used as received.

1, 6-Bis(triethoxysilyl)hexane **1** were prepared by the chloroplatinic acid-catalyzed hydrosilation of 1,5-hexadiene with triethoxysilane. The pure monomer was obtained by distillation (2X) at reduced atmosphere: b.p. = 105-108 C @ 200 mtorr.



Scheme 1. Hydrosilation of 1, 5-hexadiene with triethoxysilane to give **1**.



Scheme 2. Sol-gel polymerization of **1** to give hexylene-bridged polysilsesquixanes.

Sol-Gel Polymerizations

Sol-gel polymerizations of **1** were carried out in ethanol with both acid (10.8 mol% HCl) and base (10.8 mol% NaOH) catalysts and six equivalents H_2O. The amount of monomer and volume of aqueous catalyst for each concentration experiment is shown in Table 1. In all cases, **1** was weighed in a 5 mL volumetric flask and thoroughly mixed with approximately 2.0 mL of freshly distilled ethanol to form a clear colorless solution. In a separate vessel, aqueous catalyst (either HCl or NaOH) was dissolved in ethanol and mixed quickly with the monomer solution. After diluting to 5 mL, the resulting solution was transferred to a scintillation vial, and tightly capped to avoid solvent evaporation. Once gelation occured, the gels were allowed to age for two weeks before further processing.

Processing Gels to Xerogels

The aged gels were removed from the scintillation vials and crushed in water (100 mL). The water was filtered off under vacuum through a Buchner frit, and the resulting white gel was washed with water (2 x 100 mL) and diethyl ether (100 mL) before drying under vacuum for 24 hours at 100 °C.

Table 1. Formulations for sol-gel polymerizations.

Concentration **1**	Monomer	Catalyst (1 N HCl or NaOH)	Yields for NaOH cat. xerogels	Yields for HCl cat. xerogels
0.1M	0.206 g	0.054 mL	111%	0 %
0.2M	0.412 g	0.108 mL	108%	81 %
0.4M	0.824 g	0.216 mL	105%	116 %
0.6M	1.236 g	0.324 mL	96%	94 %
0.8M	1.823 g	0.480 mL	100%	91 %
1.2M	2.733 g	0.720 mL	97%	95 %

Nomenclature

In this report, the polymers are designated (e.g. **X-0.1-NaOH**) with an X to signify xerogel, a number corresponding to the concentration of monomer **1** used, and NaOH or HCl to represent the catalyst.

Characterization Of Xerogels

^{13}C CP MAS NMR spectra were obtained with a Chemagnetics spectrometer at 50.19 MHz. ^{29}Si CP MAS NMR spectra were obtained on a Chemagnetics spectrometer at 39.65 MHz. The latter spectra were deconvoluted using a Lorentz-Gaussian (50:50) fit. Surface area analyses were conducted with a Quantachrome Autosorb6 multiport nitrogen porosimeter. Scanning electron micrographs were obtained with a JEOL 6400 scanning electron microscope.

RESULTS

Sol-gel hydrolysis-condensation of monomer **1** was carried out under acidic and basic conditions. Addition of catalyst and water to the monomer afforded clear, colorless solutions. As the polymerizations proceeded, solutions less than 0.8 M gelled to light blue, translucent monolithic alcogels free of cracks or shrinkage. In solutions with concentrations greater than 0.8 M, the sol remained clear and colorless even after gelation. The latter alcogels underwent massive shrinkage with small cracks forming throughout the monoliths. For example, the reaction of **1** at 1.2 M concentration led to cracking of the clear gel into pieces within minutes.

In both acid and base catalysts, gelation rates increased with monomer concentration. While **X-0.1-NaOH** solutions gelled after 3 hours, **X-0.1-HCl** solutions remain unchanged after nearly 1 year. The strongest differentiations in catalyst effect were found by examining the stages of gelling in respect to concentration. Base-catalyzed gels exhibited relatively stable gel rates and polymerization characteristics with increasing concentration (Table 2). In contrast, acid-catalyzed gels showed two trends with increasing monomer concentration: 1) an exponential increase in gel rate and 2) an increasingly exothermic reaction.

Table 2. Gelation rates for 1, 6-bis(triethoxysilyl)hexane **1** at concentrations ranging from 0.1-1.2 M with HCl or NaOH as catalyst. Experiments were performed in triplicate.

Monomer	**Gel Times**	
Concentration	**HCl**	**NaOH**
0.1	none	3 hours
0.2	5 months	62 min.
0.4	24 hours	38 min.
0.6	20 min.	38 min.
0.8	1 min.	26 min.
1.2	<1 min.	3 min.

Solid State NMR Spectroscopy

Solid state NMR gives structural details of the hexylene-bridged polysesquioxanes' architecture at the molecular level. Specifically, ^{13}C CP MAS NMR (Cross Polarization Magic Angle Spinning) spectroscopy can be used to determine if the bridging hexylene group has survived the hydrolytic polymerization conditons. Previous work has shown the Si-C bond in alkylene-bridged polysilsesquioxanes is hydrolytically stable. This is confirmed in this study by the presence of the expected three bridging carbons (α, β, and γ) in the ^{13}C CP MAS NMR spectrum (Figure 3). The spectrum also allows the degree of hydrolysis to be evaluated (semi-quantitatively) by the magnitude of the peaks at 58 ppm and 18 ppm arising from the residual ethoxy groups on silicon. In all cases, less than 5% ethoxy groups remained.

Degrees of condensation in the polymers were evaluated by ^{29}Si CP MAS NMR spectroscopy. The ^{29}Si CP MAS NMR spectrum (Figure 4) of a polysilsesquioxane is composed of three peaks representing Si atoms in the network with one (T^1), two (T^2), and three (T^3) siloxane linkages respectively. Deconvolution and integration of the resonances in the spectra allows the degree of condensation to be calculated (4)(Table 3). There were no significant changes in the degree of condensation with concentration of **1**. As in other sol-gel processed silica gels, siloxanes, and silsesquioxanes, the degree of condensation of xerogels prepared under basic conditions is higher than those prepared under acidic conditions.

Surface Area Measurements

The most interesting result was the effect of monomer concentration on the surface areas of the xerogels (Figure 5). With base-catalyzed polymerizations, the average surface areas remained fairly constant near 600 m^2/g with the exception of **X-1.2-OH** (200 m^2/g). The drop in surface area is probably due to the rapid gelation of the hexylene-bridged polysilsesquioxane at this concentration. However, the opposite trend was observed with the acid-catalyzed polymerizations. Xerogels prepared at 0.2 and 0.4 M monomer concentrations were non-porous to nitrogen soprtion. Yet, the xerogels prepared at higher concentrations (**X-0.6-HCl**, **X-0.8-HCl**, and **X-1.2-HCl**) were porous with surface areas as high as 300 m^2/g.

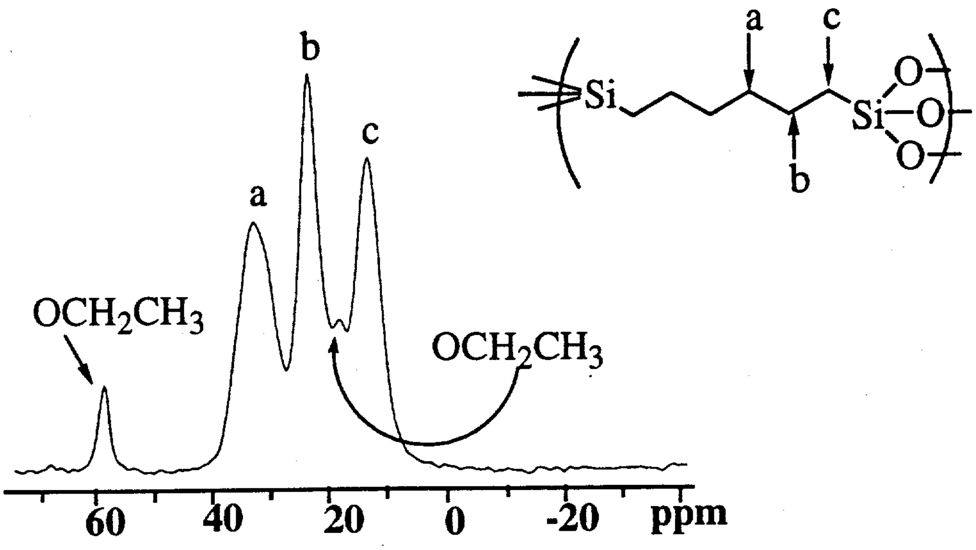


Figure 3. ^{13}C CP MAS NMR spectrum of hexylene-bridged polysilsesquioxane.

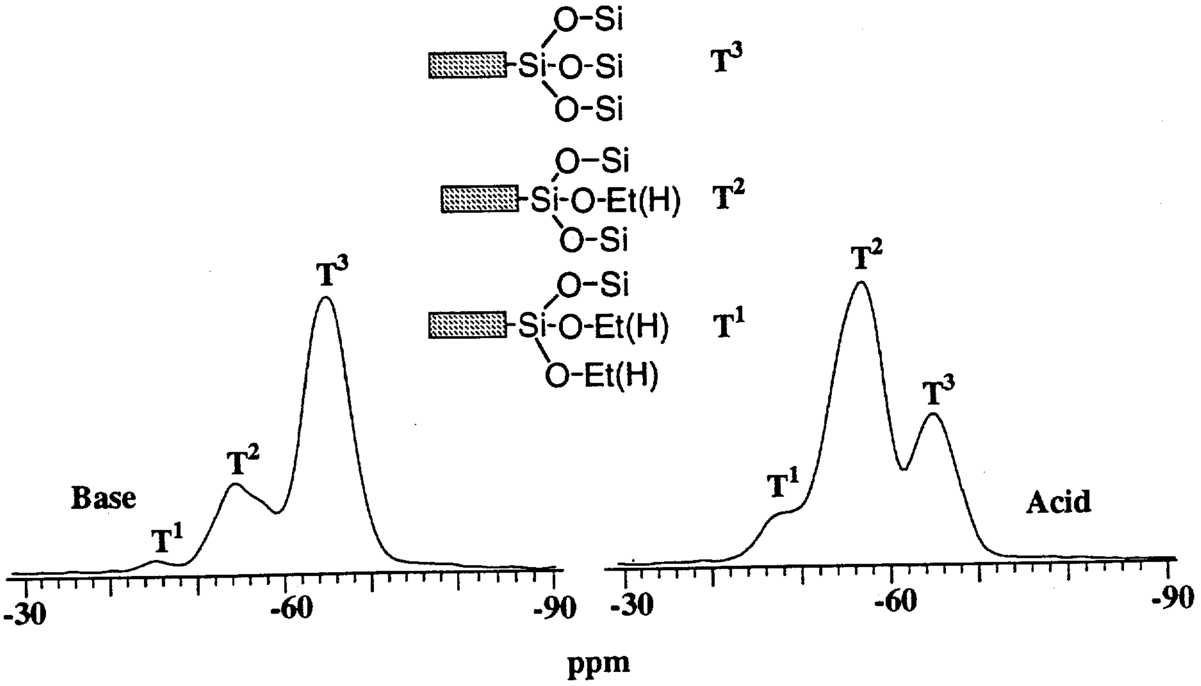


Figure 4. The ^{29}Si CP MAS NMR spectrum of hexylene-bridged polysilsesquioxane prepared with base (left) and acid (right) catalysts.

Table 3. Degrees of condensation calculated from ^{29}Si CP MAS NMR data (4) for hexylene-bridged polysilsesquioxanes prepared at different concentrations by acid- (HCl) or base- (NaOH) catalyzed polymerizations.

	Degree of Condensation (%)	
Monomer Concentration	Base Catalyzed Xerogels	Acid Catalyzed Xerogels
0.1	88.2	No gel
0.2	88.9	78.3
0.4	90.3	75.2
0.6	90.1	75.3
0.8	89.9	76.2
1.2	88.5	78.7

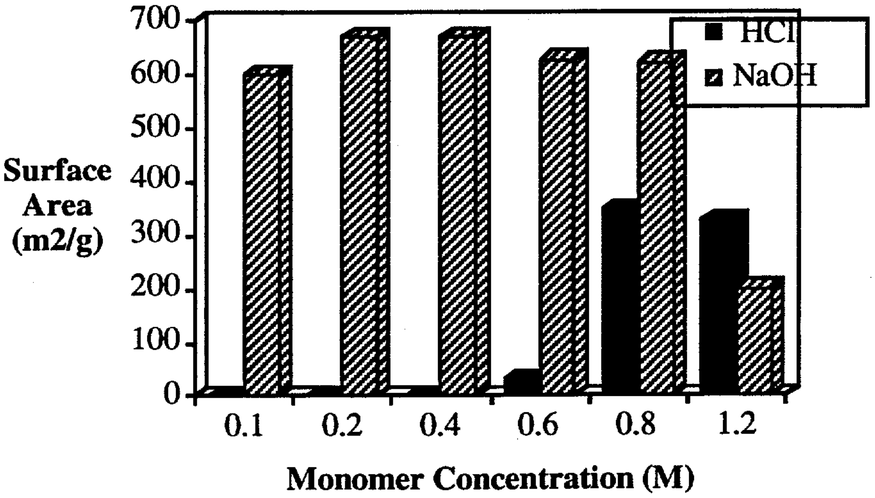


Figure 5. Surface areas of hexylene-bridged polysilsesquioxanes prepared at concentrations ranging from 0.1-1.2 M **1** in ethanol with HCl or NaOH as catalysts (10.8 mol%). The experiments at 0.1 M under acidic condtions failed to gel even after six months.

Scanning Electron Microscopy

Examination of the xerogels with scanning electron microscopy (SEM) revealed no significant differences with concentration with one exception. While the xerogels prepared under acidic and basic conditions all appeared to be formed from tightly aggregated particles between 10-20 nm in diameter with no evidence of macroporosity (>500 Å). However, the xerogels prepared at 0.2 M monomer concentration with HCl as catalyst (**X-0.2-HCl**) while mesoporous like the xerogels prepared at higher concentrations, also exhibited a number of pores in the micron size range.

CONCLUSIONS

Concentration of 1, 6-bis(triethoxysilyl)hexane was discovered to have significant impact on porosity of hexylene-bridged polysilsesquioxane xerogels. As expected, the rate of gelation in both acid- and base-catalyzed polymerizations of **1** increased with concentration. Only the reaction of 0.1 M **1** under acidic conditions failed to yield gels. No marked differences in structure of the xerogels were observed by SEM, save some large pores observed in **X-0.1-OH**. By nitrogen sorption porosimetry, xerogels prepared under acidic conditions at concentrations lower than 0.6 M were non-porous. However, xerogels prepared with acid catalyst from **1** at higher concentrations (≥ 0.6 M) displayed increasing porosity with concentration. In contrast, base catalyzed polymer revealed no surface area dependence on concentration up to xerogels prepared from 1.2 M **1**.

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REFERENCES

1. J. H. Small, K. J. Shea, D. A. Loy, *J. Non Cryst. Solids* **160**, 234-46 (1993).
2. H. W. Oviatt Jr., K. J. Shea, J. H. Small, *Chem. Mater.* **5**, 943-50 (1993).
3. D. A. Loy, et al., *J. Non Cryst. Solids* , (1995).
4. K. J. Shea, D. A. Loy, O. Webster, *J. Am. Chem. Soc.* **114**, 6700-10 (1992).