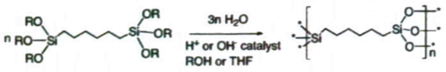
LA-UR-04-2103

Introduction

Hexylene-bridged polysilsesquioxanes are hybrid organic-inorganic materials prepared by the sol-gel polymerization of 1,6-bis(trialkoxysilyl)hexane monomers **1-3**.



Monomer **1**: R = Methyl; Monomer **2**: R = Ethyl; Monomer **3**: R = n-Propyl

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. The object of this study was to ascertain the influences of monomer alkoxide group, solvent, catalyst, and monomer concentration on gelation time, and the properties of the resulting xerogels.

Experimental

Monomers **1** and **2** were prepared by hydrosilation of 1,5-hexadiene with trimethoxysilane and triethoxysilane, respectively. Monomer **3** was prepared by reacting 1,6-bis(trichlorosilyl)hexane (Gelest) with six equivalents of *n*-propanol in the presence of six equivalents of triethylamine in benzene. 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.

The concentration study was performed with monomer **2** in ethanolic solutions at 0.1M, 0.2M, 0.4M, 0.6M, 0.8M, 1.0M, and 1.2M concentrations with six equivalents of water. 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

Under most of the polymerization conditions, gels formed fastest from monomer **1**. The differences between gelation times of the ethoxide and propoxide monomers showed no consistent trend, highlighting the danger of relating gelation times to the relative reactivities of monomers.

Chart 1. Gelation times for Monomers **1-3** (0.4 M) & six equivalents of water.

		Gel Times	(Hrs)
Monomer	Solvent	HCl	NaOH
1	MeOH	0.38	1.40
1	THF	Immed.	Immed.
2	EtOH	24	0.63
2	THF	0.08	72
3	*n*-PrOH	5	4
3	THF	2.4	48

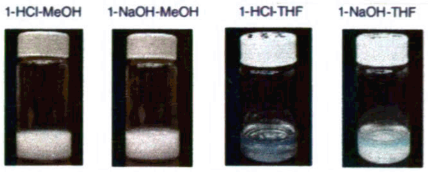
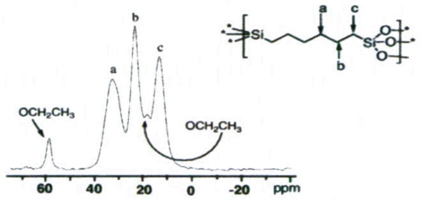


Chart 2. Appearance of Gels prepared from **1-3** (0.4M) with six equivalents of water.

		Appearance of Gels	
Monomer	Solvent	HCl Catalyst	NaOH Catalyst
1	MeOH	Opaque, white; no syneresis	Opaque, white; no syneresis
1	THF	translucent, blue; slight syneresis	Cloudy, blue; syneresis
2	EtOH	translucent, blue; no syneresis	Cloudy, blue; syneresis
2	THF	Clear, colorless	cloudy
3	*n*-PrOH	Cloudy, blue; no syneresis	Cloudy, blue; high syneresis
3	THF	Translucent, blue; slight syneresis	Cloudy, white; moderate syneresis

With drying, the gels became white, brittle glassy xerogels that are insoluble in organic solvents and water. Structural characterization was carried out by solid state ^{13}C and ^{29}Si NMR and IR spectroscopies. X-ray diffraction revealed no signs of order. Xerogels' porosity was examined with scanning electron microscopy and nitrogen sorption porosimetry.

Solid state ^{13}C NMR spectroscopy provides evidence of the organic components of the xerogels: three different bridging methylenes and residual alkoxides.



Solid state ^{29}Si NMR spectroscopy shows the extent of condensation in the xerogels by the populations of T^1, T^2, & T^3 silicons.

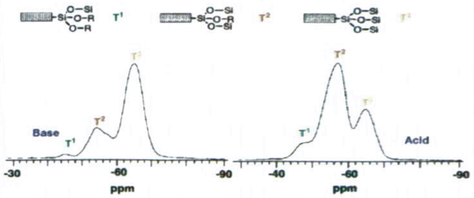


Chart 3. Deconvolution of the peaks in the solid state ^{29}Si NMR is used to calculate the degree of condensation for the xerogels. The NaOH-catalyzed sol-gels afford xerogels with higher degrees of condensation than those prepared with acid.

		Degree of Condensation	
Monomer	Solvent	HCl Catalyst	NaOH Catalyst
1	MeOH	72%	78%
1	THF	77%	87%
2	EtOH	75%	90%
2	THF	76%	89%
3	*n*-PrOH	76%	90%
3	THF	75%	91%

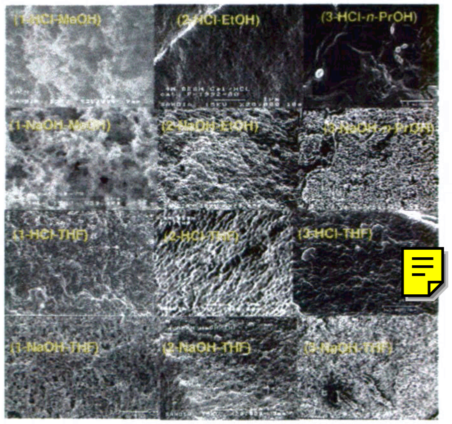
Porosity

Surface Areas (BET) and mean pore diameters (BJH) for hexylene-bridged polysilsesquioxanes show that non-porous xerogels can be prepared with acid-catalyzed polymerizations. High surface area xerogels are obtained from all of the NaOH-catalyzed polymerizations.

Chart 4. Surface areas and pore sizes obtained by nitrogen sorption porosimetry.

		Surface Area (m^2/g)/Pore Diameter (Å)	
Monomer	Solvent	HCl Catalyst	NaOH Catalyst
1	MeOH	364/110	444/109
1	THF	0.	612/34
2	EtOH	0	688/51
2	THF	0	610/35
3	*n*-PrOH	0	682/78
3	THF	0	626/37

Scanning electron micrographs of xerogels prepared from **1-3** in alcohol or THF with acid or base catalysts. Xerogels prepared from **1** showed the greatest meso- and macroporosity. The xerogels prepared from **2** and **3** in alcohols with acid were visibly non-porous.

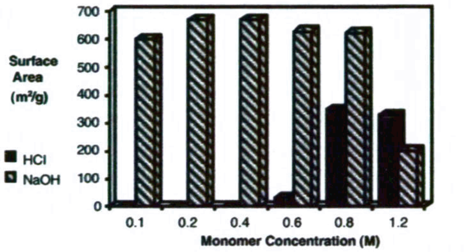


Concentration Study To ascertain the influence of monomer concentration on gelation times and surface areas, monomer **2** was polymerized at 0.1, 0.2, 0.4, 0.6, 0.8, 1.2M concentrations with acid and base catalysts.

Chart 5. Gelation Times with Concentration of **2**

	Gelation Time (Hrs)	
Concentration of **2** (M)	HCl Catalyst	NaOH Catalyst
0.1	No Gel	3
0.2	3600	1
0.4	24	0.63
0.6	0.3	0.63
0.8	0.02	0.43
1.2	< 0.02	0.03

In ethanol, gels formed fastest with base catalyst. At 1.2 M, gels formed as soon as the solutions were mixed.



Base-catalyzed xerogels exhibited high surface areas. Acid-catalyzed polymerizations afforded non-porous xerogels at 0.2 & 0.4 M concentration. Porosity was observed in the xerogels prepared at higher concentrations and may be a function of the rapid gelation times.

Conclusions

This study has provided some insight into the chemical parameters that affect the ultimate structure in bridged polysilsesquioxanes. First, gelation times do not necessarily directly reflect the hydrolysis and condensation rates expected for different alkoxide groups. The collapse of porosity during the drying of hexylene-bridged polysilsesquioxanes occurs in nearly all acid-catalyzed samples, save those that form quickly due to concentration or from the methoxide monomer **1** in methanolic solution. This suggests that that there may be a kinetic contribution to creating porosity in addition to the network compliance model. It would also appear that syneresis of gels during aging may be the symptom of changes resulting in increased porosity. Whatever these changes may be due to, they do not appear to significantly alter the structural composition. Experiments are underway to provide more information and test some of these hypotheses.

Acknowledgements

Roger Assink (SNL) for NMR, Gary Zender (SNL) for SEM's. Los Alamos National Laboratory, is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-36.