

SAND--98-0539C
CONF-980314--

Polymerization of Bis(triethoxysilyl)ethenes. The Impact of Substitution Geometry on the Formation of Ethenyl- and Vinylidene-Bridged Polysilsesquioxanes

Joseph P. Carpenter*, Stacey A. Yamanaka*, Mark D. McClain*, Douglas A. Loy*, John Greaves**, Kenneth J. Shea**

*Department of Encapsulants and Foams, Sandia National Laboratories, Albuquerque, NM 87185-1407. **Department of Chemistry, University of California, Irvine, CA 92717

Introduction

Preparation of organically-bridged polysilsesquioxanes has been achieved by polymerizing organic monomers with two or more trialkoxysilyl groups per monomer repeat unit.¹ The nature of the organic bridging group has been shown to strongly impact the final properties (surface area, pore size, and thermal stability) of the end product. For example, rigid arylene bridging groups have been shown to give rise to materials with high surface areas with a relatively large contribution from micropores (<20Å).² The length of alkylene-bridging groups can be used to control the size and dispersity of pores in hydrocarbon-bridged xerogels.³ In this study, we have examined the preparation of ethylene-bridged polysilsesquioxanes from the E-(1) and Z-(2) isomers of 1,2-bis(triethoxysilyl)ethene and vinylidene-bridged polysilsesquioxanes from 1,1-bis(triethoxysilyl)ethene-(3). This study was intended to determine the effects of substitution geometry about the carbon-carbon double bond on the condensation chemistry of the monomers and on the resulting architectures of the final materials.

Experimental

General Methods. Ethanol was distilled from magnesium before use. Anhydrous THF, triethoxyvinylsilane, RuCl₂(PPh₃)₃ were used as received from Aldrich. ¹H nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AM300 (300 MHz) using C₆D₆ as the solvent. The spinning band apparatus was from BR Instrument Corporation. Mass Spectra were obtained on a Fisons Autospec (CI, ammonia).

Monomer Preparation. E-1,2-bis(triethoxysilyl)ethene (1) and 1,1-bis(triethoxysilyl)-ethene (3). A mixture of 1 (84%) and 3 (16%) was prepared by the reaction of triethoxyvinylsilane (125 mL, 0.593 mol) with RuCl₂(PPh₃)₃ (0.304 g, 0.317 mmol) at reflux for 24 hours.^{4,5} Residual triethoxyvinylsilane was distilled off at atmospheric pressure and the remaining liquid was purified by spinning band vacuum distillations (2x). Monomer 1 (62.6 g, 98% by GC, yield = 60%) was collected at 90 °C/15μ; ¹H NMR (300 MHz, C₆D₆) δ 7.05 (s, 2 H, CHSi(OEt)₃), 3.83 (q, 12 H, J = 7.0 Hz, OCH₂CH₃), 1.16 (t, 18 H, J = 7.0 Hz, OCH₂CH₃); ¹³C NMR (75.5 MHz, C₆D₆) δ 146.34, 58.79, 18.48; ²⁹Si NMR (79.5 MHz, ethanol) δ -61.13. High resolution mass spectrometry (CI, ammonia) m/z calcd for C₁₄H₃₂O₆Si₂+H: 353.1815; found 353.1812. Monomer 3 (6.3 g, 99% by GC, yield = 6%) was collected as a clear, colorless oil at 65 °C/15μ; ¹H NMR (300 MHz, C₆D₆) δ 6.96 (s, 2 H, CH₂), 3.92 (q, 12 H, J = 7.0 Hz, OCH₂CH₃), 1.16 (t, 18 H, J = 7.0 Hz, OCH₂CH₃); ¹³C NMR (75.5 MHz, C₆D₆) δ 150.46, 139.54, 58.73, 18.47; ²⁹Si NMR (79.5 MHz, CD₃CD₂OD) δ -58.02. High resolution mass spectrometry (CI, ammonia) m/z calcd for C₁₄H₃₂O₆Si₂+H: 353.1815; found 353.1812.

Z-1,2-bis(triethoxysilyl)ethene (2). A photolysis tube was charged with E-1,2-bis(triethoxysilyl)ethene (280 g, 0.795 mol) and benzophenone (100 mg, 0.549 mmol). Irradiation for 25 h with a 1000 Watt mercury lamp, under an argon atmosphere, yielded a mixture of the E (71%) and Z (25%) isomers. Spinning band vacuum distillation (2x) of the mixture afforded 26.6 g (10 %) of Z-1,2-bis(triethoxysilyl)ethene (>96% by GC) as a colorless oil: bp 65-70 °C/20μ; ¹H NMR (300 MHz, C₆D₆) δ 6.74 (s, 2 H, CHSi(OEt)₃), 3.86 (q, 12 H, J = 7.0 Hz, OCH₂CH₃), 1.22 (t, 18 H, J = 7.0 Hz, OCH₂CH₃); ¹³C NMR (75.5 MHz, C₆D₆) δ 146.29, 58.60, 18.45; ²⁹Si NMR (79.5 MHz, ethanol) δ -61.91. High resolution mass spectrometry (CI, ammonia) m/z calcd for C₁₄H₃₂O₆Si₂+H: 353.1815; found 353.1820.

Sol-Gel Processing. Polysilsesquioxane xerogels were typically prepared by dissolving the monomer in ethanol or THF. This solution was then mixed with a second ethanol or THF solution containing 6 eq. of water from 1N HCl or from 1N NaOH. The volume was then adjusted with solvent to make the concentration of monomer 0.4 M. The solution was then transferred to a vial and sealed. Two weeks after gelation, the gel was crushed and washed with 3 x 50 mL of water and 2 x 25 mL of ether. The gel was dried in vacuo at 100 °C.

Characterization of Xerogels. Surface area analyses were conducted with a Quantachrome Autosorb6 multiport nitrogen porosimeter. The samples were coated with 100-200 Å chrome using a Gatan Model 681 High Resolution Ion Beam coater. These were analyzed using a high resolution Hitachi S4500 field emission scanning electron microscope. Secondary electron images were taken using 5 KV accelerating voltage. The images were acquired digitally from the SEM using a PGT Imix imaging system.

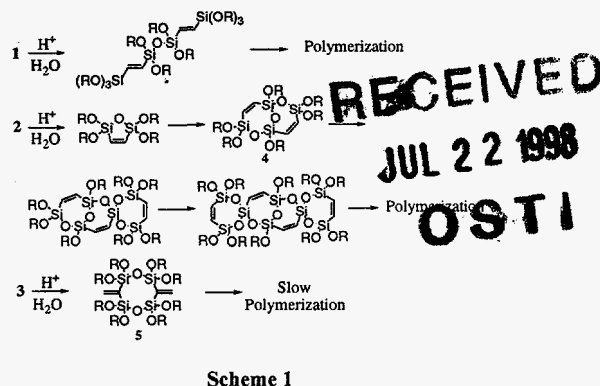
Results and Discussion

Sol-Gel Polymerizations. Monomers 1-3 exhibit remarkably different gelation behavior under identical sol-gel polymerization conditions. Acid-catalyzed polymerizations of ethanol solutions (0.4 M) of monomers 1 and 2 produce rigid transparent gels in 5 days (Table I). However, when THF is utilized as the cosolvent in the same polymerizations, 1 forms a cloudy white gel in 4 hours while 2 requires 10 days to set up as a rigid colorless transparent gel. Contrasting sharply with 1 and 2, the vinylidene monomer 3 is apparently extremely resistant towards polymerization; under identical sol-gel conditions, the monomer does not form a gel or a precipitate even after 1 year! When basic conditions are employed, slightly opaque rigid free standing gels can be produced from 1 in 20 minutes (EtOH) or 36 hours (THF). In the presence of a basic catalyst, monomer 2 reacts very rapidly to produce a white precipitate in both EtOH and THF as gels could not be obtained under these conditions. Again, 3 is very slow to polymerize with gelation occurring only after 9 months in EtOH with NaOH catalyst.

Table 1. Sol-Gel Polymerizations and Gel Times for 1, 2, and 3.

Monomer (Catalyst)	Gel Time (Polymer)	
	EtOH	THF
1(acid)	5 days (1A)	4 hours (1A-THF)
1(base)	20 min. (1B)	2 days (1B-THF)
2(acid)	5 days (2A)	10 days (2A-THF)
2(base)	precipitated (2B)	precipitated (2B-THF)
3(acid)	no gel after 1 year	-
3(base)	9 months (3B)	-

The early hydrolysis and condensation chemistry of 1, 2, and 3 was examined under acidic conditions by solution ²⁹Si NMR spectroscopy and chemical ionization mass spectrometry. Each monomer was found to have its own unique polymerization process as outlined in Scheme I. While the E and Z isomers polymerize through acyclic and cyclic condensations respectively, 3 forms a bicyclic dimer (5) that is resistant towards further condensation reactions.



Scheme 1

There are four types of silicon centers present during the sol-gel polymerization of organotrialkoxysilanes since there may be from 0 to 3

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED
MASTER

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

**Portions of this document may be illegible
electronic image products. Images are
produced from the best available original
document.**

siloxane bonds at any one silicon atom. These silicon atoms are considered to be trifunctional with respect to the alkoxide ligands and are denoted as T^n which is a modification of the General Electric Q notation.⁶ The reaction of **1** with 1 eq. of water from 1N HCl after 24 hour gave a ²⁹Si NMR spectrum which consisted of two main peaks of roughly equal intensity at -61.5 ppm and -68.7 ppm. The chemical shift of -61.5 ppm is the same as that for unreacted monomer and must arise from T^0 silicon nuclei while the second signal is shifted 7.2 ppm upfield and is thus assigned to T^1 silicon nuclei. No T^2 or T^3 silicons are observed under the controlled hydrolysis and condensation reactions with 1 eq. of H₂O indicating that oligomerization is occurring by linear acyclic chain growth. The reaction was also followed by mass spectroscopy (CI MS, ammonia) and the two major ions observed were at m/z 852 [trimer+NH₃-EtOH]⁺ and 648 [dimer+NH₄]⁺. These two ions are assigned to acyclic trimer and dimer which is consistent with acyclic chain growth. This type of polymerization is expected under acidic conditions.

The addition of 2 eq. of water from 1 N HCl to a solution of **2** results in a ²⁹Si NMR spectrum which has two signals of equal intensity at -65.9 and -68.6 ppm which are upfield from the starting monomer (**2**, -61.9 ppm). The mass spectrum of the reaction shows basically one major product which is represented by the parent ions at m/z 500 [4+NH₄]⁺ and 483 [4+H]⁺. The only structure that is consistent with the spectral data is the bicyclic dimer **4** shown in Scheme 1. The observed chemical shifts for the T^1 and T^2 silicons are not shifted as far upfield as is normally expected for such condensation products (ca 7-8 ppm). This is due to the ring strain present in the bicyclic structure which shifts the signals downfield from where they would normally appear in an acyclic product. A small concentration of trimer (m/z = 704 [trimer+NH₄]⁺ and 687 [trimer+H]⁺) and tetramer (m/z = 909 [tetramer+NH₄]⁺ and 846 [tetramer-OEt]⁺) are observed in the mass spectrum and these masses are consistent with the additional cyclization products shown in Scheme 1.

The same reaction conditions employed for **1** and **2** were repeated for **3** using 1 eq. of H₂O. Initially, only the hydrolysis products of **3** were observed in the ²⁹Si NMR spectrum. After 24 hours, the dominant peak in the spectrum appeared at δ_{Si} = -66.1 ppm which is shifted 8.1 ppm upfield from the starting monomer **3**. The mass spectrum shows only the presence of monomer and dimer. The masses of m/z 574 [5+NH₄]⁺ and 557 [5+H]⁺ and the ²⁹Si NMR spectrum are consistent with the dimer of **3** having the cyclic structure (**5**) shown in Scheme 1. Apparently, this structure is the bottleneck in the polymerization of **3** since there are no higher oligomers present after 24 hours even though hydrolysis products of **3** and **5** are observed in the mass spectrum.

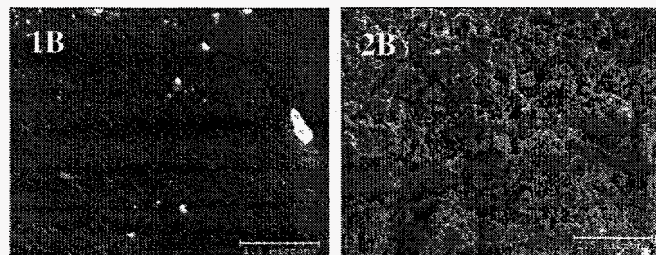
Characterization of Xerogels. To determine what effect the different polymerization processes have on the final properties of the polymers, the xerogels prepared from each monomer were studied by nitrogen sorption porosimetry and scanning electron microscopy. Due to the difficulty in polymerizing **3** to a highly condensed xerogel, most of the analytical data was obtained on ethenylene-bridged polysilsesquioxanes prepared from monomers **1** and **2**. Nitrogen sorption porosimetry was utilized to evaluate the pore structure and surface area of each xerogel. The surface areas were determined by the multi-point BET method and are tabulated along with mean pore diameters (BJH) and pore volumes in Table II. Most of the ethenylene-bridged polysilsesquioxanes are characterized by a small average pore diameter of 22-24 Å. However, the xerogels prepared from **2** under basic conditions, which precipitated rather than gelled, had average pore diameters of 46-47 Å and xerogel **3B** had an average pore diameter of 62 Å. A general trend in the ethenylene-bridged polysilsesquioxanes is that xerogels prepared using a basic catalyst exhibit much higher surface areas (473-779 m²/g) than those prepared with an acid catalyst (307-447 m²/g).

Table 2. Summary of Surface Areas and Pore Diameters Determined by Nitrogen Sorption Porosimetry for Materials from 1, 2, and 3.

Polymer	BET Surface Areas (m ² /g)	Av. Pore Diam. (Å)	Pore Vol. (cc/g)
1A	352	22	0.190
1B	691	22	0.387
2A	447	22	0.248
2B	473	47	0.561
3B	631	62	0.973
1A-THF	379	22	0.206
1B-THF	779	24	0.466
2A-THF	307	24	0.180
2B-THF	742	46	0.850

Pore size distributions derived from the BJH method were studied to determine which pore sizes contribute to the pore volume and to what extent. The polymers prepared from **1** and **2** under acidic conditions were found to be almost exclusively microporous (pore diameter < 20 Å) with small contributions to the pore volume from the lower end of the mesopore range (pore diameter 20-50 Å). The materials prepared from **1** under basic conditions exhibit a similar porosity to those prepared under acidic conditions. However, the polymerization of **2** utilizing a basic catalyst yielded materials with very broad distributions of pore sizes. When the polymerization is performed in ethanol, precipitation occurs almost immediately and a material (**2B**) is obtained that shows significant pore volume throughout the mesopore regime with a spike occurring in pores with a diameter around 90 Å. The polymer prepared from **2** in THF shows a similar mesoporosity. The pore size distributions account for the larger average pore diameters observed in **2B** and **2B-THF**.

To provide some insight into the origin of the meso and macroporosity in materials **2B**, **2B-THF**, and **3B** the polymers were examined by scanning electron microscopy. The electron micrographs shown in Figure 1 show distinctly different morphologies for the polymers prepared from **1** and **2**. Xerogel **1B** exhibits a very smooth morphology with very fine features consistent with the microporous structure identified in the porosimetry studies. However, **2B** has a very rough surface composed of globular structures and fused particulates with diameters of approximately 50-150 nm. The materials prepared in THF show a similar pattern. The voids between the particles and globules which make up xerogels **2B** and **2B-THF** are most certainly the source of the meso and macroporosity observed in these materials.



Although the porosimetry studies did not reveal any profound differences between the acid-catalyzed gels of **1** and **2**, SEM studies exposed significantly different morphologies similar to those observed in the base-catalyzed materials. Both **1A** and **1A-THF** have continuous textures with no well defined particulates while **2A** and **2A-THF** are characterized by rough particulate or globular structures that are much finer (< 50 nm in diameter) than those produced from **2** under basic conditions. The formation of mesoporous or macroporous domains in **2A** and **2A-THF** is precluded by the smaller particulates from which the xerogels are comprised.

Conclusions

The sol-gel polymerization studies of monomers **1**, **2**, and **3** reveal unique reactivity patterns for each monomer under acidic conditions. Acyclic linear chains predominate in the polymerization of **1** while the hydrolysis and condensation of **2** is characterized by the formation of seven-membered rings to build up the polymer network. The polymerization of **3** is apparently

inhibited by the formation of the sterically congested cyclic dimer **5** which is resistant to further condensation reactions. The different polymerization processes for the Z and E isomers leads to materials with vastly different morphologies and porosities. The trans monomer yields polymers with very fine structural features that are strictly microporous. The materials produced from the cis monomer are characterized by aggregates of globular or spherical particles which under basic conditions leads to polymers that are mesoporous.

Acknowledgements

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

References

- (1) Baney, R. H.; Itoh, M.; Sakakibara, A.; Suzuki, T. *Chem. Rev.* **1995**, *95*, 1409.
- (2) Shea, K. J.; Loy, D. A.; Webster, O. *J. Am. Chem. Soc.* **1992**, *114*, 6700.
- (3) Oviatt, H. W., Jr.; Shea, K. J.; Small, J. H. *Chem. Mater.* **1993**, *5*, 943.
- (4) Marciniac, B.; Maciejewski, H.; Gulindki, J.; Rzefak, J. *J. Organomet. Chem.* **1989**, *362*, 273.
- (5) Marciniac, B.; Pietraszuk, C. *J. Chem. Soc., Chem. Commun.* **1995**, 2003.
- (6) Brinker, C. J.; Scherer, G. W. *Sol-Gel Science: the physics and chemistry of sol-gel processing*; 1st ed.; Academic Press, Inc.: San Diego, **1990**.