

POLYMERIZATION OF THE E AND Z ISOMERS OF BIS-(TRIETHOXSILYL)-2-BUTENE

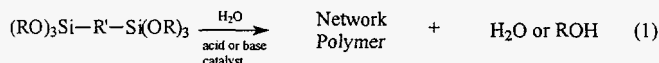
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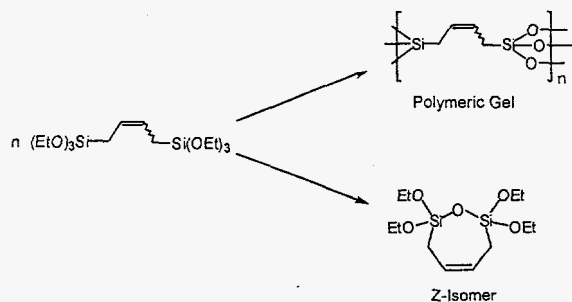
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Introduction

Hydrolysis and condensation of monomers of the general form, (EtO)₃Si-R-Si(OEt)₃ (equation 1; R = arylene-, alkylene-, and alkenylene-bridging groups) results in the formation of highly crosslinked polymeric gels. Properties, such as porosity, of these materials have been shown to be affected by the nature of the organic bridging group, R. Rigid bridging groups such as arylene-, alkynylene-, or alkenylene- afford microporous materials.¹ Monomers with flexible alkylene-spacers longer than five carbons in length polymerize under acidic conditions to give non-porous materials.² Short alkylene spacers such as the ethylene-, propylene-, and butylene- bridging groups permit the monomers to readily undergo cyclization reactions that, under acidic conditions, lengthen gelation times from minutes to months.³ The preferred ring sizes formed in these cyclization reactions were six and seven membered rings. Studies of the sol-gel polymerization of E- and Z-ethenylene-bridged monomers demonstrated that the type of cyclic intermediates could be strongly influenced by the substitution geometry without affecting gelation times.⁴ Furthermore, the substitution geometry had a pronounced effect on the porosity of the ethenylene-bridged polysilsesquioxane xerogels with the Z-monomer producing mesoporous xerogels and the E monomer producing microporous materials.



Here we have extended the study of the effects of substitution geometry to the E and Z 2-butenylene-bridged monomers. Lengthening the bridging group from the 2-carbon ethenylene-bridged system to the four carbon-bridge while still keeping the carbon-carbon double bond, was intended to have two effects. The Z-butenylene monomer should be able to undergo a cyclization reaction to form a seven-membered cyclic disilsesquioxane. The *trans* double bond would still be expected to prevent the formation of monomeric cyclic disilsesquioxanes (Scheme 1) and readily allow for gel formation. The more flexible bridging group, due to the extra methylene units, should make the resultant gels more compliant. This, in turn, should permit the pores to collapse during drying and cause the formation of non-porous gels.



Scheme 1. Condensation of E (top) and Z(bottom) isomers of bis-(triethoxysilyl)-2-butene.

Experimental

The E⁶ and Z^{4,5} isomers of bis-(triethoxysilyl)-2-butene were prepared by the copper (I) catalyzed silation of E and Z 1,4-dichloro-2-butene with trichlorosilane followed by esterification with triethylorthoformate.

The monomers were polymerized under a variety of conditions which involved varying the solvent (THF or ethanol) and the catalyst (HCl, NaOH or

NH₃). The monomer concentration was maintained at 0.4 M and the water/monomer ratio at 6/1 equivalents.

Results and Discussion

To determine if there were differences between the products from the E and Z isomers the polymers were tested by several physical techniques. Solid state and solution ²⁹Si NMR revealed differences in extent of polymerization and presence or absence of fine structure (indicating cyclics/oligomers). Nitrogen sorption porosimetry and Scanning Electron Microscopy showed differences in pore sizes and molecular weight measurements on soluble polymers indicated extent of polymerization. Also, differences in gelation time were good indicators of reactivity differences.

The sol gel polymerization of the two monomers led to gel formation under most conditions studied (Table I). The exceptions were the Z isomer under acidic conditions (entries 2 and 3, Table I) which did not gel even after several months. The products, though ungelled, were relatively high molecular weight polymers with molecular weights of 8.5 X 10⁴ (entry 1) and 1.8 X 10⁵ Daltons (entry 3).

Table I. Gelation Times for E and Z bis-(triethoxysilyl)-2-butene

Expt. #	Isomer	Catalyst	Solvent	Gel Time
1	Z	HCl	EtOH	No gel
2	E	HCl	EtOH	14 days
3	Z	HCl	THF	No gel
4	E	HCl	THF	3 days
5	Z	NH ₃	THF	2 months
6	E	NH ₃	THF	28 days
7	Z	NaOH	EtOH	1 hour
8	E	NaOH	EtOH	1 hour

The solid state ²⁹Si NMR spectra of the materials that gelled under basic conditions (entries 6, 7 and 8 in Table I) were very similar – all displaying three broad peaks assigned to T¹, T² and T³ silicons with the T³ peak being largest and the T¹ the smallest. Under acidic conditions, the gelled polymers (E only, entries 2 and 4) were almost identical in structure. It was apparent from the data that basic conditions resulted in more condensed polymers than acidic conditions.

Solution ²⁹Si NMR of ungelled Z butenylene-bridged polysilsesquioxanes were quite different from the solid state spectra described above. As shown in Fig. 1, the spectra contain many sharp peaks due to monomeric cyclics, cyclic oligomers and their hydrolysis products. The broader resonances farther upfield represent less well defined, higher condensed silsesquioxanes. In an attempt to determine the identity of the compounds giving rise to the sharp peaks, we synthesized the cyclic disilsesquioxane and its dimer shown in Fig. 2 and measured their NMR spectra. Although neither was observed in the solution NMR's of the polymers, the chemical shifts of several prominent, sharp resonances are consistent with their hydrolysis products (Figure 1).

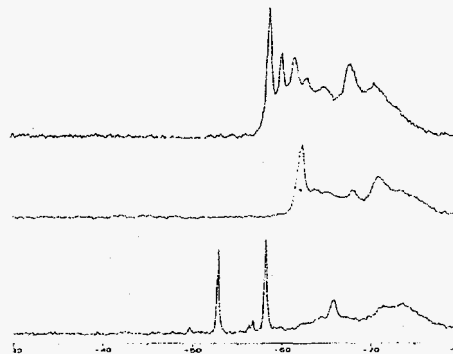


Figure 1. Solution ²⁹Si NMR of soluble non-gelled polymers produced from the Z isomer. Top - HCl catalyst, ethanol solvent; middle - HCl catalyst, THF solvent; bottom - NH₃ catalyst, THF solvent.

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The condensation of the Z ethenylene bridged system results in the initial formation of cyclic products which eventually form gels under acidic conditions (Scheme 2, left side).³ The butenylene bridged system, however, does not form gels under acidic conditions. Comparison of the cyclic species obtained with the two systems reveals that those formed with the former contain monoethoxy (bridgehead) and diethoxy substituted silicons. The cyclic species formed with the Z butenylene monomer contain only the less reactive monoethoxy substituted bridgehead silicons. The presence of the diethoxysilyl groups in the ethenylene bridged monomer allow it to more readily form network structures and therefore gel (Scheme 1).

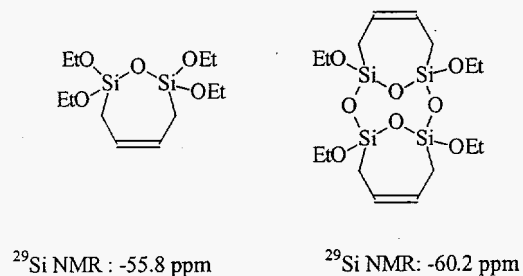
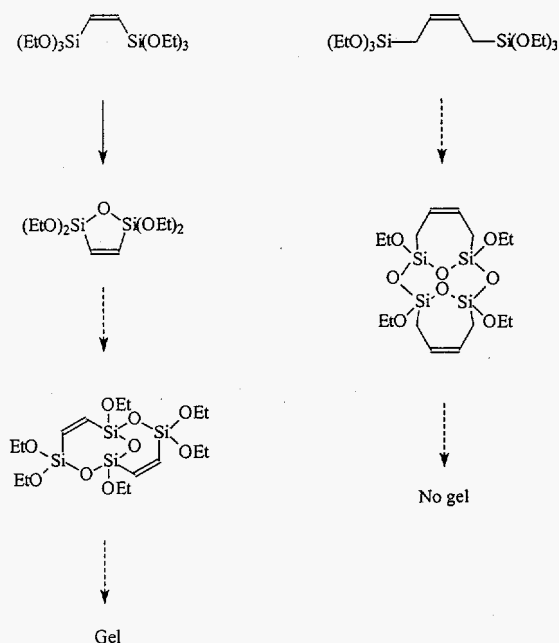


Figure 2. Compounds (or derivatives Thereof) That May Be Present in Soluble Resins.



Scheme 2. Cyclics formed with Z-ethenylene monomer (left) and Z butenylene monomer (right).

The X-ray crystal structure of the tricyclic dimer formed from the Z bis-(triethoxysilyl)-2-butene (Fig. 3) is of interest because it indicates that the dimer has a *cis* syndiotactic geometry. If the oligomerization process could be continued with the same stereochemical preference, a highly regular *cis* syndiotactic ladder polymer would be obtained. Further, the presence of the carbon-carbon double bond in the butenylene bridging group could provide the means for controlling the polymer tacticity through coordination to transition metals.

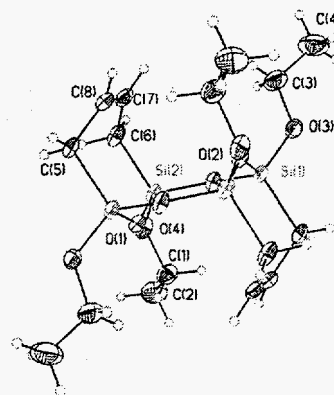


Figure 3. X-Ray Structure of $C_{16}H_{32}O_8Si_4$.

The gels that formed from the E and Z monomers were examined by nitrogen sorption porosimetry. All the gels were non-porous except the two that formed within one hour (entries 7 and 8, Table I) which were meso porous. Scanning electron microscopy revealed a rough aggregate structure for the meso porous gels. The lack of microporosity in all the gels indicated that they were, in fact, more compliant than ethenylene-bridged polysilsesquioxanes.

Conclusions

We have synthesized the Z and E isomers of 1,4-bis(triethoxysilyl)-2-butene and polymerized them under acid and base catalyzed sol-gel conditions. As expected the E system formed crosslinked, insoluble gels. The Z isomer, by nature of its geometry, formed high molecular weight, soluble polymeric products under acidic conditions. We were able to prepare and isolate both the cyclic disilsesquioxane monomer, and its dimer. Comparison of their spectral characterization with that of the soluble polymers suggests that the cyclics are present within the polymers. The synthesis of a dimer likely present at some early stage of the polymerization suggests that we may be able to control the reaction and form rigid polymers with controllable tacticity. In addition, most of the gels were found to be non-porous indicating that the gels were, in fact, more compliant than ethenylene-bridged polysilsesquioxanes leading to collapse of pores during drying.

Acknowledgement. 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.

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The E and Z isomers of bis-(triethoxysilyl)-2-butene were polymerized by the sol-gel method under various conditions. The E isomer formed gels under all conditions studied. The Z isomer formed gels only under basic conditions. Under acidic conditions it formed soluble resins of molecular weight ranging from 88000 to 180000. Solid state and solution ^{29}Si NMR revealed that the E isomer formed condensed gels, and that the resins formed by the Z isomer contained cyclic monomers including a tricyclic *cis* syndiotactic species. The gelled materials were characterized by solid state NMR, SEM and nitrogen porosimetry.