

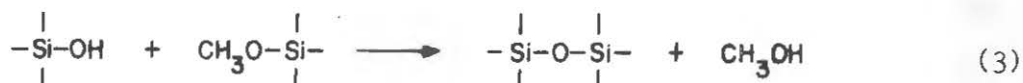
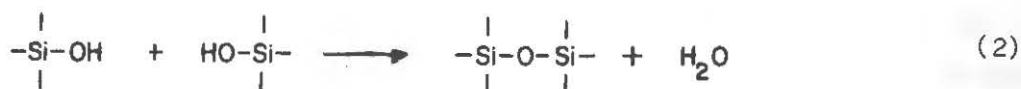
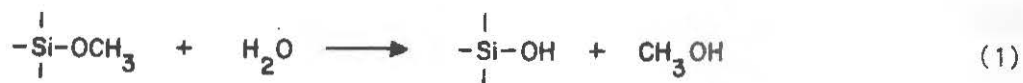
Polysilicic Acid Esters as Precursors to New Ceramic Materials

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Final Seminar

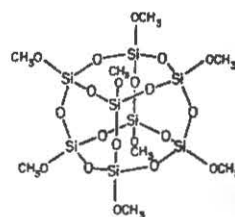
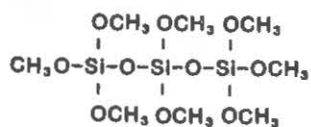
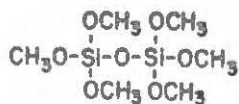
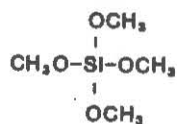
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Since 1846 [1] it has been known that silicic acid esters such as $(\text{CH}_3\text{O})_4\text{Si}$ (1) hydrolyze and condense according to equations 1-3 to yield sols of oligomeric silicic acids.



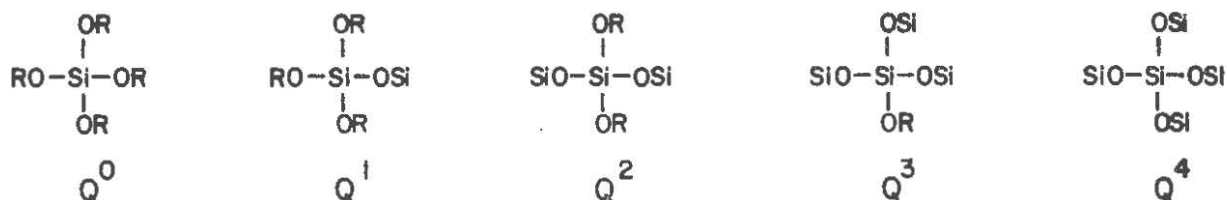
From these sols, a number of silica gel and glass products may be obtained [2]. In the last 10 years, extensive work has been performed aimed at chemically characterizing the sol-to-gel process [3] and applying these techniques to many materials problems [4]. The "Sol-Gel" method holds many advantages over traditional silica glass preparation techniques, perhaps the greatest being that the gel network is obtained under chemically mild conditions and densifies at relatively low temperatures. These mild conditions lend themselves to the synthetic approach of polymer science, where small reactive monomers are polymerized and the properties of the final products tailored by modification of the chemical and structural nature of the monomers [5]. The focus of the work presented here has been the extension of this molecular approach to the preparation of silica gels and glasses using "Sol-Gel" processing.

The first step of this investigation involved the synthesis and characterization of suitable polysilicic acid ester monomers. Two simple siloxane ester chains, $[\text{Si}_2\text{O}](\text{OCH}_3)_6$ (2) and $[\text{Si}_3\text{O}_2](\text{OCH}_3)_8$ (3), and a more complex monomer based on the cubic $[\text{Si}_8\text{O}_{12}]$ core, $[\text{Si}_8\text{O}_{12}](\text{OCH}_3)_8$ (4), were prepared.



Synthesis of 2 and 3 was achieved by reaction of their commercially available chlorosiloxane precursors, $[\text{Si}_2\text{O}]_2\text{Cl}_6$ and $[\text{Si}_3\text{O}_2]\text{Cl}_8$, with either CH_3ONO or $\text{HC}(\text{OCH}_3)_3$. Similar reactions with $[\text{Si}_8\text{O}_{12}]\text{Cl}_8$, prepared by photochlorination of $[\text{Si}_8\text{O}_{12}]\text{H}_8$ (5) [7], with CH_3ONO or $\text{HC}(\text{OCH}_3)_3$ produce 4 with good yields. Retention of the corresponding chain or cage structures were confirmed by ^{29}Si NMR and, in the case of 4, single-crystal X-ray analysis.

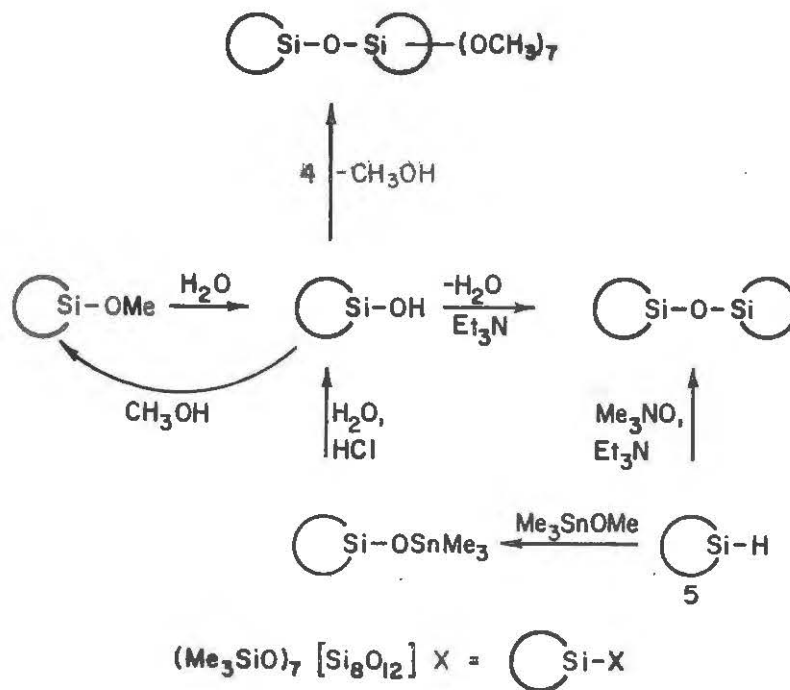
^{29}Si NMR was used to investigate whether the structural integrity of 1 - 4 is retained upon gel and glass formation. Hydrolysis and condensation produces silicon centers in different chemical environments dependent on the degree of hydrolysis and condensation, designated $\text{Q}^0 - \text{Q}^4$, with each Q-type silicon falling into characteristic chemical shift ranges [8].



Spectra obtained in the early stages of hydrolysis-condensation clearly demonstrate that for 2 and 3, monomer degradation is indeed occurring, although at low rates. Similar experiments following the behavior of 4 show that these reactions appear to proceed without monomer degradation. The overall rates of hydrolysis and condensation of 4 are considerably slower than those of 1 - 3.

Solid-state NMR techniques were used to follow the later stages of gelation and drying and to determine if differences between gels from different monomers could be observed. ^{29}Si FTMAS and CPMAS NMR experiments [9] show that gels from 1 - 3 have essentially identical distributions of Q^2 , Q^3 , and Q^4 centers, even after drying the gels to 400°C . The spectra of gels obtained from 4, however, show very different distributions of $\text{Q}^2 - \text{Q}^4$ environments, having much higher concentrations of Q^3 relative to Q^2 and Q^4 sites. The observation of Q^2 centers demonstrates that, even though not observed in the early stages of reaction, monomer degradation has occurred. Since 4 contains only Q^3 silicons, any Q^2 centers observed must be a result of reactions which cleave siloxane bonds in the $[\text{Si}_8\text{O}_{12}]$ core. Further differences between gels from 1 - 3 and 4 were observed in the spin-lattice relaxation (T_1) values for the Q^4 silicons. T_1 measurements made from gels dried from 60°C to 400°C , show that gels from 4 consistently demonstrate much longer Q^4 T_1 values than those observed in gels from 1 - 3. At 60°C , this difference is only 30 seconds, but by 400°C , nearly a 200 second difference is observed.

In an effort to study the primary hydrolysis and condensation reactions at the Q^3 $[\text{Si}_8\text{O}_{12}]$ centers, a series of $[\text{Si}_8\text{O}_{12}]$ -based molecules bearing only one reactive site were synthesized. $[\text{Si}_8\text{O}_{12}][\text{OSi}(\text{CH}_3)_3]_7\text{H}$ (6) was prepared from 5 by reaction with $(\text{CH}_3)_3\text{NO}$ and excess $(\text{CH}_3)_3\text{SiCl}$. A summary of the reactions studied is shown in the following scheme.



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