

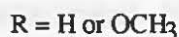
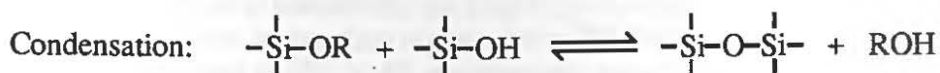
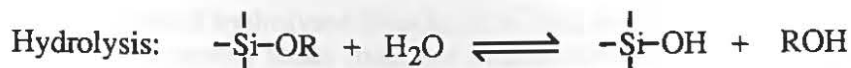
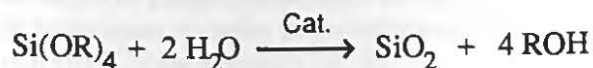
The Sol-Gel Polymerization of $[\text{Si}_8\text{O}_{12}](\text{OCH}_3)_8$

Phillip C. Cagle

Final Seminar

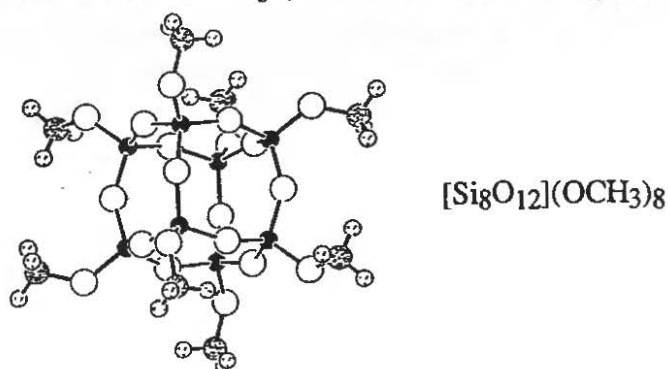
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Multifunctional silicate esters are known to undergo hydrolytic polymerization due to a series of hydrolysis and condensation steps [1-5]:



The reaction proceeds through the formation of a complex mixture of high molecular weight species $\text{Si}_a\text{O}_b(\text{OR})_c$ ($\text{R} = \text{H or CH}_3$), and ultimately results in the formation of amorphous silica.

Much work has been done on optimizing silica sol-gel conditions for the processing of silica films, fibers, monoliths and aerogels by the hydrolytic polymerization of tetraalkyl-orthosilicates $\text{Si}(\text{OR})_4$ [1-5]. However, Millar et al. were the first to address the notion of actually modifying the structure of silica on an atomic scale through the synthesis and sol-gel polymerization of the novel octafunctional silicate ester $[\text{Si}_8\text{O}_{12}](\text{OCH}_3)_8$ [6-8]. In contrast to more traditional silicate esters such as $\text{Si}(\text{OCH}_3)_4$, the octasilicate has a rigid cube structure [6]:



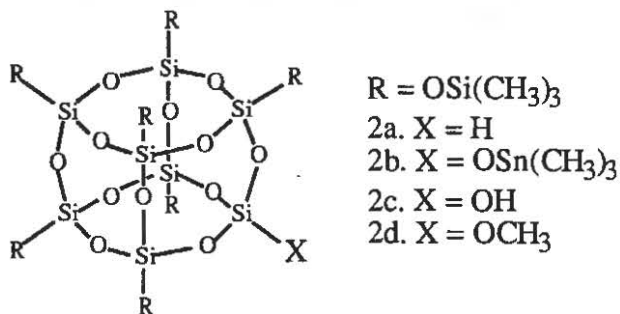
The rigidity of this molecular "building block" generates very different materials on a molecular size scale under sol-gel conditions [9,10]. Sol-gel polymerization of $[\text{Si}_8\text{O}_{12}](\text{OCH}_3)_8$ in CH_3CN under neutral conditions yields very high surface area ($S_{\text{BET}} > 900 \text{ m}^2/\text{g}$) xerogels, although lower surface areas result when acidic or basic catalysts are used [11]. These trends have been explained [9,10] in terms of the rigidity of cube polymers derived from $[\text{Si}_8\text{O}_{12}](\text{OCH}_3)_8$; polymers containing the $[\text{Si}_8\text{O}_{12}]$ repeat unit are relatively rigid and resist extensive crosslinking, thus generating materials with high surface areas.

The molecular building block approach assumes that the linkage of $[\text{Si}_8\text{O}_{12}](\text{OCH}_3)_8$ cubes by hydrolysis/condensation proceeds with retention of the cubic $[\text{Si}_8\text{O}_{12}]$ core. The

[Si₈O₁₂] cube contains 24 siloxane (Si-O) bonds, and cleavage of any one of these by water, alcohol, or a silicic acid (Si-OH) group would correspond to opening up of a cube edge. Although small amounts of [Si₈O₁₂] degradation would not affect the rigidity of cube polymers, extensive degradation would have an adverse effect. In principle, degradation of the silicate cube may be detected by ²⁹Si NMR. ²⁹Si NMR studies by Ramamurthi et al. of Si(OCH₃)₄ sol-gel polymerization were able to show quite conclusively how the molecular growth pathways are affected by acidic and basic catalysts [11,12]. In light of these results, it was hoped that the initial stages of [Si₈O₁₂](OCH₃)₈ sol-gel polymerization could be followed by a combination of such techniques in order to provide a molecular understanding of the trends observed for [Si₈O₁₂](OCH₃)₈ xerogels [9,10].

²⁹Si NMR studies of hydrolysed [Si₈O₁₂](OCH₃)₈ solutions showed that polymerization occurred much more rapidly under basic and neutral conditions than under acidic conditions. Under basic and neutral conditions, the [Si₈O₁₂](OCH₃)₈ resonance decreased in intensity with a concurrent rise in the glass region of the ²⁹Si NMR (the glass region is an extremely broad peak observed in ²⁹Si NMR spectroscopy associated with resonances from the glass in the NMR tube and the spectrometer probe). No distinct resonances due to oligomeric condensation products (dimers, trimers, etc.) were detected under sol-gel conditions (≥ 4 equiv. H₂O). Furthermore, intermediate hydrolysis products [Si₈O₁₂](OCH₃)_n(OH)_{8-n} were only present in low concentrations. These results are in stark contrast to those obtained under acidic conditions. Under acidic conditions condensation was extremely slow. After 2 weeks 99% of the total silicon concentration was present as [Si₈O₁₂](OCH₃)₈ and [Si₈O₁₂](OCH₃)_n(OH)_{8-n}, and [Si₈O₁₂](OCH₃)_n(OH)_{8-n} species were present in significant concentrations. The results observed under neutral and basic conditions are readily explained by a statistical approach to polymerization, namely Flory-Stockmayer theory [13,14]. Flory-Stockmayer theory predicts that the molecular weight distribution for an octafunctional monomer will be extremely broad, and that intermediate polymerization products (dimer, trimer, etc.) will be present in concentrations too low to detect by ²⁹Si NMR.

A study of the chemistry responsible for the differences under neutral, acidic, and basic conditions was hindered due to the complexity of the high molecular weight species present, even at the initial stages of polymerization. In order to avoid these difficulties, a model system initially explored by Millar [8] was used to model fundamental reactions at [Si₈O₁₂](OCH₃)₈ sites. This model is based on an [Si₈O₁₂] core in which seven of the eight reactive cube vertex sites are occupied by inert trimethylsiloxy units and the eighth is a reactive hydroxyl or methoxy group, which allows the study of fundamental hydrolysis and condensation reactions under a variety of conditions:



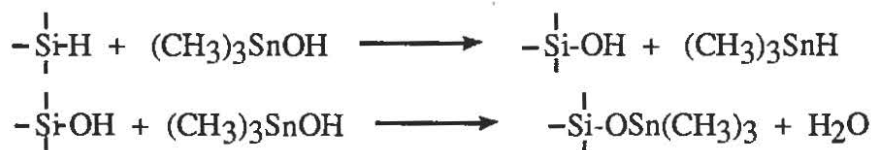
The reaction of $[\text{Si}_8\text{O}_{12}]\text{H}_8$ with $\text{Me}_3\text{NO}\cdot\text{Me}_3\text{SiCl}$ in THF gave a mixture of $((\text{CH}_3)_3\text{SiO})_n[\text{Si}_8\text{O}_{12}]\text{H}_{8-n}$, where $n = 7, 8$, as shown by GC/MS, $^{29}\text{Si}\{^1\text{H}\}$ and ^1H NMR spectroscopy, and elemental analysis. $[\text{Si}_8\text{O}_{12}](\text{OSi}(\text{CH}_3)_3)_7\text{OCH}_3$ is readily prepared from **2a** and Me_3SnOMe or Bu_3SnOMe . ^{119}Sn and ^1H NMR spectroscopy detected Me_3SnH as a byproduct, suggesting the following reaction [15]:



$[\text{Si}_8\text{O}_{12}](\text{OSi}(\text{CH}_3)_3)_7\text{OCH}_3$ was characterized by GC/MS, $^{29}\text{Si}\{^1\text{H}\}$ and ^1H NMR spectroscopy, and elemental analysis.

The hydrolysis of $[\text{Si}_8\text{O}_{12}](\text{OSi}(\text{CH}_3)_3)_7\text{OCH}_3$ was followed by ^{29}Si and ^1H NMR spectroscopy in 50:50 v/v $\text{C}_6\text{D}_6/\text{CD}_3\text{CN}$. Hydrolysis under neutral, basic, and acidic conditions gave the silanol, although some trimethylsiloxy group cleavage occurred under acidic conditions. Condensation to the cube dimer $((\text{CH}_3)_3\text{SiO})_7[\text{Si}_8\text{O}_{12}]\text{O}[\text{Si}_8\text{O}_{12}](\text{OSi}(\text{CH}_3)_3)_7$ occurred only under basic conditions. Surprisingly, the relative rates of hydrolysis were found to be: base \gg neutral $>$ acid. This is unusual because acids are usually considered *catalysts*, not inhibitors, in the hydrolysis of silicon alkoxides [16].

The reaction of **2a** with Me_3SnOH gave the stannoxy derivative, $[\text{Si}_8\text{O}_{12}](\text{OSi}(\text{CH}_3)_3)_7\text{OSn}(\text{CH}_3)_3$. The reaction requires two equivalents of Me_3SnOH , and is proposed to occur in two steps:



Hydrolysis of the stannoxy derivative with aqueous acid in C_6H_6 gives the silanol $[\text{Si}_8\text{O}_{12}](\text{OSi}(\text{CH}_3)_3)_7\text{OH}$, which was characterized by GC/MS, $^{29}\text{Si}\{^1\text{H}\}$ and ^1H NMR spectroscopy, and elemental analysis.

The self-condensation of $[\text{Si}_8\text{O}_{12}](\text{OSi}(\text{CH}_3)_3)_7\text{OH}$ to the cube dimer was followed by GC/MS, ^1H and ^{29}Si NMR. Condensation was only observed under basic conditions; no condensation was detected after one week under neutral or acidic conditions in 50/50 v/v $\text{C}_6\text{D}_6/\text{CD}_3\text{CN}$. In the presence of high concentrations of acids (> 1 equiv.), no condensation occurred although some trimethylsiloxy group cleavage was detected.

The base catalyzed condensation of $[\text{Si}_8\text{O}_{12}](\text{OSi}(\text{CH}_3)_3)_7\text{OH}$ with silicon alkoxides $\text{Si}(\text{OCH}_3)_4$, $[\text{Si}_2\text{O}](\text{OCH}_3)_6$, and $[\text{Si}_3\text{O}_2](\text{OCH}_3)_8$ occurred readily to give the corresponding condensation products, although in some cases the reactions were complicated by the competing self-condensation reaction, which produced water as a by-product. The reactions were followed by a combination of GC/MS and ^1H and ^{29}Si NMR.

The reactivity trends observed with the $[\text{Si}_8\text{O}_{12}](\text{OSi}(\text{CH}_3)_3)_7\text{X}$ model compounds effectively model the hydrolysis/condensation behavior of hydrolysed $[\text{Si}_8\text{O}_{12}](\text{OCH}_3)_8$ solu-

tions. The reactivity of these compounds also has relevance to various aspects of the $\text{Si}(\text{OCH}_3)_4$ sol-gel system [14].

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