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Cyclization Phenomena in the Sol-Gel Polymerization of α,ω-Bis(triethoxysilyl)alkanes and Incorporation of the Cyclic Structures into Network Silsesquioxane Polymers

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Abstract

Intramolecular cyclizations during acid-catalyzed, sol-gel polymerizations of α,ω-bis(triethoxysilyl)alkanes substantially lengthen gel times for monomers with ethylene- (**1**), propylene- (**2**), and butylene-(**3**)-bridging groups. These cyclizations reactions were found, using mass spectrometry and ^{29}Si NMR spectroscopy, to lead preferentially to monomeric and dimeric products based on six and seven membered disilsesquioxane rings. 1,2-Bis(triethoxysilyl)ethane (**1**) reacts under acidic conditions to give a bicyclic dimer (**5**) that is composed of two annelated seven membered rings. Under the same conditions, 1,3-bis(triethoxysilyl)propane (**2**), 1,4-bis(triethoxysilyl)butane (**3**), and Z-1,4-bis(triethoxysilyl)but-2-ene (**10**) undergo an intramolecular condensation reaction to give the six membered and seven membered cyclic disilsesquioxanes **6**, **7**, and **11**. Subsequently, these cyclic monomers slowly react to form the tricyclic dimers **8**, **9** and **12**. With NaOH as polymerization catalyst, these cyclic silsesquioxanes readily reacted to afford gels that were shown by CP MAS ^{29}Si NMR and infrared spectroscopies to retain some cyclic structures. Comparison of the porosity and microstructure of xerogels prepared from the cyclic monomers **6** and **7** with gels prepared directly from their acyclic precursors **2** and **3**, indicate that the final pore structure of the xerogels is markedly dependent on the nature of the precursor. In addition, despite the fact that the monomeric cyclic disilsesquioxane species can not be isolated from **1-3** under basic conditions due to their rapid rate of gelation, spectroscopic techniques also detected the presence of the cyclic structures in the resulting polymeric gels.

Introduction

Cyclization phenomena in the sol-gel synthesis of silica and polysilsesquioxanes play an integral role in the polymerization process and in the development of the network architecture. Six and eight membered rings have been identified in the hydrolysis and condensation of tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS).[1-6] Larger rings, which are probably present, have been more difficult to detect.[7,8] These two dimensional rings undergo further condensation reactions to generate, at least in some cases, polyhedral oligomers such as the octamethoxysilsesquioxane cube,[9] which may act as one of the primary building blocks in silica sol-gels. Similarly, the hydrolysis and condensation chemistry of silsesquioxanes, $RSiO_{1.5}$, is heavily influenced by cyclizations. Polymerization of trialkoxysilanes often leads to soluble polymers[4,10] due to the formation of numerous cyclic structures in lieu of branches or crosslinks. With sterically demanding substituents for R, discrete polyhedral oligosilsesquioxanes can be isolated in high yield.[11,12]

While studying the synthesis of a new class of hybrid organic/silica materials, a related yet unique cyclization process was discovered. Organically-bridged polysilsesquioxanes, prepared from the hydrolysis and condensation of triethoxysilanes linked by a hydrocarbon spacer, have been synthesized with a wide variety of organic groups incorporated in the polymer.[13-21] Acid- or base-catalyzed polymerization of α,ω-bis(triethoxysilyl)alkanes normally proceeds to highly condensed rigid gels within a few hours.[21] However, when the alkylene bridge is ethylene (**1**), propylene (**2**), or butylene (**3**), gelation under acidic conditions requires 2-6 months. Upon closer examination, it was discovered that these monomers were undergoing intramolecular cyclization reactions to form six and seven-membered rings (Scheme 1) that are designated as "cyclic disilsesquioxanes".[22] Ring closure to form cycloalkanes is well known to be governed by both the kinetic and the thermodynamic demands of cyclization generally favoring the formation of five and six membered rings.[23] Similarly, dihalodimethylsilanes are known to preferentially cyclo-oligomerize to eight and ten membered siloxane rings.[1,24,25] Since cyclic disilsesquioxanes can be considered hybrids of the hydrocarbon and siloxane ring systems, it is not surprising that cyclizations to six and seven membered rings are the most favorable in the alkylene-bridged series.

Naturally, the fate of these cyclic disilsesquioxanes was of interest with regards to the final molecular structure of the resulting polymeric networks and gels. By monitoring the hydrolysis and condensation reactions of the bridged monomers **1-3**, **10**, **13** with mass spectrometry and ^{29}Si NMR spectroscopy it was possible to detect not only the monomeric cyclic disilsesquioxanes, but a variety of oligomeric products based predominantly on six and seven membered rings. By performing the reactions with sub-stoichiometric quantities of water we were able to isolate and characterize the monocyclic (**6**, **7**, **11**, **14**), bicyclic (**5**) and tricyclic (**8**, **9**, **12**, **15**) silsesquioxanes formed during these reactions (Scheme 2). Furthermore, we were able to demonstrate, using infrared and ^{29}Si CP MAS NMR spectroscopies, that polymerization of the cyclic disilsesquioxane monomers could be accomplished without significant ring-opening to afford a new class of polysilsesquioxane materials. Discovery of *cis*-syndiotactic stereochemistry about the ring junctions of the tricyclic dimers **8**, **9**, **12**, **15** suggests that it might be possible to prepare ladder-like polysilsesquioxanes structures as well.

Results and Discussion

Gelation of monomers with two or more triethoxysilyl groups has been shown to occur as quickly as minutes, even at monomer concentrations as low as 0.2 M.[16,20,21] This ease of gelation, relative to tetraethoxysilane under identical conditions, has been attributed to the higher degree of functionality and additional connectivity built into these monomers with the organic bridging group.[16] With base-catalyzed polymerization of α,ω-bistriethoxysilyl)alkanes, gelation is rapid regardless of the length of the bridging alkylene group; if cyclic species are forming they are not interfering with the growth of polymers capable of forming gels. Under acidic conditions, the length of the bridging group had a remarkable effect on the gel times (Figure 1). Gelation occurred after months for monomers **1-3**, but only hours for monomers with bridging alkylenes longer than six carbons in length. Gelation would readily occur even with only two equivalents of water. It was this disparity in gelation times that gave us the first indication that different reaction manifolds could be accessed based on the length of the alkylene-bridging group.[22] The fact that bridging alkylenes longer than six carbons gave no evidence of soluble cyclic monomers and oligomers in either mass spectrometric or ^{29}Si NMR studies, coupled with their short gel times, indicated that acyclic and intermolecular condensation reactions predominate.

Dimerization-Cyclization Reactions of Monomer 1. Ethylene-bridged monomer **1** gelled immediately under base-catalyzed sol-gel conditions, but required one month for gelation under acidic conditions. It was suspected that the prolonged gel times were due to a cyclization process that was similar to that first observed with the propylene- and butylene-bridged monomers.[22] However, we were not certain whether the five membered cyclic disilsesquioxane (**4**), from the intramolecular condensation reaction of **1**, would be too strained to participate or if larger rings, based on dimers of **1**, would dominate the early stages of the sol-gel chemistry (Scheme 3). Examination of the solutions before gelation with ^{29}Si NMR demonstrated that the expected pattern of resonances from monomer hydrolysis and condensation products was not in evidence.

Typically in sol-gel chemistry, the ^{29}Si NMR chemical shift of peaks moves progressively downfield in increments between 1-3 ppm per ethoxide group replaced with a hydroxide, and upfield 5-10 ppm with each additional siloxane bond to the silicon atom.[26] To illustrate this, a series of ^{29}Si NMR spectra for 1,10-bis(triethoxysilyl)decane before hydrolysis (top), monomer treated with 1 equivalent water (middle), and monomer treated with 2 equivalents water (bottom), both with aqueous HCl as catalyst are shown in Figure 2. The group of peaks labeled T^0 (middle) represent the unreacted monomer ($\delta = -45.3$) and singly ($\delta = -43.2$) and doubly hydrolyzed ($\delta = -41.2$) monomer. A second group of peaks (T^1) appears upfield from the T^0 resonances arising from silsesquioxanes with a single siloxane bond with no hydrolyzed ethoxide groups (δ = -52.9) and with one ethoxide hydrolyzed to a silanol (δ = -51.2). The third spectrum (bottom) shows that the peaks due to the monomer and other T^0 silicons have been reduced in intensity while the T^1 resonances have grown to be the major contributors to the spectrum. T^2 silicons from additional condensation reactions can be seen near -60 ppm. After one hour, the solution of 1,10-bis(triethoxysilyl)decane and 2 equivalents of water formed a gel. In comparison, the spectra of the ethylene-bridged monomer **1** and its hydrolysis and condensation products are quite different (Figure 3). Hydrolysis affords a more complex pattern of peaks downfield from the monomer resonance (δ = -45.9) due to long range substituent effects.[27] However, the most notable difference between the spectra for the sol-gel polymerization of **1** and those for 1,10-bis(triethoxysilyl)decane is in the distribution of T^1 and T^2 peaks. Here, two peaks (δ = -50.7 and δ = -53.1) appear and remain near equal intensity even at greater extent of reaction. The chemical shift for **4**, synthesized by hydrogenating 2,2,5,5,-tetraethoxy-2,5-disilaoxacyclopent-3-ene (Scheme 4), lies *downfield* (δ = -41.3) from the resonance due to **1**.[28-30] Only a small peak near –41 ppm can be observed in the spectra shown in Figure 3.

A mass spectrum of an identical solution of **1** after 10 minutes of reaction shows that most of the monomer has been converted into the bicyclic dimer or its hydrolysis products (Figure 4). The unhydrolyzed bicyclic dimer has parent ions at m/z 487 $[\mathbf{5}+H]^+$ and m/z 504 $[\mathbf{5}+NH_4]^+$. Ions from the hydrolysis products of the dimer are present (m/z = 476 and 459 for the singly hydrolyzed dimer, m/z = 431 and 448 for the doubly hydrolyzed dimer, and m/z = 403 and 420 for the triply hydrolyzed dimer). Two structures (**5** and **5a**) for the dimer are consistent with the observed masses and the hydrolysis and condensation chemistry of alkoxysilanes. The five-membered cyclic disilsesquioxane **4** was not observed in the mass spectrum; the analogous 2,2,5,5-tetramethyl-2,5-disila-1-oxacyclopentanes are significantly strained (8-12 kcal/mol) and readily undergo ring-opening polymerization.[29] It is unlikely that such a strained species would be present under sol-gel polymerization conditions.

The dimer was identified as **5** based on the ^{29}Si NMR data (Figure 3) and by isolating and characterizing the pure compound from the reaction mixture; the product was shown to have two silicon resonances at δ = -50.3 and δ = -52.9. T^1 silicons in **5a** would be expected to give rise to a peak with a chemical shift close to that observed for **4** (δ = -41.3). The ^{29}Si NMR of **5** would also have T^1 and T^2 resonances, but because they would be in seven-membered rings, the peaks should lie farther upfield of the monomer and downfield of acyclic T^1 and T^2 resonances (Figure 2). Furthermore, when **1** was reacted with only *one equivalent* of water under acidic conditions, intermediates in the formation of **5** were observed in the mass spectrum (Scheme 5). Within the first hour of reaction, the major ions in what should be the dimer region for **1** were masses at m/z = 589 [**1a**-OEt]$^+$, 561, and 515 which are consistent with the acyclic dimer **1a** along with ions attributable to **5** and its hydrolysis products. The next intermediate in the formation of **5** would result from the first of two intramolecular cyclizations of the acyclic dimer to yield **1b**. The presence of **1b** was supported by the presence of the parent ion with m/z = 561 [**1b**+H]$^+$ and its fragmentation product at m/z = 515 [**1b**-OEt]$^+$. After several hours, the ions due to intermediates **1a** and **1b** had diminished and only peaks assigned to **5** and its hydrolysis products remained. Only traces of ions with masses consistent with the five-membered disilsesquioxane ring were observed.

Once formed, **5** was slow to react, even in the presence of excess water. Oligomers larger than dimer were not observed in the mass spectrum. The reaction of two equivalents of water with **1** was monitored for several hours and the only significant change in the mass spectrum is an increase in the amount of hydrolyzed dimer as hydrolysis products of **5** account for the major ions in the spectrum (m/z = 448, 420, and 374). Apparently, the relatively slow condensation chemistry of **5** serves as a bottleneck in the acid-catalyzed polymerization of **1**. The limited amount of water employed in the experiment cannot account for the paucity of higher oligomers since extensive hydrolysis of **5** is detected in the mass spectrum. The impact of the cyclization of the ethylene-bridged monomer on polymerization and gelation is highlighted by the ease with which 1,10-bis(triethoxysilyl)decane forms a gel under identical conditions.

Cyclization Reactions of Monomers 2 and 3. Polymerization of monomers **2** and **3** (0.4 M in ethanol) with six equivalents of water and HCl (10 mol%) as catalyst gave transparent, colorless solutions that took over six months to gel. Analyses of these solutions indicated the presence of the six (**6**) and seven (**7**) membered cyclic disilsesquioxane monomers, respectively. In the ^{29}Si NMR of the reaction of **2** with one equivalent of water under acidic conditions, a single peak assignable to the T^1 silicon (δ = -47.2) in **6** appeared between where T^0 (monomer; δ = -45.8) and T^1 resonances are typically expected (Figure 5). Hydrolysis and condensation of monomer **3** under identical conditions gave a single resonance (δ = -49.1) for **7** (Figure 6) that was shifted slightly farther upfield from that of **6**, but still farther downfield than would be expected for an acyclic or unstrained T^1 resonance. Conversions to **6** and **7** were quantitative with one equivalent of water and the cyclic products could be isolated in good yields from the reaction mixtures by simple distillation. Intramolecular cyclization under acidic conditions was also observed with 1,4-bis(triethoxysilyl)but-2-ene (**10**) to give the unsaturated cyclic disilsesquioxane **11** and with 1,3-bis(diethoxymethylsilyl)propane (**13**) to give the cyclic disiloxane **14** as a mixture of its syn and anti diastereomers.

6

The stability of the six and seven membered cyclic disilsesquioxanes towards ring-opening is important for understanding their impact on the polymerization of the propylene- and butylene-bridged monomers. Treatment of neat **6**, **7**, and **14** with catalytic amounts of Lewis acidic ($BF_3.OEt_2$) or basic (Bu_4NOH) catalysts had no effect, indicating that insufficient ring strain was present to facilitate ring-opening polymerizations. The reversibility of the cyclization reaction under sol-gel conditions will impact how well the cyclic structures are incorporated into polymeric architectures. It has been shown with tetraalkoxysilanes that the condensation reaction is essentially irreversible in these types of sol-gels.[31] Because acyclic species were not detected in the mass spectra and ^{29}Si NMR during the formation of **6** and **7**, we prepared an isotopically labeled cyclic disilsesquioxane **6***. If the cyclic species was equilibrating with an acyclic one, isotopic exchange between the ^{17}O/^{18}O-labeled cyclic disilsesquioxane and unlabeled water would be detected. ^{17}O/^{18}O-labeled cyclic disilsesquioxane **6*** was prepared from **2** using isotopically labeled water ($H_2{}^*O$; $^*O$ = 42% ^{18}O and 27% ^{17}O). The reaction of **6*** with 1N aqueous HCl, which was monitored by mass spectrometry, showed a gradual decrease in **6*** (m/z = 296 and 297) with a concomitant increase in unlabeled **6** (m/z = 295) as unlabeled water was incorporated. These observations imply that a small amount of acyclic product was generated from **6*** in the presence of water. ^{17}O NMR spectroscopy of the same sample also revealed the single peak from the labeled **6*** (δ = 64.0 ppm) gradually being replaced by low frequency resonances due to labeled silanols (δ = 30.7 ppm) and labeled water (δ = -5.7 ppm).[32] Loss of ^{17}O from **6*** is consistent with exchange due to the reversibility of the cyclization reaction.

Synthesis and Characterization of Tricyclic Dimers. When **2** or **3** were reacted with *two equivalents* of water for several hours, new resonances at δ = -50.4 and δ = -53.5, respectively, slowly appeared in the ^{29}Si NMR. These resonances fall between where acyclic or unstrained cyclics with T^1 and T^2 silicons would be expected to appear (Figure 5 & 6). Even after 3 weeks of acid-catalyzed hydrolysis of **6** with six equivalents of water, gelation was not observed and the ^{29}Si NMR spectrum was dominated by the resonance at δ = -50.4. In the mass spectra of identical solutions, peaks with masses consistent with dimers of **6** and **7** were observed for each monomer. The dimers were tentatively assigned as tricyclic compounds **8** and **9** (m/z 458 [M+NH_4] and m/z 486 [M+NH_4], respectively).

Verification of these tricyclic structures was achieved by careful hydrolysis of the cyclic disilsesquioxane **6** and **7** to give the pure tricyclics **8** and **9**, respectively. However, the most efficient route was to prepare **8** and **9** directly from the acyclic monomers **2** and **3**. Complete conversion of the monomers to dimers required several days in refluxing ethanol or THF with two equivalents water and HCl as catalyst. Tricyclic dimer **8** was isolated as a crystalline solid directly from the reaction in ethanol. Dimer **9** was isolated as a crude oil and all attempts to crystallize it from the reaction mixture failed, probably due to the high solubility of the dimer and to the additional flexibility in the structure imparted by the longer alkylene groups. It was possible, however, to prepare pure **9**, still as an oil, by hydrogenating its unsaturated analog (**12**; Scheme 6). Pure, crystalline tricyclic dimer (**12**) was obtained directly from the acid-catalyzed hydrolysis of Z-1,4-bis(triethoxysilyl)but-2-ene (**10**) with two equivalents of water.

Formation of bridged tricyclic structures appears to be common to both *silsesquioxane* and *siloxane* monomers with three or four carbon bridging groups as the same series of cyclization reactions was also observed for **13**. Tricyclic dimer **15**, a crystalline white solid, was of interest because it possesses no ethoxide groups, making it a relatively unreactive model compound. ^{1}H NMR spectra of **8**, **12**, and **15** are consistent with the rigid tricyclic structure. Compounds **8** and **15** have similar spectra which are best described as AA'BB'MX. The portion of the ^{1}H NMR spectrum arising from the propylene bridge of **8**, shown in Figure 7, was simulated and decoupling experiments were performed to assist in making assignments and obtaining coupling constants. The large $^3J_{XA}$ and $^3J_{XA'}$ of 13.1 Hz is indicative of an axial to axial coupling while the smaller methylene $^3J_{HH}$ are consistent with axial to equatorial and equatorial to equatorial couplings. These coupling constants indicate that the structure of the two six-membered rings in the tricyclic system are in the expected chair conformation. The ^{1}H NMR spectrum of **15** exhibited chemical shifts and coupling constants for methylene groups in its propylene bridge that were nearly identical to those observed for **8**.

While the structures of tricyclic dimers **8**, **12**, and **15** could be assigned from NMR and mass spectral data, the configuration (syn or anti) of the dimers was determined by X-ray crystallographic studies.[33] The structures consist of two cyclic monomer units linked in an anti configuration about a distorted eight-membered siloxane ring (Figure 8). None of the syn stereoisomer was isolated from any of the reactions. This is in good agreement with the calculated MM2 structures[34] that predicted that the anti diastereomer would be more stable than the syn form by 7.55 kcal/mole (Figure 9). The anti-configuration of the bridging groups is the same orientation displayed in *cis*-syndiotactic ladder structures that have often been proposed for soluble polysilsesquioxanes.[35] While the tricyclic dimer may represent the beginning of a ladder polymer structure, continued growth of the polymer would be severely limited by slow hydrolysis and condensation at the remaining ethoxysilyl functionalities; no discrete, higher oligomers have been isolated. X-ray crystallographic studies of **12** and **15** disclosed that these dimers have virtually the same structural features as those described for **8**.

Synthesis of Polysilsesquioxanes

Finding that monomers **1-3** form substantial amounts of cyclic monomers and dimers early in the acid-catalyzed sol-gel polymerization process raises the question: are cyclic structures incorporated in the resulting xerogels? To answer this, polysilsesquioxanes were prepared by the sol-gel polymerization of monomers **1-3** and **6-8** with aqueous NaOH as the catalyst. Formation of polysilsesquioxane gels using an acidic catalyst was not practical since the formation of cyclics under these conditions resulted in gel times of several months (Figure 1). Under basic conditions, monomers **1-3** and **6-8** polymerized to rigid, free standing gels in less than 24 hours. Gels prepared from the acyclic monomers were generally cloudy or fully opaque, while the cyclic monomers polymerized to give colorless, transparent gels. All of the dried gels or xerogels were obtained as glassy white fragments.

There is no reason to expect that intramolecular condensation of monomers **1-3** to form cyclic disilsesquioxanes does not occur in the base-catalyzed polymerizations. Unfortunately, it is much more difficult to study the initial hydrolysis and condensation products under basic sol-gel conditions. With sodium hydroxide-catalysis, the first hydrolysis and condensation are the slowest while the rates of subsequent hydrolysis and condensation reactions increase with the extent of the reactions.[41] Consequently, the initial condensation products are very short-lived and difficult to observe spectroscopically. Xerogels **1X-3X** and **6X-8X** were studied by CP MAS ^{29}Si NMR and infrared spectroscopies to try to determine if the cyclic structures of **6-8** were present in these polymers.

Characterization of Polysilsesquioxanes.

^{29}Si CP MAS NMR Spectroscopic Analyses. Because ^{29}Si NMR chemical shifts are sensitive to variations in the bond angles at the silicon atom, this analytical method is a powerful tool for differentiating between cyclic and acyclic structures. As the bond angles becomes smaller in the cyclic systems, the chemical shift of the silicon-29 resonance moves downfield. If the cyclic structures are incorporated into the final polysilsesquioxanes, there should be a distinct difference in the ^{29}Si CP MAS NMR spectra of these materials and those in which the formation of the small cyclic structures do not occur. The solid state CP MAS ^{29}Si NMR spectra of alkylene-bridged polysilsesquioxanes usually contain three distinguishable peaks which are assigned to the T^1, T^2, and T^3 silicons present in the polymer.[21] A typical spectrum observed for these materials is shown in Figure 10 for a polymer prepared from 1,10-bis(triethoxysilyl)decane as well as the spectra for the polymers **1X-3X** and **6X-8X**. The decylene-bridged monomer does not form the small organosiloxane rings observed in **1**, **2**, and **3** and the T^2 and T^3 peaks for this polymer are observed

at -59.3 ppm and -66.8 ppm, respectively. However, the spectra for the polymers prepared from the ethylene-, propylene-, and butylene-bridged monomers, whether the monomer is cyclic or acyclic, contain a single broad unresolved peak. The T^3 resonance is generally the largest peak in the ^{29}Si NMR spectra of polysilsesquioxanes prepared from monomers with hexylene- or longer bridging groups and it is observed between -66 ppm to -67 ppm. It is expected that the unresolved peaks for the polymers prepared from **1-3** and **6-8** arise mostly from T^3 silicons since they are also prepared under basic conditions. These peaks are shifted significantly downfield from the typical alkylene-bridged material. We interpret this *downfield* shift as an indication of the presence of the cyclic disilsesquioxane structures in the polysilsesquioxanes **1X-3X** and **6X-8X**.

The poor resolution in the ^{29}Si NMR spectra of the polymers prepared from **1-3** and **6-8** may be explained by a combination of phenomena. The presence of cyclic structures in the xerogels adds to the variety of chemical environments in which the T^2 and T^3 silicons may be found compared to the simple acyclic structures of longer alkylene-bridged materials. Also, there may be some ring opening occurring during the polymerization of **6-8** and ring closure may not be quantitative during the polymerization of **1-3**, yielding polymer networks that are composed of both cyclic and acyclic structures.

Infrared Spectroscopic Analyses. Infrared spectroscopy was also utilized to probe the solid state structure of the polysilsesquioxanes. Siloxanes typically exhibit one or more very strong bands in the region 1130-1000 cm^{-1} for ν(Si-O).[42] The location of this absorption band in the infrared spectrum is influenced by the structure of the siloxane. For example, when the siloxane bonds are confined to a small cyclic structure such as $[R_2SiO]_3$, the ν(Si-O) occurs at a low frequency of 1020-1010 cm^{-1} while larger cyclics, $[R_2SiO]_{4-5}$, are observed at 1090-1075 cm^{-1}.[42-44] This same phenomenon is observed in the series of cyclic organo-siloxane compounds 2,2,5,5-tetramethyl-2,5-disilaoxacyclopentane, 2,2,6,6-tetramethyl-2,6-disilaoxacyclo-hexane, and 2,2,7,7-tetramethyl-2,7-disilaoxacycloheptane which exhibit ν(Si-O) bands at 920, 987, and 1020 cm^{-1}, respectively.[42,45] All of these Si-O bands involved in the small cyclic structures are observed at lower frequencies than the acyclic siloxanes $R_3SiOSiR_3$ which show Si-O absorption bands in the range of 1040-1080 cm^{-1}.[42] We observed a similar trend in the SiO bands for cyclic disilsesquioxanes. These differences in the absorption bands between cyclic and acyclic siloxanes were used to help characterize the network architectures of xerogels **1X-3X** and **6X-8X**.

The prominent absorption bands in the infrared spectra in the range 1200-1000 cm^{-1} for both monomers and xerogels are listed in Table 1. The cyclic monomers, **4** and **6-8**, exhibit a very strong absorption band around 1034-950 cm^{-1} which is conspicuously absent in the spectra of the acyclic monomers. These low frequency absorptions are consistent with ν(Si-O) absorptions in small cyclic structures. Most of the xerogels also show absorption bands in this range indicative of the presence of the cyclic structures. A polymer prepared from 1,10-bis(triethoxysilyl)decane, which cannot form strained disilsesquioxane rings, has a very strong absorption band at 1122 cm^{-1} with a shoulder at 1050 cm^{-1} and no low frequency absorptions in the range of 1034-950 cm^{-1}. This spectrum is typical of alkylene-bridged polysilsesquioxanes which have bridging groups of six carbons or longer.

A band at 1030 cm^{-1} is observed in the xerogel **1X** which is very close to that of the seven-membered rings in **5** (1011 cm^{-1}) and **7** (1034 cm^{-1}). This observation suggests that the seven-membered disilsesquioxane rings observed for **1** under acid-catalyzed hydrolysis and condensation conditions are also formed under basic conditions. Xerogels prepared from the propylene-bridged monomers **2**, **6**, and **8** have absorption bands at 1024, 1018, and 1008 cm^{-1}, respectively. These bands are also in the low frequency range indicative of the presence of cyclic structures in the final polymers. The band for **2X** occurs at a slightly higher frequency than those for **6X** or **8X**, which may be due to the presence of a greater fraction of acyclic propylene-bridged moieties. Furthermore, the absorption for **8X** is shifted to a lower frequency than that for **6X**, which is expected if the more highly strained tricyclic structure **8** is present to a greater extent in **8X** than in **6X**. The absorption of 1054 cm^{-1} for **3X** is in the range (1040-1080 cm^{-1}) of ν(Si-O) bands expected for acyclic structures. Thus, under base-catalyzed conditions, infrared analysis suggests that ring closure of **3** and incorporation of the cyclic structure into the final polymer does not seem to predominate as it did for **2**. However, xerogel **7X** has a strong absorption band at 1039 cm^{-1}, indicating that the cyclic structure of the starting monomer is at least partially preserved in the final polymer. Clearly, the choice of acyclic or cyclic silsesquioxane monomer does have influence on the contribution of cyclic structures in the resulting xerogels.

Surface Area Analyses. The structures of the polysilsesquioxanes were also studied by nitrogen sorption porosimetry and scanning electron microscopy to determine what effect the structures of the starting monomers have on the surface areas and porosity of the final polymers. All of the materials were found to have high surface areas ranging from 590 m^2/g, for **1X**, to 880 m^2/g, for **3X** (Table 2). Most of the porosity of the xerogels resides in pores with average diameters in the lower end of the mesoporous domain (mesopore diameter range = 20-500 Å).[46] The average pore diameters and pore volumes for the polymers prepared from **1-3** decrease as the alkylene-bridge is lengthened.

The effect of the cyclic versus acyclic monomer structure on the porosity of the final polysilsesquioxanes was examined in greater detail through the incremental pore volume plots[47] for each polymer. These plots, derived from the desorption branch of the nitrogen isotherm, reveal the distribution of pore sizes and the extent to which they contribute to the pore volume. At each step during the desorption phase of the porosimetry experiment, the volume of liquid nitrogen removed from the pores of the material is measured and a corresponding pore diameter is calculated from the relative pressure using the BJH method.[48] A distribution of the pore sizes in the material can be observed by plotting the measured pore volumes versus the calculated pore diameters.

Incremental pore volume plots for the propylene-bridged polysilsesquioxanes, prepared from the acyclic monomer **2** and the cyclic monomers **6** and **8**, exhibit a stark difference in their pore size distributions (Figure 11). In **2X**, contributions to the pore volume are observed from pores with diameters that extend over the entire mesopore range.

However, xerogels **6X** and **8X** have very narrow pore size distributions with the pore diameters lying mostly between 30-45 Å. Since all three polymers were prepared using identical conditions, these differences must originate from the cyclic or acyclic structures of the starting monomers. This same trend is not observed in the butylene-bridged polysilsesquioxanes as the porosimetry data and pore volume plots for **3X** and **7X** are very similar. Both polymers have fairly narrow pore size distributions with a range of pore diameters of 30-50 Å for **3X** and 40-100 Å for **7X** (Figure 12).

The differences in porosity between **2X** and xerogels **6X** and **8X** are reflected in the scanning electron micrographs of the polymers shown in Figure 13. Xerogel **2X** appears to have a very coarse morphology with the macrostructure of the polymer being comprised of large globular particles ranging in size from fifty to several hundred nanometers. These structural features result in an open framework that is responsible for the larger mesopores and macropores (macropore = diameter > 500 Å) in the polymer. Xerogels **6X** and **8X** have smoother and more continuous morphologies with more compact structures eliminating the larger pores.

Conclusions

Novel cyclization phenomena during the synthesis of alkylene-bridged polysilsesquioxanes were discovered for monomers with short alkylene bridges of 2-4 carbons (**1-3**). These cyclic products were found to inhibit the polymerization of the monomers under acidic sol-gel conditions. The ethylene-bridged monomer formed an unusual bicyclic dimer (**5**) which consisted of two fused seven-membered organosiloxane rings. Monomers with three or four carbon bridges underwent a series of intramolecular cyclizations to form a fused tricyclic dimeric product. Many of the cyclic products including some the tricyclic dimers were isolable. These cyclic products were shown to be reactive monomers for the base-catalyzed sol-gel synthesis of polysilsesquioxanes that incorporate the ring structures into the network architecture. Solid state ^{29}Si NMR and infrared spectroscopy indicate that cyclic structures were preserved in the final polymers.

It was also discovered that the structures of the monomers (cyclic or acyclic) can have a profound influence on the porosities and morphologies of the sol-gel materials derived from them. The synthesis of propylene-bridged polysilsesquioxanes from the acyclic monomer **2** resulted in polymers with a very broad pore size distribution spanning several hundred nanometers. However, when the propylene-bridged materials are prepared from the cyclic monomers **6** and **8**, the polymers exhibit very narrow pore size distributions of just a few nanometers. Both the acyclic and cyclic butylene-bridged monomers yield materials with fairly narrow pore size distributions in the lower end of the mesopore regime between 20 and 100 Å. Manipulation of the structures of the starting monomers in polysilsesquioxane syntheses may be an important technique for creating materials with well-defined mesoporous domains.

Experimental

General Methods. All reactions were run under dry argon using standard Schlenk techniques unless otherwise noted. Ethanol was dried and distilled off magnesium turnings under argon and benzene was distilled from calcium hydride. 3-Triethoxysilylpropene, 4-triethoxysilylbutene, triethoxysilane were obtained from Geleste and were used as received. Chloroplatinic acid was purchased from Aldrich and was kept stored under argon until needed. Isotopically enriched water (27% ^{17}O, 42% ^{18}O) was purchased from ISOTEC, Inc. 1,10-Bis(triethoxysilyl)decane was prepared by chloroplatinic acid catalyzed hydrosilation of 1,9-decadiene with triethoxysilane and was spectroscopically identical to the report in literature.[21] Z-1,4-bis(trichlorosilyl)but-2-ene was prepared by a procedure used to prepare the analogous E-isomer.[49]

Infrared spectra were obtained on a Perkin-Elmer 1750 Fourier Transform Infrared spectrophotometer. ^{1}H, ^{13}C and ^{29}Si solution NMR spectra were recorded on Bruker AM

300 and DRX 400 MHz spectrometers. ^1H NMR spectra of **8** and **11** were recorded on an DRX 400 at a resonant frequency of 400.16 MHz, using standard single pulse sequences on a 5 mm BB probe. The relaxation delay was 5 seconds, with 8K to 32K complex points. Experiments were performed at 298 K, using 16-32 scans. Iterative simulations of the ^1H spectra of **8** and **11** were performed using commercial software (ACORN NMR) on a PC to make peak assignments and to determine coupling constants. ^{17}O NMR experiments were conducted with an AMX 400 at a resonant frequency of 54.25 MHz, using a 5 mm BB probe. The relaxation delay was 200 ms, with 32-64 scan averages as a function of time. Residual solvent peaks or tetramethylsilane were used as internal references for ^1H and ^{13}C spectra. An external tetramethylsilane ($\delta = 0.0$) sample was used as the reference for ^{29}Si NMR spectra and an external H_2O ($\delta = 0.0$) was used to reference ^{17}O spectra.

Solid state ^{13}C and ^{29}Si CP MAS NMR spectra were obtained with a Bruker AMX-400 MHz spectrometer at 100.63 MHz and 79.5 MHz, respectively, and were acquired with magic angle spinning (MAS) speeds of ~5 kHz and ~3-5 kHz, respectively. ^{13}C NMR spectra were acquired using cross polarization (CP) with a relaxation delay of 1 sec and a cross polarization time of 2 msec. ^{13}C referencing was performed on the carbonyl resonance of solid glycine ($\delta = 176.0$). Since the gels in this study are similar, these parameters were optimized on only one of the gels to obtain spectra with a satisfactory signal to noise ratio. ^{29}Si NMR spectra were acquired using single pulse excitation with a relaxation delay of 480 sec. With ^{29}Si T_1 values ranging from 19 to 135 sec, the relaxation delay is $3T_1$ which is sufficient for quantitative spectra. ^{29}Si CP MAS NMR spectra were deconvoluted using a Lorentz-Gaussian (50:50) fit. Mass spectra were obtained on a Fisons Autospec (CI, ammonia). Monomer purity was determined by GC with an HP Series II 5890 and a packed column with HP-1 (crosslinked methyl siloxane), 15m x 0.32mm. Microscopy studies were performed using a Hitachi S4500 field emission scanning electron microscope. The samples were coated with 100-200 Å chromium using a Gatan Model 681 High Resolution Ion Beam coater. Secondary electron images were taken using 5 KV accelerating voltage. The images were acquired digitally from the SEM using a PGT Imix imaging system. Porosimetry measurements were determined using a Quantachrome Autosorb-6 multiport nitrogen porosimeter.

Monomer Preparation

1,2-Bis(triethoxysilyl)ethane (1). A flask was charged with vinyltriethoxysilane (45.0 g, 237 mmol), triethoxysilane (44.5 g, 271 mmol), benzene (200 mL), and chloroplatinic acid (130 mg, 0.320 mmol). The flask was fitted with a drying tube loaded with Drierite such that the reaction was exposed to dry air. The mixture darkened after a few minutes and it was allowed to stir for 24 h. Benzene was removed *in vacuo* leaving a dark liquid that was vacuum distilled (0.025 Torr, 86-88 °C) yielding a clear colorless liquid (63.7 g, 76%). ^1H NMR (300 MHz, C_6D_6): $\delta = 3.76$ (q, 12H, OCH_2CH_3, J = 7.0 Hz), 1.13 (t, 18H, OCH_2CH_3, J = 7.0 Hz), 0.89 (s, 4H, $SiCH_2CH_2Si$, J = 8.2 Hz). ^{13}C NMR (75 MHz, C_6D_6): $\delta = 58.5$ (OCH_2CH_3), 18.5 (OCH_2CH_3), 2.5 ($SiCH_2CH_2Si$). ^{29}Si NMR (99 MHz, EtOH): $\delta = -45.8$. IR (neat): ν = 2975, 2927, 2887, 1483, 1443, 1409, 1391, 1366, 1295, 1168, 1147, 1103, 1083, 957, 781 cm^{-1}. HRMS (CI, isobutane): Anal. Calcd for $C_{14}H_{35}O_6Si_2$ $[M + H]^+$: 355.1972. Found: 355.1972.

1,3-Bis(triethoxysilyl)propane (2).[22] A flask was charged with 3-triethoxysilylpropene (50.0 g, 245 mmol), triethoxysilane (48.3 g, 294 mmol), benzene (100 mL), and chloroplatinic acid (0.10 g, 0.24 mmol). The flask was fitted with a drying tube loaded with Drierite such that the reaction was exposed to dry air. While stirring for 24 h, the solution gradually turned yellow-brown. Additional chloroplatinic acid (0.10 g, 0.24 mmol) was added to the reaction mixture and stirred for another 24 h. Benzene was removed *in vacuo* leaving a dark liquid that was distilled (0.025 Torr, 85-90 °C) to yield a clear colorless liquid (52 g, 58%). ^1H NMR (300 MHz, C_6D_6): $\delta = 3.78$ (q, 12H, OCH_2CH_3, J = 7.0 Hz), 1.84 (m, 2H, $SiCH_2CH_2CH_2Si$), 1.15 (t, 18H, OCH_2CH_3, J = 7.0 Hz), 0.85 (t, 4H, $SiCH_2CH_2CH_2Si$, J = 8.2 Hz). ^{13}C NMR (75 MHz, C_6D_6): $\delta = 58.4$ (OCH_2CH_3), 18.5 (OCH_2CH_3), 17.2 ($SiCH_2CH_2CH_2Si$), 15.0 ($SiCH_2CH_2CH_2Si$). IR (neat): ν = 2975, 2928, 2884, 1484, 1444, 1391, 1366, 1341, 1295, 1229, 1168, 1078, 960, 900, 820, 774, 710 cm^{-1}. ^{29}Si NMR (99 MHz, EtOH): δ = -45.8. HRMS (CI, isobutane): Anal. Calcd for $C_{15}H_{37}O_6Si_2$ $[M + H]^+$: 369.2129. Found: 369.2113.

1,4-Bis(triethoxysilyl)butane (3).[21,22] To a solution of 4-triethoxysilylbutene (25.0 g, 114 mmol), triethoxysilane (24.3 g, 148 mmol), and benzene (100 mL) was added chloroplatinic acid (0.10 g, 0.24 mmol). Within 10 min, the solution turned yellow and an exothermic reaction occurred. After stirring for 48 h, chloroplatinic acid (0.05 g, 0.12 mmol) was again added and the mixture was refluxed for 20 h. The benzene was removed *in vacuo*. Distillation (95-105 C, 0.050 Torr) afforded a clear colorless liquid (21.1 g, 48%). The analytical data was in agreement with previously published data for this compound.[21] ^1H NMR (300 MHz, C_6D_6): δ = 3.78 (q, 12H, OCH_2CH_3, J = 7.0 Hz), 1.84 (m, 4H, $SiCH_2CH_2CH_2CH_2Si$), 1.15 (t, 18H, OCH_2CH_3, J = 7.0 Hz), 0.85 (t, 4H, $SiCH_2CH_2CH_2CH_2Si$, J = 8.2 Hz). ^{13}C NMR (75 MHz, C_6D_6): δ = 58.4 (OCH_2CH_3), 26.7 ($SiCH_2CH_2CH_2CH_2Si$), 18.6 (OCH_2CH_3), 10.9 ($SiCH_2CH_2CH_2CH_2Si$). IR (neat): ν = 2975, 2928, 2884, 2765, 1444, 1391, 1366, 1295, 1226, 1201, 1168, 1104, 1083, 1006, 958, 861, 820, 795, 761 cm^{-1}.

2,2,5,5,-Tetraethoxy-2,5-disilaoxacyclopentane (4). To a solution of 2,2,5,5,-tetraethoxy-2,5-disilaoxacyclopent-3-ene[50] (470 mg, 1.70 mmol.) and benzene-d_6 in a 250 mL, glass pressure vessel, palladium on carbon (10wt%, 10 mg) was added. The solution was thoroughly degassed and the vessel was pressurized with hydrogen to 50 psig. The mixture was stirred for 4 hours at room temperature. After depressurizing and purging the residual hydrogen, the solution was filtered through a 0.25 micron filter and the solvent removed *in vacuo* to give a clear colorless oil (**4**, 260 mg, 54.6%). ^1H NMR (400 MHz, C_6D_6): δ = 3.85 (q, 8H, J = 7.1, OCH_2CH_3), 1.17 (t, 12H, J = 7.1, OCH_2CH_3), 0.91 (s, 4H, $SiCH_2CH_2Si$; ^{13}C NMR (75 MHz, C_6D_6): δ = 59.3 (OCH_2CH_3), 19.0 (OCH_2CH_3), 5.4 (SiCH_2CH_2Si); ^{29}Si NMR (99 MHz, EtOH): δ = -41.2; IR (neat): ν = 2976, 2929, 2894, 1484, 1445, 1392, 1296, 1226, 1169, 1082, 952, 829, 780, 718 cm^{-1}.

Bicyclic dimer (5). To a solution of **1** (23.5 g, 66.3 mmol) in ethanol (120 mL) was added 1 N HCl (2.36 mL, 131 mmol H_2O) dissolved in ethanol (20 mL). The reaction was stirred for 24 h and the solvent was removed *in vacuo* leaving a viscous oil. The oil was distilled (0.05 Torr, 110-120 °C) yielding a clear colorless liquid (**5**, 93% by GC, 2.33 g, 7.2 %). ^{1}H NMR (300 MHz, C_6D_6): δ = 3.82 (m, 12H, O$CH_2$$CH_3$), 1.13 (m, 18H, $OCH_2$$CH_3$), 0.98 (m, 4H, Si$CH_2CH_2$Si). ^{13}C NMR (75 MHz, C_6D_6): δ = 58.7 (Si(T^2)OCH_2CH_3), 58.5 (Si(T^1)OCH_2CH_3), 18.5 (OCH_2CH_3), 18.4 (OCH_2CH_3), 4.4 (Si(T^2)CH_2CH_2Si(T^1)), 4.2 (Si(T^2)CH_2CH_2Si(T^1)). ^{29}Si NMR (99 MHz, EtOH): δ = -50.3 (T^1_{cyclic}), -52.9 (T^2_{cyclic}). IR (neat): ν = 2975, 2886, 1392, 1268, 1169, 1103, 1079, 1055, 1011, 960, 757, 736, 697, 662 cm^{-1}. HRMS (CI, isobutane): Anal. Calcd for $C_{16}H_{39}O_9Si_4$ $[M + H]^+$: 487.1671. Found: 487.1663.

2,2,6,6-Tetraethoxy-2,6-disilaoxacyclohexane (6)^{22}: To a solution of **2** (15.0 g, 40.7 mmol) in ethanol (150 mL) was added 1 N HCl (0.733 mL 40.7 mmol H_2O) dissolved in ethanol (50 mL). After stirring for 24 h, the ethanol was removed *in vacuo*. The remaining liquid was distilled (0.05 Torr, 47-55 °C) yielding a clear colorless liquid (**6**, 9.67 g, 81%). ^{1}H NMR (300 MHz, C_6D_6): δ = 3.85 (q, 8H, O$CH_2$$CH_3$, J = 7.0 Hz), 1.78 (m, 2H, $SiCH_2$$CH_2$$CH_2Si$), 1.23 (t, 12H, $OCH_2$$CH_3$, J = 7.0 Hz), 0.71 (t, 4H, Si$CH_2$$CH_2$$CH_2$Si, J = 3.8 Hz). ^{13}C NMR (75 MHz, C_6D_6): δ = 58.3 (OCH_2CH_3), 18.2 (OCH_2CH_3), 17.2 ($SiCH_2CH_2CH_2Si$), 11.2 (Si$CH_2CH_2CH_2$Si). ^{29}Si NMR (99 MHz, neat): δ = -47.2 (T^1_{cyclic}). IR (neat): ν = 2977, 2923, 2889, 1442, 1296, 1246, 1219, 1168, 1106, 1084, 1007, 968, 898, 821, 786, 705 cm^{-1}. HRMS (CI, ammonia): Anal. Calcd for $C_{11}H_{26}O_5Si_2$ $[M]^+$: 294.1319. Found: 294.1322.

^{17}O/^{18}O-Labeled (6*): To a solution of **2** (19.3 g, 52.4 mmol) in ethanol (100 mL) was added H_2O^* (1.00 g, 52.3 mmol , 27% ^{17}O, 42% ^{18}O) dissolved in ethanol (10 mL). After stirring for 24 h, the ethanol was removed *in vacuo*. The remaining liquid was distilled (0.065 Torr, 63-77 °C) yielding a clear colorless liquid (**6***, 10.3 g, 66%) determined to be 97.9% pure by GC. ^{1}H NMR (300 MHz, C_6D_6): δ = 3.85 (q, 8H, $OC\mathit{H}_2CH_3$, J = 7.0 Hz), 1.78 (m, 2H, $SiCH_2C\mathit{H}_2CH_2Si$), 1.23 (t, 12H, $OCH_2C\mathit{H}_3$, J = 7.0 Hz), 0.71 (t, 4H, $SiC\mathit{H}_2CH_2C\mathit{H}_2Si$, J = 3.8 Hz). ^{13}C NMR (75 MHz, C_6D_6): δ = 58.3 ($O\mathit{C}H_2CH_3$), 18.2 ($OCH_2\mathit{C}H_3$), 17.2 ($SiCH_2\mathit{C}H_2CH_2Si$), 11.2 ($Si\mathit{C}H_2CH_2\mathit{C}H_2Si$). ^{29}Si NMR (99 MHz, neat): δ = -47.2 (T^1_{cyclic}). ^{17}O NMR (54.25 MHz, 1M **6*** in EtOH): δ = 64.0. IR (neat): v = 2976, 2926, 2888, 2737, 1483, 1444, 1392, 1367, 1296, 1246, 1219, 1169, 1105, 1079, 969, 898, 824, 789, 757, 738, 702 cm^{-1}. HRMS (CI, ammonia): Anal. Calcd for $C_{11}H_{26}O_5Si_2$ $[M]^+$: 294.1319. Found: 294.1324.

2,2,7,7-tetraethoxy-2,7-disilaoxacycloheptane (7): [22] To a solution of **3** (15.0 g, 39.2 mmol) in ethanol (185 mL) was added 1 N HCl (0.705 mL, 39.2 mmol of H_2O) in ethanol (10 mL). After stirring for 48 h, the ethanol was removed *in vacuo*. The remaining liquid was distilled (0.05 Torr, 65-70 °C) to give a clear colorless liquid (**7**, 8.22 g, 68%). ^{1}H NMR (300 MHz, C_6D_6): δ = 3.83 (q, 8H, $OC\mathit{H}_2CH_3$, J = 7.0 Hz), 1.64 (m, 4H, $SiCH_2C\mathit{H}_2C\mathit{H}_2CH_2Si$), 1.16 (t, 12H, $OCH_2C\mathit{H}_3$, J = 7.0 Hz), 0.76 (m, 4H, $SiC\mathit{H}_2CH_2CH_2C\mathit{H}_2Si$). ^{13}C NMR (75 MHz, C_6D_6): δ = 58.4 ($O\mathit{C}H_2CH_3$), 26.7 ($SiCH_2\mathit{C}H_2\mathit{C}H_2CH_2Si$), 18.6 ($OCH_2\mathit{C}H_3$), 10.9 ($Si\mathit{C}H_2CH_2CH_2\mathit{C}H_2Si$). ^{29}Si NMR (79.5 MHz, neat): δ = -49.1 (T^1_{cyclic}). IR (neat): v = 2975, 2927, 2885, 2736, 1484, 1444, 1392, 1366, 1347, 1307, 1296, 1212, 1169, 1106, 1083, 1034, 961, 884, 849, 800, 762, 737 cm^{-1}. HRMS (CI, isobutane): Anal. Calcd for $C_{12}H_{28}O_5Si_2$ $[M]^+$: 308.1475. Found: 308.1473.

Tricyclic dimer (8): A flask was charged with **2** (42.5 g, 115 mmol), ethanol (180 mL), and 1 N HCl (4.14 mL, 230 mmol) dissolved in ethanol (100 mL). The mixture was stirred for 24 h and then refluxed for 5 days. The solvent was removed in vacuo and the viscous oil was cooled to -20 °C to produce a white solid. The solid was filtered and recrystallized from ethanol yielding white crystals. After filtration, the crystals were washed with cold ethanol and dried *in vacuo* (**8**, 2.74 g, 10.8 %, mp 83-84 °C). ^{1}H NMR (300

MHz, C_6D_6): δ = 3.83 (q, 8H, OCH_2CH_3, J = 6.9 Hz), 1.97 (dtt, 2H, $SiCH_2CH_{ax}H_{eq}CH_2Si$, J = 13.6, 13.1, 2.8 Hz), 1.83 (dtt, 2H, $SiCH_2CH_{ax}H_{eq}CH_2Si$, J = 13.6, 6.0, 4.4 Hz), 1.16 (t, 12H, OCH_2CH_3, J = 7.0 Hz), 0.89 (ddd, 4H, $SiCH_{eq}H_{ax}CH_2$, J = 15.2, 6.0, 2.8 Hz), 0.63 (ddd, 4H, $SiCH_{eq}H_{ax}CH_2$, J = 15.2, 13.1, 4.4 Hz). ^{13}C NMR (75 MHz, C_6D_6): δ = 58.5 (OCH_2CH_3), 18.4 (OCH_2CH_3), 16.3 ($SiCH_2CH_2CH_2Si$), 12.3 ($SiCH_2CH_2CH_2Si$). ^{29}Si NMR (79.5 MHz, C_6D_6): δ = -50.8 (T^2_{cyclic}). IR (neat): ν = 2967, 2917, 2879, 1413, 1333, 1260, 1214, 1102, 1052, 1026, 997, 932, 901, 840, 801, 744, 662, 598 cm^{-1}. HRMS (CI, isobutane): Anal. Calcd for $C_{14}H_{33}O_8Si_4$ $[M]^+$: 440.1174. Found: 440.1171.

Tricyclic Dimer (9): A solution of **15** (500 mg, 1.1 mmol) in benzene (50 mL) with 10% palladium on carbon (20 mg) was treated with hydrogen (50 psig) for 24 h. After filtering through celite and removing the solvent *in vacuo*, **9** was isolated as (360 mg, 70%). ^1H NMR (400 MHz, C_6D_6): δ = 3.87 (q, 8H, J = 7.0, OCH_2CH_3), 1.68 (m, 8H, $SiCH_2CH_2CH_2CH_2Si$), 1.20 (t, 12H, J = 7.0, OCH_2CH_3), 0.92 (s, 8H, $SiCH_2CH_2CH_2CH_2Si$; ^{13}C NMR (75 MHz, C_6D_6): δ = 58.9 (OCH_2CH_3), 24.2 ($SiCH_2CH_2CH_2CH_2Si$), 18.9 (OCH_2CH_3), 13.2 ($SiCH_2CH_2CH_2CH_2Si$); ^{29}Si NMR (79.5 MHz, C_6D_6): δ = -53.5 (T^2); IR (neat) 2975, 2927, 1456, 1392, 1212, 1170, 1117, 1045, 963, 848, 792, 757, 613 cm^{-1}. HRMS (CI, isobutane): Anal. Calcd for $C_{16}H_{37}O_8Si_4$ $[M+1]^+$: 469.1556. Found: 469.1556.

Z-1,4-Bis(trichlorosilyl)but-2-ene: To a mixture of triethylamine (62.0 mL, 0.440 moles) and copper (I) chloride (0.4 g) in anhydrous diethyl ether (40 mL), trichlorosilane (60.3 g, 0.445 mole) and 1, 2-dichlorobut-2-ene (25 g, 0.2 mole) in diethyl ether (50 mL) were added at a rate sufficient to keep the reaction at reflux (2 hours). After addition, the reaction was refluxed for an additional two hours, before filtering and removing solvent *in vacuo* to give a clear yellow liquid. Distillation under vacuum (85 C, 9 Torr) afforded a colorless liquid (55.0 g, 85%).

Z-1,4-bis(triethoxysilyl)but-2-ene (10): Z-1,4-Bis(trichlorosilyl)but-2-ene was added dropwise to 200 mL of refluxing triethylorthoformate. The resulting solution was heated at reflux for 24 hours before removing the remaining orthoformate *in vacuo*. The desired product was isolated by distillation at 132 C/8 mTorr (**10**, 40.2 g, 53.0%). ^1H NMR (400 MHz, C_6D_6): $\delta = 5.35$ (t, 2H, $SiCH_2CH{=}CHCH_2Si$, $J = 3.7$ Hz), 3.77 (q, 12H, OCH_2CH_3, $J = 7.5$ Hz), 1.55 (d, 4H, $SiCH_2CH{=}CHCH_2Si$, $J = 3.7$ Hz), 1.17 (t, 18H, OCH_2CH_3, $J = 7.4$ Hz). ^{13}C NMR (100.5 MHz, C_6D_6): $\delta = 58.1$ (OCH_2CH_3), 18.7 (OCH_2CH_3), 18.5 ($SiCH_2CH_2CH_2Si$), 17.1 ($SiCH_2CH_2CH_2Si$), -4.5 ($SiCH_3$). ^{29}Si NMR (79.5 MHz, C_6D_6): $\delta = -50.4$. (IR (neat): v = 3016, 2975, 2927, 2887, 1703, 1686, 1643, 1483, 1443, 1391, 1295, 1168, 1104, 1083, 959, 883, 798, 747, 535 cm^{-1}. HRMS (CI, isobutane): Anal. Calcd for $C_{16}H_{37}O_6Si_2$ $[M+1]^+$: 381.6324 Found: 381.2116.

2,2,7,7-tetraethoxy-2,7-disilaoxacyclohept-4-ene (11): To a solution of **10** (10.2 g, 26.8 mmol) in ethanol (50 mL) was added 1N HCl (0.48 mL 26.6 mmol of H_2O) dissolved in ethanol (15 mL). After stirring for 24 h, the solvent was removed *in vacuo* and the crude oil was vacuum distilled (0.05 Torr, 65-75 °C) yielding a colorless liquid (**11**, 6.2 g, 76%). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 5.52$ (m, 2H, $CH_2CH{=}CHCH_2$), 3.78 (q, 8H, OCH_2CH_3, $J = 7.3$ Hz), 1.54 (m, 4H, $SiCH_2$), 1.17 (t, 12H, OCH_2CH_3, $J = 7.4$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 122.8$ ($CH{=}CH$), 58.5 (OCH_2CH_3), 18.1 (OCH_2CH_3), 12.9 ($SiCH_2$). ^{29}Si NMR (79.5 MHz, C_6D_6): $\delta = -55.8$. IR (neat): v = 3028, 2975, 2928, 2886, 1631, 1484, 1444, 1392, 1296, 1169, 1104, 1085, 1044, 963, 912, 804, 775, 704, 682, 595 cm^{-1}. HRMS (CI, isobutane): Anal. Calcd for $C_{12}H_{26}O_5Si_2$ $[M]^+$: 306.1319. Found:.

Tricyclic dimer (12): To a solution of **10** (33.1 g, 87.0 mmol) in ethanol (150 mL) was added 1N HCl (3.132 mL, 174 mmol of H_2O) dissolved in ethanol (50 mL). The mixture was refluxed for 1 week and then additional 1N HCl (0.783 mL, 43.5 mmol of H_2O) was added and the mixture was refluxed for another week. The solvent was removed *in vacuo* and the crude oil was stored at -20 °C overnight. A crude white solid crystallized and was filtered. The solid was recrystallized in hot ethanol to give white needle-like crystals. The crystals were filtered and washed with cold ethanol (3 x 1 mL) and dried in vacuo (**12**, 1.24 g, 6.1%). ^{1}H NMR (300 MHz, C_6D_6): δ = 5.64 (m, 4H, C*H*=C*H*), 3.81 (q, 8H, OCH_2CH_3, *J* = 7.4 Hz), 1.71, 1.59 (m, 8H, $SiCH_2$), 1.17 (t, 12H, OCH_2CH_3, *J* = 7.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 123.5 (*C*H=*C*H), 58.6 (OCH_2CH_3), 18.4 (OCH_2CH_3), 14.1 ($SiCH_2$). ^{29}Si NMR (79.5 MHz, C_6D_6): δ = -60.1 (T^2_{cyclic}). IR (neat): ν = 3027, 2977, 2929, 2886, 1633, 1443, 1393, 1372, 1189, 1164, 1109, 1046, 968, 908, 837, 813, 784, 755, 701, 610 cm^{-1}. HRMS (CI, isobutane): Anal. Calcd for $C_{16}H_{32}O_8Si_4$ $[M]^+$: 464.1174. Found: 464.1168.

1,3-Bis(diethoxymethylsilyl)propane (13): To a solution of 3-diethoxymethylsilylpropene (37.2 g, 213 mmol), diethoxymethylsilane (31.5 g, 234 mmol), and benzene (200 mL) under air was added chloroplatinic acid (80 mg, 0.2 mmol). The mixture immediately turned dark yellow. After stirring for 24 h, the solvent was removed *in vacuo* and the viscous oil was vacuum distilled (0.05 Torr, 70-78 °C) yielding a clear colorless liquid (**13**, 49.9 g, 76%). ^{1}H NMR (400 MHz, C_6D_6): δ = 3.70 (q, 8H, OCH_2CH_3, *J* = 7.2 Hz), 1.70 (p, 2H, $SiCH_2CH_2CH_2Si$, *J* = 8.2 Hz), 1.14 (t, 12H, OCH_2CH_3, *J* = 6.8 Hz), 0.82 (t, 4H, $SiCH_2CH_2CH_2Si$, *J* = 8.4 Hz), 0.15 (s, 6H, $SiCH_3$). ^{13}C NMR (100.5 MHz, C_6D_6): δ = 58.1 (OCH_2CH_3), 18.7 (OCH_2CH_3), 18.5 ($SiCH_2CH_2CH_2Si$), 17.1 ($SiCH_2CH_2CH_2Si$), -4.5 ($SiCH_3$). IR (neat): ν = 2974, 2926, 2878, 1483, 1444, 1391, 1339, 1257, 1166, 1107, 1081, 953, 901, 796, 764 cm^{-1}.

2,6-diethoxy-2,6-dimethyl-2,6-disilaoxacyclohexane (14): A flask was charged with 1,3-bis(diethoxymethylsilyl)propane (49.4 g, 160 mmol), 1 N HCl (2.88 mL, 160 mmol of H_2O), and ethanol (350 mL) and the solution was stirred for 24 h. The solvent was removed *in vacuo* and the remaining oil was vacuum distilled (0.10 Torr, 30-33 °C) yielding a mixture of *syn* and *anti* diastereomers as a clear colorless liquid (**14**, 29.3 g, 78%). ^{1}H NMR (300 MHz, C_6D_6): δ = 3.73 (q, OCH_2CH_3), 3.67 (q, OCH_2CH_3), 1.75 (m, $SiCH_2CH_2CH_2Si$), 1.15 (t, OCH_2CH_3), 1.12 (t, OCH_2CH_3), 0.572 (m,

$SiCH_2CH_2CH_2Si$), 0.138 (s, $SiCH_3$), 0.099 (s, $SiCH_3$). ^{13}C NMR (75 MHz, C_6D_6): δ = 58.1, 58.0 (OCH_2CH_3), 18.6 (OCH_2CH_3), 17.7 ($SiCH_2CH_2CH_2Si$), 15.3 ($SiCH_2CH_2CH_2Si$), -2.1, -2.2 ($SiCH_3$). IR (neat): v = 2973, 2908, 2879, 1444, 1415, 1392, 1328, 1259, 1238, 1168, 1110, 1081, 956, 902, 811, 789, 666 cm^{-1}. HRMS (CI, isobutane): Anal. Calcd for $C_9H_{22}O_3Si_2$ $[M]^+$: 234.1107. Found: 234.1107.

Tricyclic dimer (15): To a flask containing **14** (15 g, 64 mmol) and ethanol (150 mL) was added 1 N HCl (1.15 mL, 64.0 mmol of H_2O) dissolved in ethanol (10 mL). The mixture was stirred at room temperature for 4 h and then refluxed for 24 h. The solvent was removed *in vacuo* and some solid crystallized from the crude oil. The mixture was dissolved in a minimum of hot ethanol and cooled to -20 °C for 3 h yielding needle-like white crystals. The crystals were filtered and dried *in vacuo* (**15**, 3.17 g, 31%, mp 100-101.5 °C). ^1H NMR (300 MHz, C_6D_6): δ = 2.19 (dtt, 2H, $SiCH_2CH_{ax}H_{eq}CH_2Si$, J = 13.4, 12.8, 2.8 Hz), 1.88 (dtt, 2H, $SiCH_2CH_{ax}H_{eq}CH_2Si$, J = 13.4, 6.3, 4.2 Hz), 0.85 (ddd, 4H, $SiCH_{eq}H_{ax}CH_2$, J = 14.5, 6.3, 2.8 Hz), 0.48 (ddd, 4H, $SiCH_{eq}H_{ax}CH_2$, J = 14.5, 12.8, 4.2 Hz), 0.20 (s, 12H, $SiCH_3$). ^{13}C NMR (75 MHz, C_6D_6): δ = 16.82, 16.79, -0.3. ^{29}Si NMR (79.5 MHz, C_6D_6): δ = -13.0 (T^2_{cyclic}). HRMS (CI, isobutane): Anal. Calcd for $C_{14}H_{33}O_8Si_4$ $[M]^+$: 320.0752. Found: 320.0751.

X-ray Structure Determinations. All single crystal X-ray diffraction data were collected on a Siemens SMART CCD system at reduced temperatures over an entire hemisphere of the reciprocal lattice. Specific pertinent parameters for the data collection can be found in supplementary materials. The reflection lists for all structures were assembled from no fewer than 900 individual images collected at a framewidth of 0.3° in phi. The images were analyzed and the peaks integrated by the SAINT routine and all reflections were used to refine the final unit cell parameters in the monoclinic cell.

Structure solution and refinement were accomplished using the SHELXL-93 software package.[51] For all structures, a substructure of Si-O was initially solved in $P2_1/c$ by direct methods. An absorption correction was applied to the data using SADABS[52] and the solutions were refined to suitable residual values. In all cases, the discrepancies in the high intensity reflections warranted refinement of a secondary extinction coefficient. Finally, all non-hydrogen atoms were refined anisotropically, but the C5 and C7 atoms of **15** showed large thermal motions and were best modeled over two disordered sites with fractional occupancies that were fixed in the final refinement cycles at 70:30 % after initially being allowed to refine independently. Consequently, no hydrogen atoms could be reasonably assigned to these carbon atoms or their neighboring carbon atoms.

Sol-Gel Processing.

Polymerizations. Sol-gel polymerizations of **1-8** were performed with a monomer concentration of 0.4 M (absolute ethanol) and with aqueous 1 N NaOH as the catalyst. The number of equivalents of water used for each polymerization was equal to the number of ethoxides present in each monomer (4 or 6). Gelation was determined as the point at which the liquid would not flow. After gelation the samples were allowed to age for 2 weeks and then processed to xerogels. Xerogels were prepared by crushing the wet gels and washing with water (3 x 50 mL) and ether (2 x 25 mL) and then drying *in vacuo* at 100 °C for 24 h.

Polysilsesquioxane Xerogel Syntheses.

1X. A dry 10 mL volumetric flask was charged with **1** (1.42 g, 4.00 mmol) and ethanol (6.0 mL). A catalyst solution of aqueous NaOH (0.432 mL, 1N, 24.0 mmol of H_2O) and ethanol (2.0 mL) was added to the volumetric and the mixture immediately became cloudy. Enough ethanol was added to the flask to bring the volume to exactly 10.0 mL and the contents were mixed thoroughly. The cloudy solution was then transferred to a dry scintillation vial and sealed. After 24 h, a rigid cloudy gel had formed. The wet gel was processed to a xerogel as outlined above and recovered as white monolithic fragments (529 mg, 100% based on complete condensation of **1**). ^{13}C CP MAS NMR $\delta = 58.4, 17.2, 4.7$; ^{29}Si CP MAS NMR $\delta = -46.0$ (T^1), -56.8 (T^2), -63.7 (T^3). IR (KBr pellet): $v = 2979$, 2894, 1413, 1272, 1090, 1030, 909, 771, 698 cm^{-1}. Elemental analysis calcd. for

$C_2H_4O_3Si_2$: C 18.2%, H 3.0%, Si 42.5%, found: C 18.9%, H 4.2%, Si 38.3%. Nitrogen sorption surface area (BET) 593 m^2/g.

2X. A 10 mL ethanol solution containing **2** (1.47 g, 4.00 mmol) and aqueous NaOH (0.432 mL, 1N, 24.0 mmol of H_2O) was prepared in the same manner as for **1** and the slightly opaque solution was sealed in a scintillation vial. After 1 h, a slightly opaque rigid gel formed and was processed to a white xerogel (585 mg, 100% based on complete condensation of **2**). ^{13}C CP MAS NMR $\delta = 57.7, 16.4, 13.3$. ^{29}Si CP MAS NMR $\delta = -51.2, -60.8$. IR (KBr pellet): ν = 2925, 1416, 1251, 1220, 1112, 1024, 932, 903, 761, 670, 592 cm^{-1}. Elemental analysis calcd. for $C_3H_6O_3Si_2$: C 24.6%, H 4.1%, Si 38.4%, found: C 24.6%, H 4.8%, Si 35.7%. Nitrogen sorption surface area (BET) 712 m^2/g.

3X. A 10 mL ethanol solution containing **3** (1.53 g, 4.00 mmol) and aqueous NaOH (0.432 mL, 1N, 24.0 mmol of H_2O) was prepared in the same manner as for **1** and the slightly cloudy solution was sealed in a scintillation vial. After 1 h, a cloudy rigid gel formed and was processed to white xerogel fragments (674 mg, 105% based on complete condensation of **3**). ^{13}C CP MAS NMR $\delta = 58.3, 25.6, 16.2, 12.7$. ^{29}Si CP MAS NMR $\delta = -55.4, -64.2$. IR (KBr pellet): ν = 2931, 1410, 1225, 1127, 1054, 852, 795 cm^{-1}. Elemental analysis calcd. for $C_4H_8O_3Si_2$: C 30.0%, H 5.0%, Si 35.0%, found: C 26.5%, H 5.7%, Si 31.4%. Nitrogen sorption surface area (BET) 882 m^2/g.

6X. A 5 mL ethanol solution containing **6** (589 mg, 2.00 mmol) and aqueous NaOH (0.144 mL, 1N, 8.00 mmol of H_2O) was prepared in the same manner as for **1** and the clear colorless solution was sealed in a scintillation vial. After 0.5 h, a clear rigid gel formed and was processed to white xerogel fragments (304 mg, 104% based on complete condensation of **6**). ^{13}C CP MAS NMR $\delta = 57.8, 16.1, 13.6$. ^{29}Si CP MAS NMR $\delta = -61.0$. IR (KBr pellet): ν = 2929, 1420, 1252, 1115, 1018, 932, 903, 762, 592 cm^{-1}. Elemental analysis calcd. for $C_3H_6O_3Si_2$: C 24.6%, H 4.1%, Si 38.4%, found: C 22.5%, H 5.0%, Si 35.0%. Nitrogen sorption surface area (BET) 807 m^2/g.

7X. A 5.0 mL ethanol solution of **7** (617 mg, 2.00 mmol) and aqueous NaOH (0.144 mL, 1N, 8.00 mmol of H_2O) was prepared in the same manner as for **1** and the clear colorless solution was sealed in a scintillation vial. After 2.5 h, a clear rigid gel formed and was processed to white xerogel fragments (344 mg, 107% based on complete condensation of **7**). ^{13}C CP MAS NMR $\delta = 57.8, 24.7, 16.5, 12.6$. ^{29}Si CP MAS NMR $\delta = -63.7$. IR (KBr pellet): v = 2932, 1408, 1311, 1127, 1039, 853, 797 cm^{-1}. Elemental analysis calcd. for $C_4H_8O_3Si_2$: C 30.0%, H 5.0%, Si 35.0%, found: C 29.4%, H 6.0%, Si 31.2%. Nitrogen sorption surface area (BET) 868 m^2/g.

8X. In a dry 2 mL volumetric flask, **8** (352 mg, 0.800 mmol) was dissolved in 1.5 mL of ethanol and then the volume was adjusted to 2.0 mL with additional ethanol. In a second 2 mL volumetric, aqueous NaOH (57.6 μL, 1N, 3.20 mmol of H_2O) was mixed with enough ethanol to bring the volume to 2.0 mL. The two solutions were mixed in a scintillation vial and after 16 h the clear solution had formed a slightly opaque gel. The wet gel was processed to a white xerogel powder (244 mg, 105% based on complete condensation of **8**). ^{13}C CP MAS NMR $\delta = 58.0, 16.1$. ^{29}Si CP MAS NMR $\delta = -59.5$. IR (KBr pellet): v = 2928, 1420, 1252, 1111, 1008, 931, 902, 757, 420 cm^{-1}. Elemental analysis calcd. for $C_3H_6O_3Si_2$: C 24.6%, H 4.1%, Si 38.4%, found: C 19.8%, H 5.1%, Si 34.9%. Nitrogen sorption surface area (BET) 785 m^2/g.

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Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **8**, **12**, and **15** (14 pages print/PDF). See any current masthead page for ordering information and Web access instructions.

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Figure 1. Gelation times for α,ω-bis(triethoxysilyl)alkanes (0.4 M in ethanol, 6 H_2O, 10.8 mol% HCl or NaOH catalyst).

Figure 2. ^{29}Si NMR spectra for 1M solutions of 1,10-bis(triethoxysilyl)decane in ethanol. The top spectrum is of the unreacted monomer. The next spectrum is of the product of the acid-catalyzed hydrolysis of themonomer with one (middle) and two (bottom) equivalents water. Spectra were obtained after 4 hours; chromium acetoacetate (5mmol/liter) was added to each solution just before analysis. T^0 refers to the monomer and its hydrolysis products. T^1 refers to the peaks from silicons with a single siloxane bond (dimer or end-groups) and their hydrolysis products. T^2 refers to peaks from silicons with two siloxane bonds.

Figure 3. ^{29}Si NMR spectra for 1M solutions of monomer **1** in ethanol. The top spectrum in each series is of the unreacted monomer. The next spectra are of the product of the acid-catalyzed hydrolysis of each monomer with one (middle) and two (bottom) equivalents water. Spectra were obtained after 4 hours; chromium acetoacetate (5mmol/liter) was added to each solution just before analysis. T^0 refers to the monomer and its hydrolysis products. T^1_{cyclic} and T^2_{cyclic} refer to the peaks due to silicons with a single siloxane bond and two siloxane bonds, respectively, that are part of a seven membered disilsesquioxane ring such as in compound **5**.

Figure 4. Mass spectrum (CI, NH_3) of the hydrolysis and condensation products of 1,2-bis(triethoxysilyl)ethane **1** with 1 equivalent water under acidic conditions. The products are predominantly the bicyclic dimer **4** and its hydrolysis products.

Figure 5 . ^{29}Si NMR spectra for 1M solutions monomers 1,3-bis(triethoxysilyl)propane **2** in ethanol. The top spectrum is of the unreacted monomer. The next spectra are of the product of the acid-catalyzed hydrolysis of each monomer with one (middle) and two (bottom) equivalents water. Spectra were obtained after 4 hours; chromium acetoacetate (5mmol/liter) was added to each solution just before analysis. T^1_{cyclic} refers to the peak due to the cyclic disilsesquioxane **6** that formed from the intramolecular condensation of **2**. T^2_{cyclic} refers to the peak due to the tricyclic dimer **8**.

Figure 6 . ^{29}Si NMR spectra for 1M solutions monomers 1,4-bis(triethoxysilyl)butane **4** in ethanol. The top spectrum is of the unreacted monomer. The next spectra are of the product of the acid-catalyzed hydrolysis of each monomer with one (middle) and two (bottom) equivalents water. Spectra were obtained after 4 hours; chromium acetoacetate (5mmol/liter) was added to each solution just before analysis. T^1_{cyclic} refers to the peak due to the cyclic disilsesquioxane **7** that formed from the intramolecular condensation of **3**. T^2_{cyclic} refers to the peak due to the tricyclic dimer **9**.

Figure 7. Expanded views of the ^{1}H resonances due to the α and β hydrogens on the cyclic disilsesquioxane ring in **7** revealing $^2J_{HH}$ and $^3J_{HH}$ couplings.

Figure 8. Ortep plots of the x-ray crystal structure of the tricyclic dimer **8** showing the anti configuration of the six-membered cyclic disilsesquioxane rings about the central eight membered tetrasiloxane ring. The methyl carbon {C(5)} in **8** was modeled at two positions with a site occupancy factor of 0.72(4) for C(5A) and 0.28 for C(5B). This was done because the anisotropic thermal ellipsoid was too large to be appropriate for one site. Packing within the structure suggests that the ends of the ethyl groups are free to move in an interpenetrating fashion between the planes of the molecules which would allow them to rotate due to thermal motion giving rise to the disorder.

Figure 9. Molecular models (MM2, Chemdraw 3D Plus) of the anti- and syn diastereomers of the tricyclic dimer **7** with calculated steric energies.

Figure 10. Comparison of solid state ^{29}Si CP MAS NMR spectrum of a decylene-bridged polysilsesquioxane (top) with spectra of xerogels (**1X-3X**) obtained from monomers **1-3** that are capable of forming cyclics and with spectra of xerogels (**6X-8X**) prepared from cyclic monomers **6-8**.

Figure 11. Incremental pore volume distribution plots of xerogels (**2X**, **6X**, and **8X**) prepared by base-catalyzed sol-gel polymerizations of the acyclic monomer **2**, cyclic disilsesquioxane **6** and tricyclic dimer **8** , respectively.

Figure 12. Comparison of the incremental pore volume distribution plots for xerogels prepared from the butylene-bridged monomer **3** and its cyclic disilsesquioxane derivative **7**.

Figure 13. Scanning electron micrographs of xerogels **2X**, **6X**, and **8X**.

Scheme 1. Polymerization and cyclization reactions of α.ω-bis(triethoxysilyl)alkanes.

Scheme 2. Cyclization of α,ω-bis(triethoxysilyl)alkanes **1-3**, **10** and 1,3-bis(diethoxymethylsilyl)propane **13** to give cyclic monomers **6-11**, bicyclic **5** and tricyclics **8, 9, 12**, and **15**.

Scheme 3. Different reaction paths for the hydrolysis and condensation of 1,2-bis(triethoxysilyl)ethane **1**.

Scheme 4. Preparation of **4** by palladium-catalyzed hydrogenation 2,2,5,5-tetraethoxy-2,5-disilaoxacyclopent-3-ene.

Scheme 5. Reaction pathway for the hydrolysis and condensation of **1** showing intermediates (**1a-b**) detected by mass spectrometry.

Scheme 6. Preparation of tricyclic **9** by palladium-catalyzed hydrogenation of unsaturated tricyclic **12**.

Table 1. Infrared ν(Si-O) Bands of Monomers and Xerogels in the Range of 1200-950 cm^{-1}.

Monomer	ν(Si-O) cm^{-1}	Xerogel	ν(Si-O) cm^{-1}
1	1168, 1148, 1106, 1078	**1X**	1090, **1030**
2	1168, 1104, 1083	**2X**	1112, **1024**
3	1168, 1104, 1083	**3X**	1127, **1054**
4	1169, 1082, 952		
5	1169, 1106, 1007		
6	1169, 1105, 1084, **1006**	**5X**	1115, **1018**
7	1169, 1106, 1083, **1034**	**6X**	1127, **1039**
8	1110, 1072, 1024, **1001**	**7X**	1111, **1008**

Table 2. Nitrogen Sorption Porosimetry Studies[a] of Polymers **1X-3X** and **6X-8X**.

Polymer	Surface Area (m^2/g)	Mean Pore Diameter (Å)	Pore Volume (cm^3/g)
1X	593	101	1.50
2X	712	81	1.45
3X	882	38	0.84
6X	807	32	0.64
7X	868	52	1.12
8X	785	32	0.63

[a] Surface areas were determined by BET, mean pore diameters by BJH theory, and pore volumes determined by single-point analysis.

Figure 1. Gelation times for α,ω-bis(triethoxysilyl)alkanes (0.4 M in ethanol, 6 H_2O, 10.8 mol% HCl or NaOH catalyst).

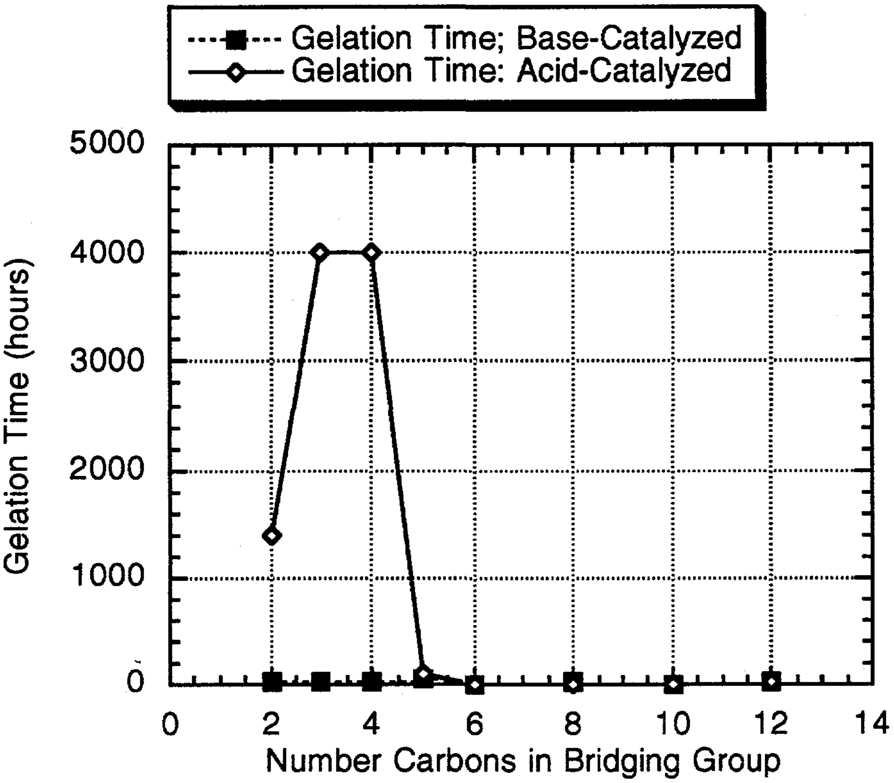


Figure 2

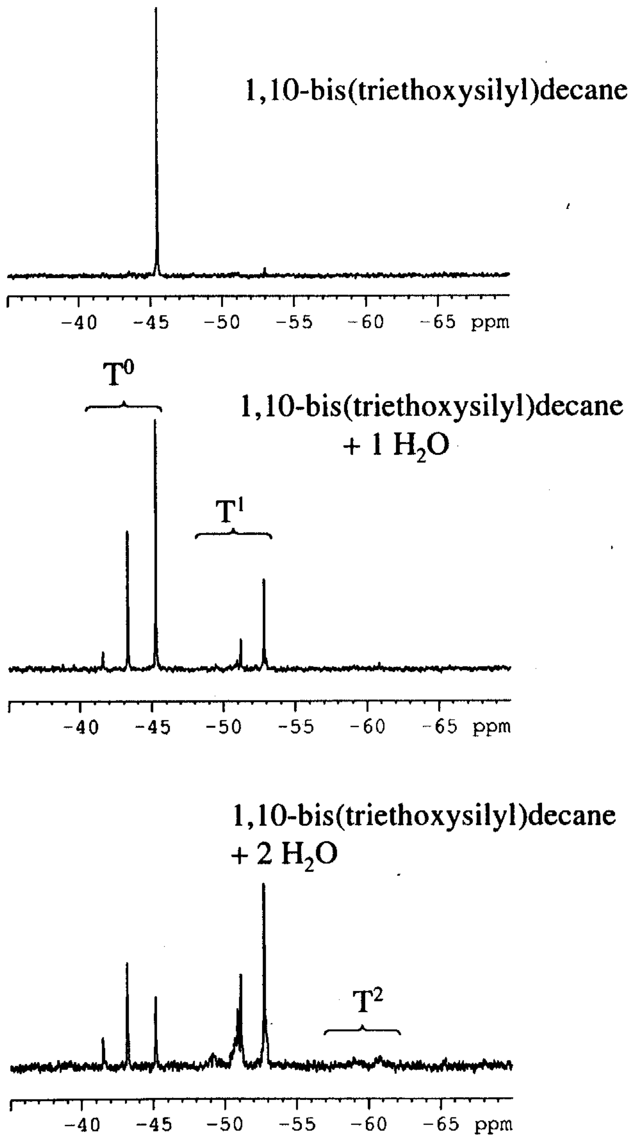

1,10-bis(triethoxysilyl)decane
-40
-45
-50
-55
-60
-65
ppm
T^0
1,10-bis(triethoxysilyl)decane
+ 1 H_2O
T^1
-40
-45
-50
-55
-60
-65
ppm
1,10-bis(triethoxysilyl)decane
+ 2 H_2O
T^2
-40
-45
-50
-55
-60
-65
ppm

Figure 3

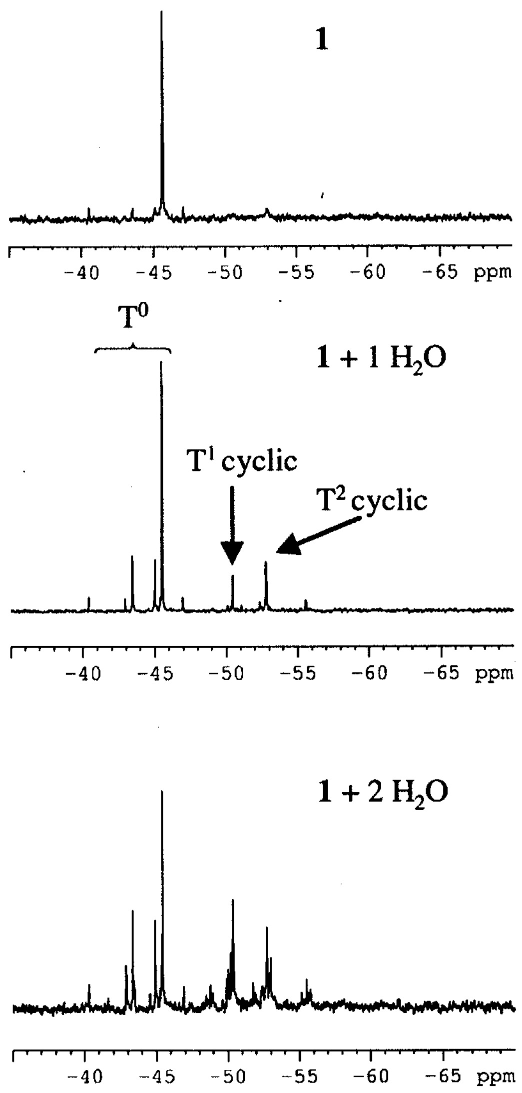
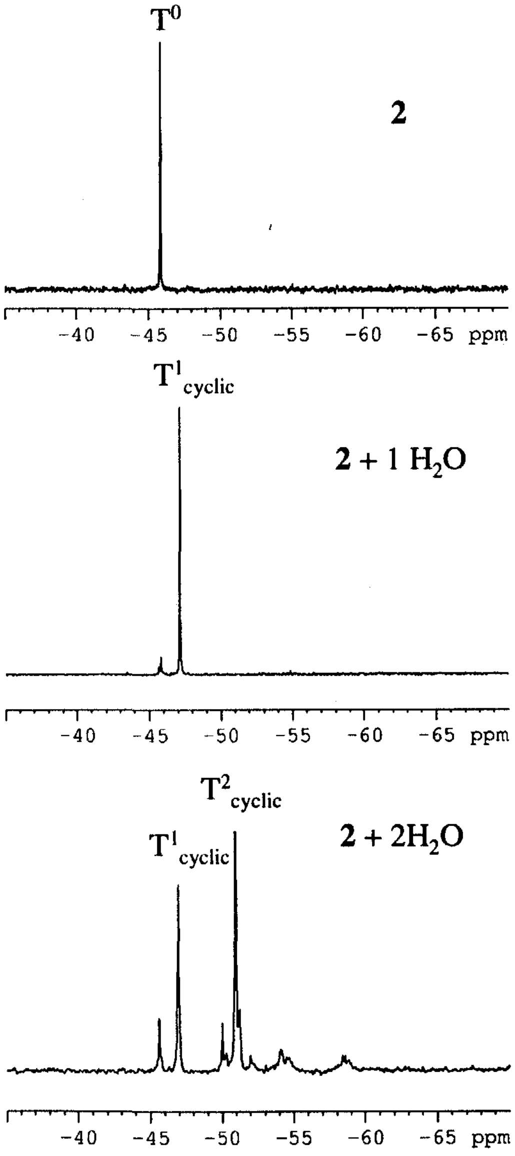

1
-40
-45
-50
-55
-60
-65
ppm
T^0
1 + 1 H_2O
T^1 cyclic
T^2 cyclic
-40
-45
-50
-55
-60
-65
ppm
1 + 2 H_2O
-40
-45
-50
-55
-60
-65
ppm

Figure 5



T^0
2
-40 -45 -50 -55 -60 -65 ppm
T^1_{cyclic}
2 + 1 H_2O
-40 -45 -50 -55 -60 -65 ppm
T^2_{cyclic}
T^1_{cyclic}
2 + $2H_2O$
-40 -45 -50 -55 -60 -65 ppm

Figure 6

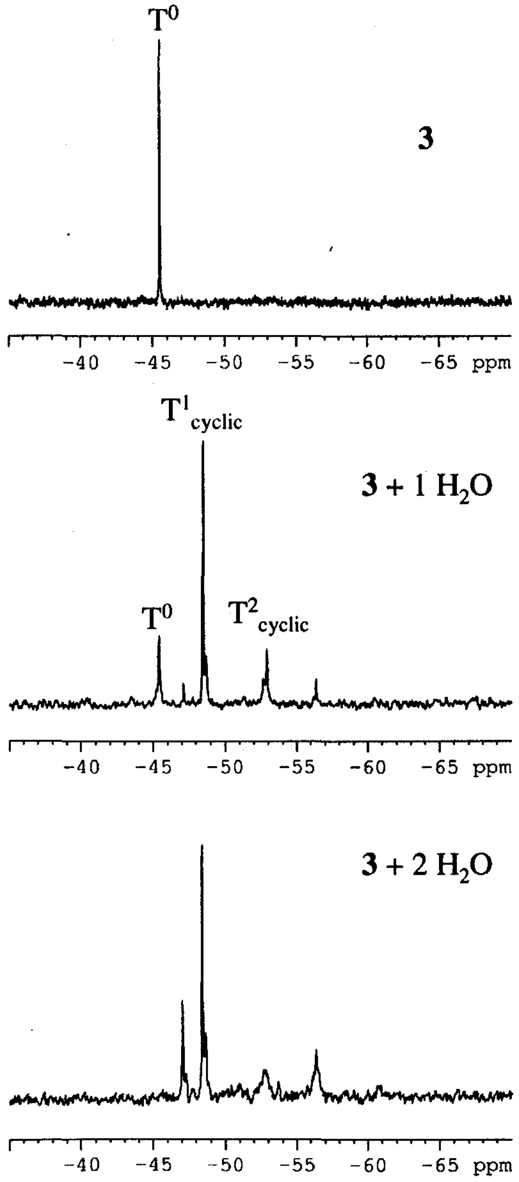
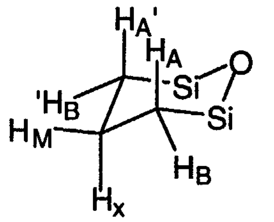

T^0
3
−40 −45 −50 −55 −60 −65 ppm
T^1_{cyclic}
3 + 1 H_2O
T^0
T^2_{cyclic}
−40 −45 −50 −55 −60 −65 ppm
3 + 2 H_2O
−40 −45 −50 −55 −60 −65 ppm

Figure 7

Coupling	$^2J_{HH}$ (Hz)	$^3J_{HH}$ (Hz)
H_AH_B	-15.2	-
H_MH_X	-13.6	-
H_XH_A	-	13.1
H_XH_B	-	2.8
H_MH_A	-	4.4
H_MH_B	-	6.0



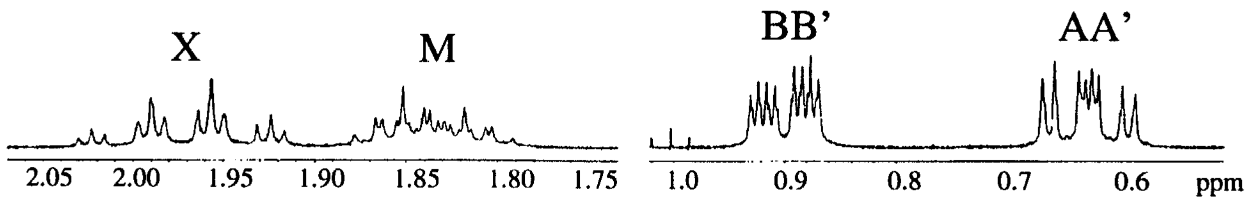


Figure 8

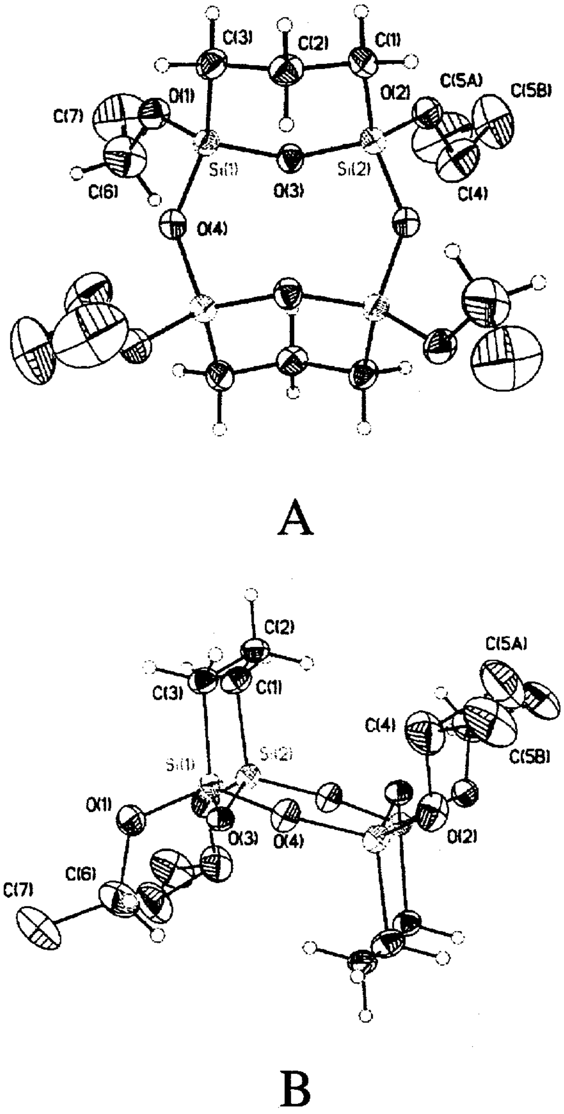
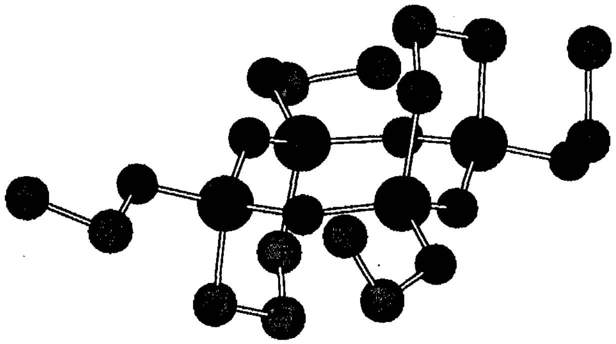
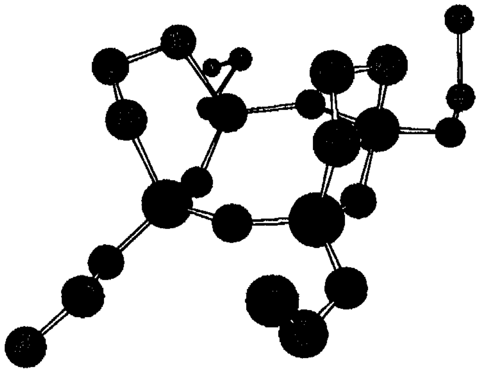

C(3)
C(2)
C(1)
C(5A)
C(5B)
O(1)
O(2)
C(7)
Si(1)
O(3)
Si(2)
C(6)
C(4)
O(4)
A
C(2)
C(5A)
C(3)
C(1)
C(4)
Si(2)
C(5B)
Si(1)
O(1)
O(3)
O(4)
O(2)
C(6)
C(7)
B

Figure 9



Anti-8
18.4 kcal/mole



Syn-8
26.0 kcal/mole

Figure 10

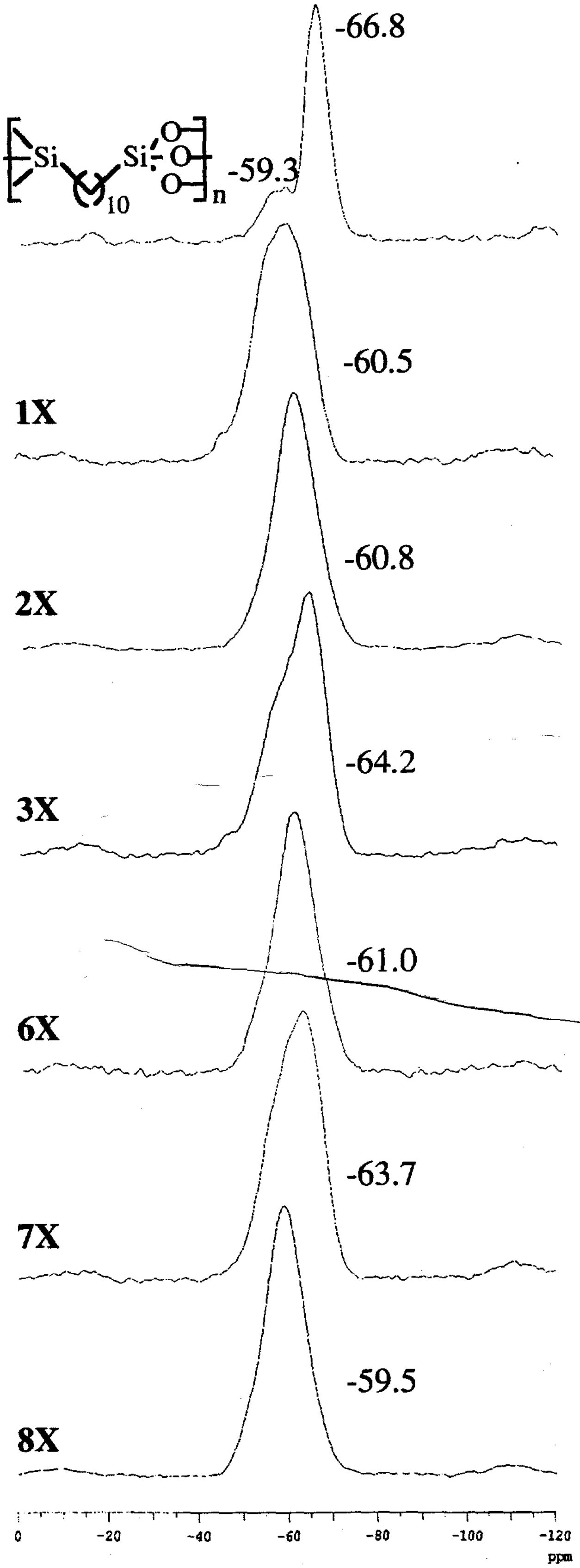
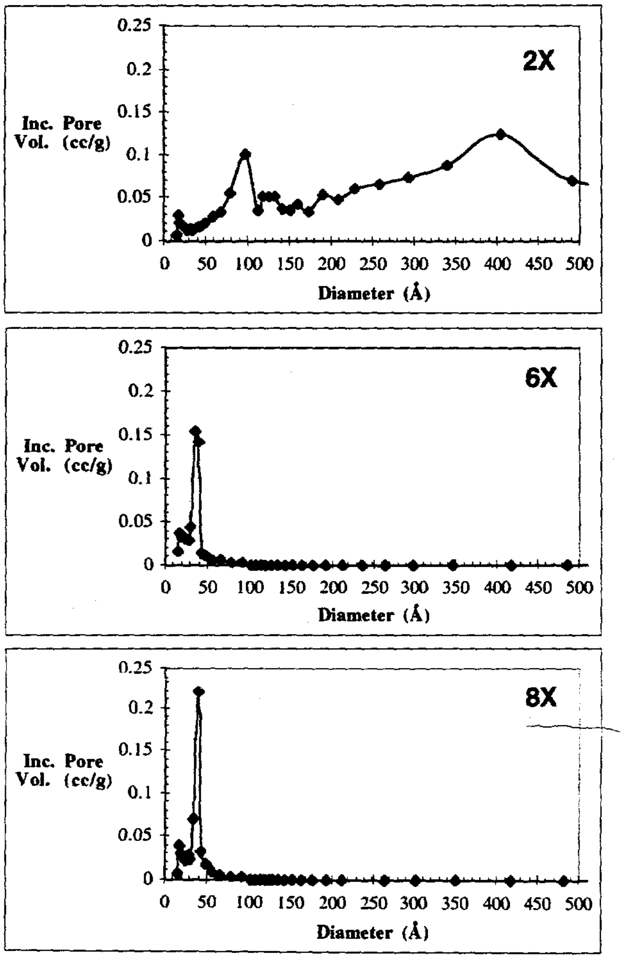

Si
Si
O
O
O
10
n
-66.8
-59.3
-60.5
1X
-60.8
2X
-64.2
3X
-61.0
6X
-63.7
7X
-59.5
8X
0
-20
-40
-60
-80
-100
-120
ppm

Figure 11



2X
6X
8X
Inc. Pore Vol. (cc/g)
0
0.05
0.1
0.15
0.2
0.25
0
50
100
150
200
250
300
350
400
450
500
Diameter (Å)

Figure 12

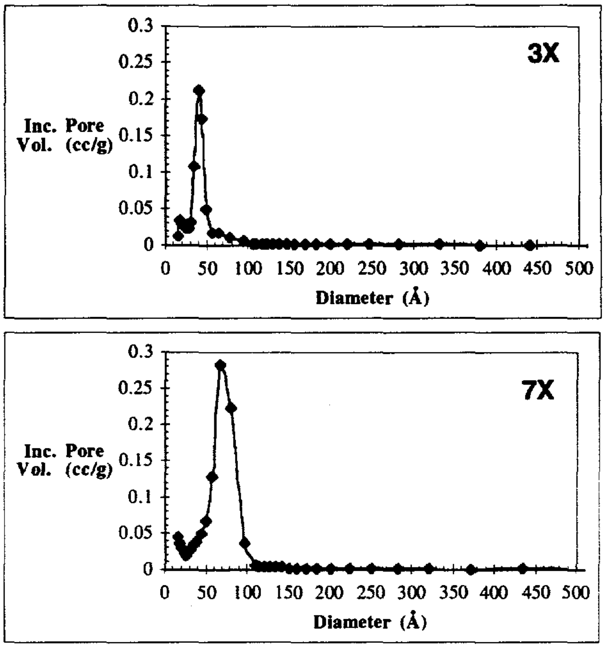
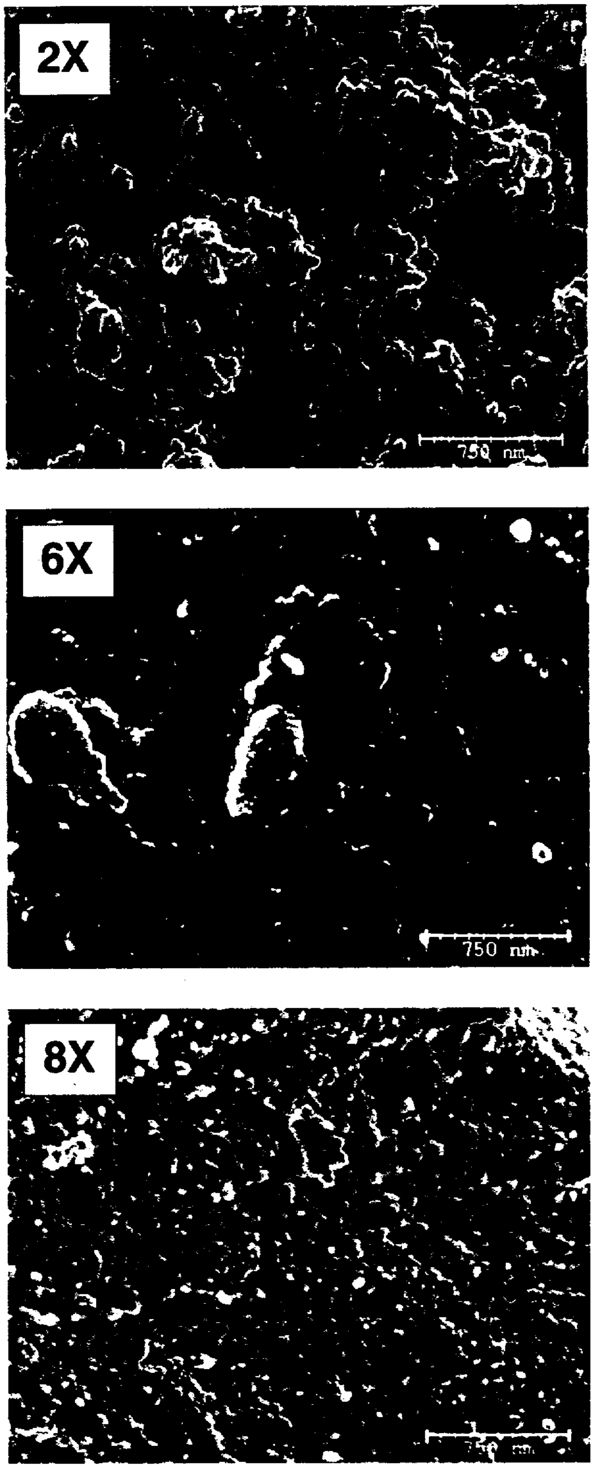
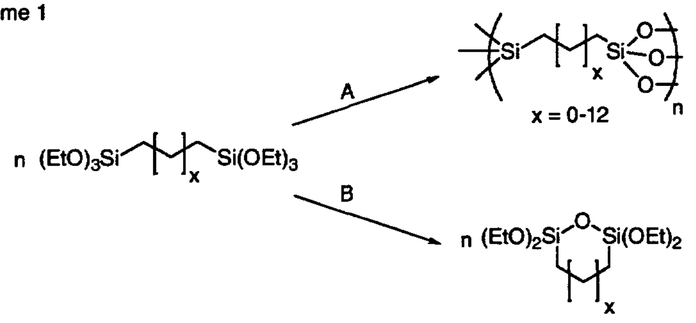

3X
Inc. Pore Vol. (cc/g)
0.3
0.25
0.2
0.15
0.1
0.05
0
0 50 100 150 200 250 300 350 400 450 500
Diameter (Å)
7X
Inc. Pore Vol. (cc/g)
0.3
0.25
0.2
0.15
0.1
0.05
0
0 50 100 150 200 250 300 350 400 450 500
Diameter (Å)

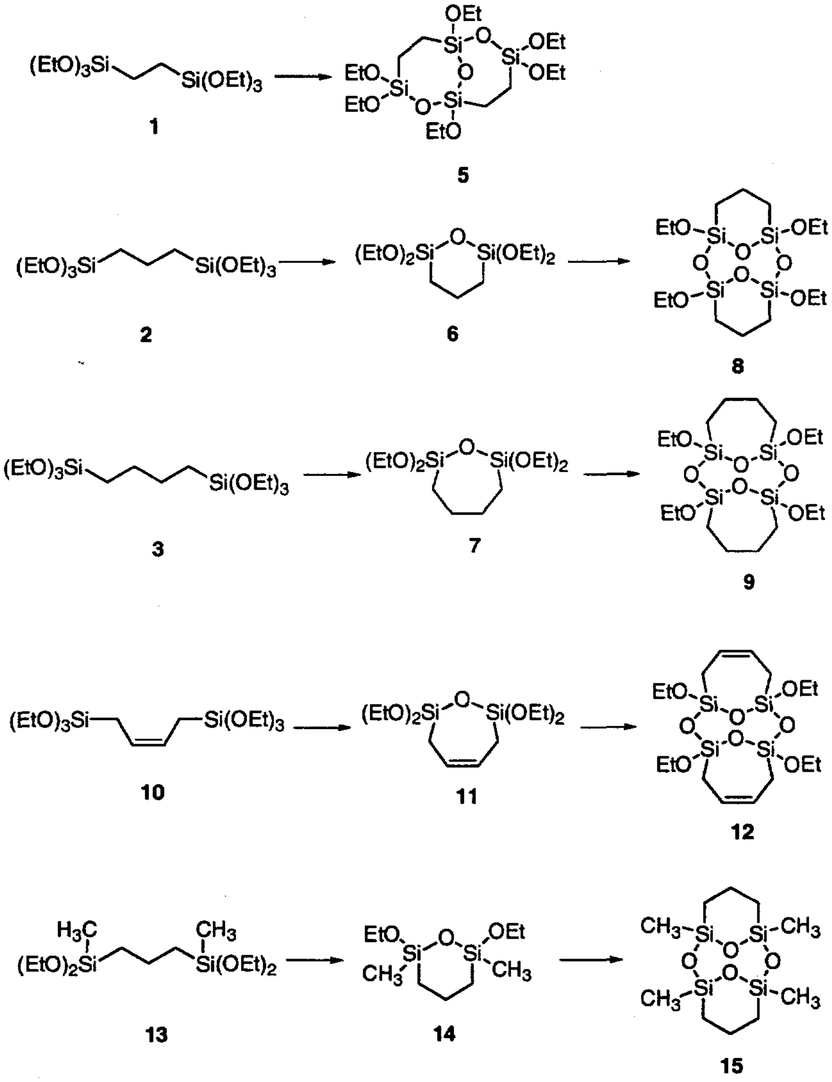
Figure 13



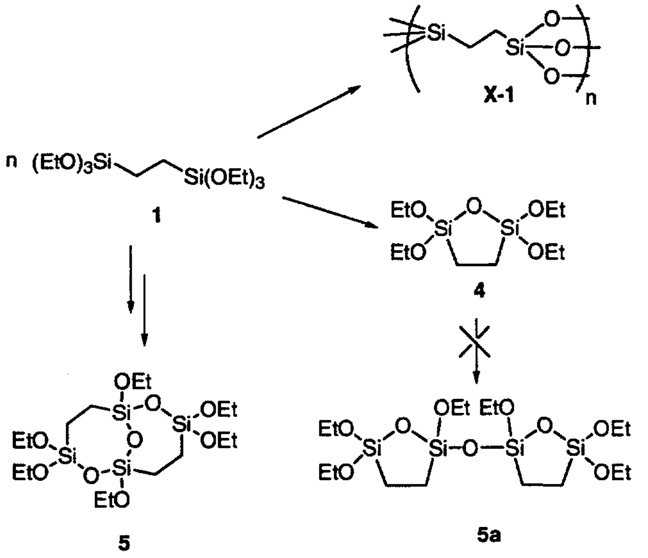
Scheme 1



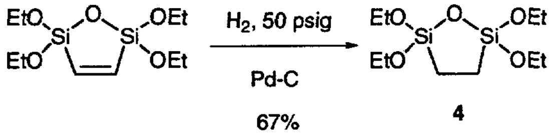
Scheme 2



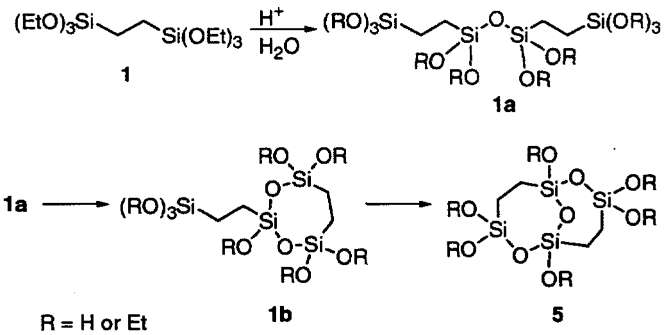
Scheme 3



Scheme 4.



Scheme 5.



Scheme 6.