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INTRAMOLECULAR CONDENSATION REACTIONS OF α, ω-BIS(TRIETHOXYSILYL)ALKANES. FORMATION OF CYCLIC DISILSESQUIOXANES

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ABSTRACT

Under acidic sol-gel polymerization conditions, 1,3-bis(triethoxysilyl)-propane **1** and 1,4-bis(triethoxysilyl)butane **2** were shown to preferentially form cyclic disilsesquioxanes **3** and **4** rather than the expected 1,3-propylene- and 1,4-butylene-bridged polysilsesquioxane gels. Formation of **3** and **4** is driven by a combination of an intramolecular cyclization to six and seven membered rings, and a pronounced reduction in reactivity under acidic conditions as a function of increasing degree of condensation. The ease with which these relatively unreactive cyclic monomers and dimers are formed (under acidic conditions) helps to explain the difficulties in forming gels from **1** and **2**. The stability of cyclic disilsesquioxanes was confirmed with the synthesis of **3** and **4** in gram quantities; the cyclic disilsesquioxanes react slowly to give tricyclic dimers containing a thermodynamically stable eight membered siloxane ring. Continued reactions were shown to perserve the cyclic structure, opening up the possiblity of utilizing cyclic disilsesquioxanes as sol-gel monomers. Preliminary polymerization studies with these new, carbohydrate-like monomers revealed the formation of network *poly(cyclic disilsesquioxanes)* under acidic conditions and polymerization with ring-opening under basic conditions.

INTRODUCTION

Sol-gel polymerization of α, ω-bis(triethoxysilyl)alkanes normally leads to alkylene-bridged polysilsesquioxanes as insoluble, highly crosslinked gels [1]. Hydrolysis of the six ethoxide groups on each monomer gives silanols that subsequently condense to form a network of siloxane bonds. Unlike most sol-gel monomers that possess a single alkoxysilane functionality, these flexible hydrocarbon-bridged monomers can participate not only in intermolecular condensation reactions that lead to oligomers and polymeric networks, but in *intramolecular* condensation reactions that afford cyclic disilsesquioxanes as well (Scheme 1). Partitioning between intermolecular and intramolecular pathways will be strongly affected by 1) the mechanism of hydrolysis (acid versus base catalysis), 2) the concentration of α, ω-bis(triethoxysilyl)alkane, and 3) the length of the alkylene-bridging group. The degree to which one of these reaction pathways is favored over the other may be an important determinant in how the network is assembled and ultimately of the final morphologies of the network polymers.

The first evidence for the formation of cyclic disilsesquioxanes, rather than polymeric gels, came from the studies of the sol-gel polymerization of α, ω-bis(triethoxysilyl)alkanes, $(EtO)_3Si\text{-}(CH_2)_n\text{-}Si(OEt)_3$ (Figure 1) [2]. Under alkaline conditions (10.8 mol% NaOH), these monomers (0.4 M) reacted rapidly with water (6 equivalents), regardless of the length of the bridging group, to afford viscous solutions of growing, highly branched polysilsesquioxanes that formed gels within a few hours. Under acidic conditions (10.8 mol% HCl), however, it was discovered that solutions of the propylene- (**1**) and butylene- (**2**) bridged monomers required more than 4000 hours for gels to form [2, 3]. In this paper, we describe the discovery that the extraordinarily slow rates of gelation exhibited by **1** and **2** resulting from dominance of the intramolecular reaction pathway leading to the cyclic disilsesquioxanes **3** and **4**, respectively, as

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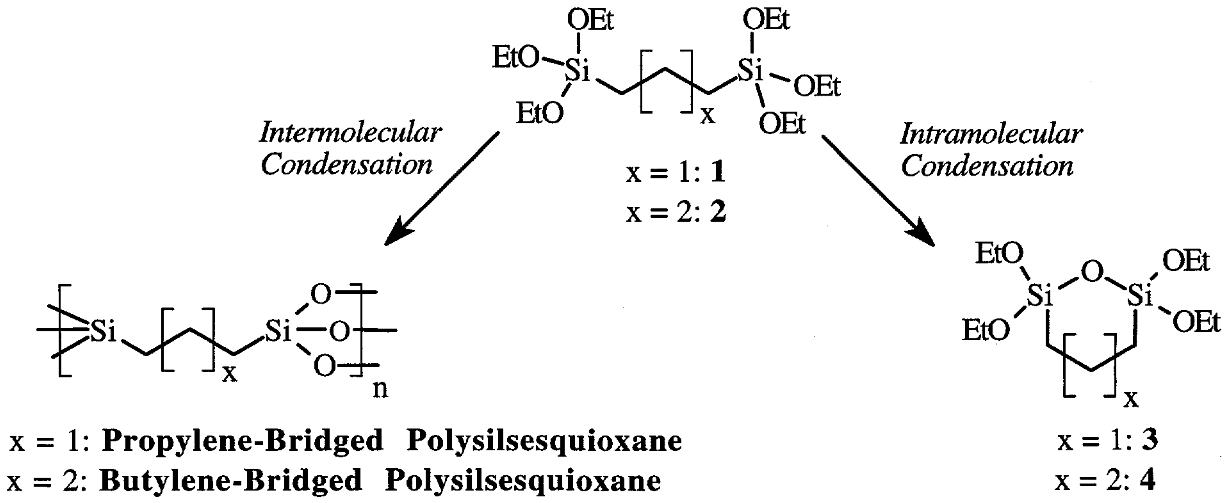


Scheme 1. Inter- and intramolecular condensation pathways for α, ω-bis(triethoxysilyl)alkanes.

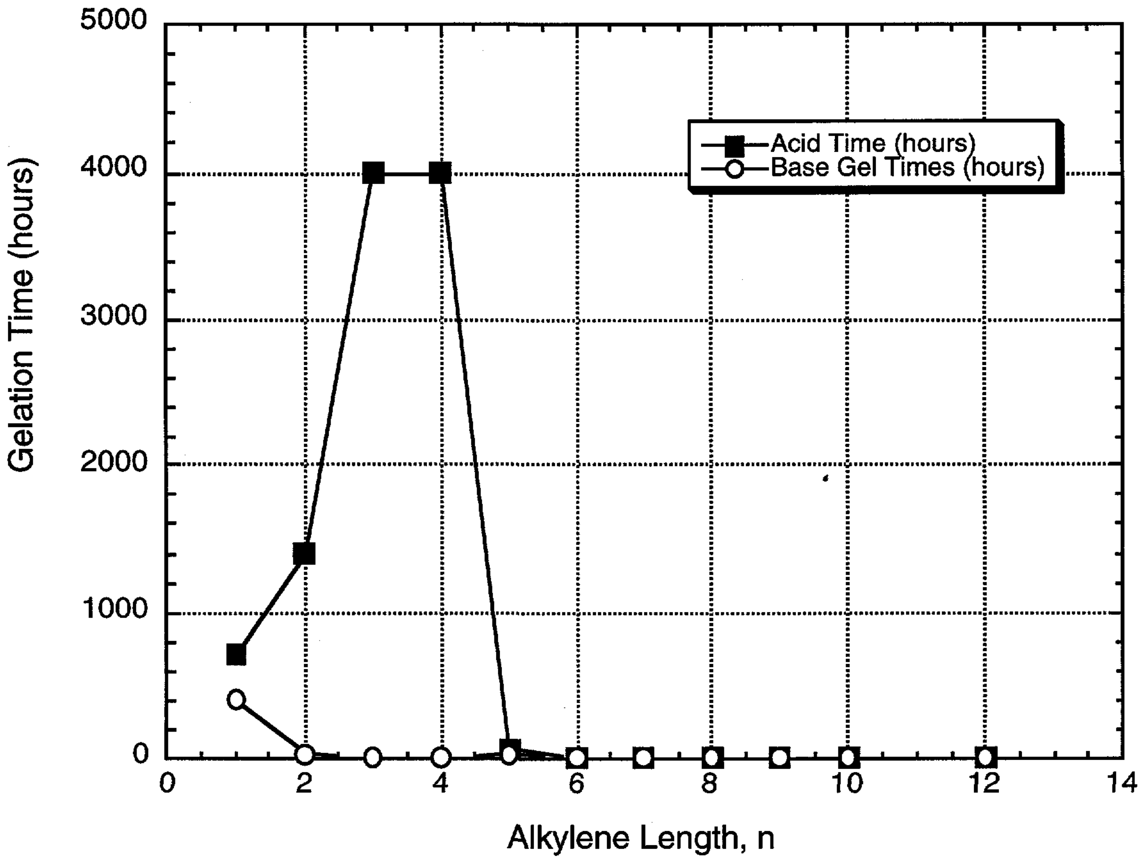


Figure 1. Gelation times for α, ω-bis(triethoxysilyl)alkanes, $(EtO)_3Si-(CH_2)_n-Si(OEt)_3$ (n = 2-14). Sol-gel polymerizations were carried out at 0.4 M monomer concentration in ethanol with 6 H_2O, 10.8 mol% HCl or NaOH.

EXPERIMENTAL

General Procedures

Reagents were distilled from appropriate drying agents: magnesium (ethanol) and calcium hydride (benzene). Anhydrous tetrahydrofuran (THF, Sure/Seal™), 4-triethoxysilylbutene, chloroplatinic acid, and 3-triethoxysilylpropene was purchased (Aldrich) and used as received. Solution NMR spectra were collected on a Brüker AM-300 spectrometer and referenced to the solvents' residual proton signal (^1H, ^{13}C) or internal tetramethylsilane (^{29}Si). The ^{29}Si and ^{13}C CPMAS NMR spectra were acquired on a Brüker AMX-400 spectrometer using $[Si_8O_{12}](OSiMe_3)_8$ (Q_8M_8)[12] and glycine as external references. Infrared spectra were collected on a Perkin-Elmer Model 1750 FTIR. Mass spectra were collected on a VG Autospec using chemical ionization (NH_3 or isobutane).

Monomer Syntheses

Monomer 1.

A flask was charged with 3-triethoxysilylpropene (50 g, 245 mmol), triethoxysilane (48.3 g, 294 mmol), benzene (100 mL), and chloroplatinic acid (0.100 g, 0.24 mmol). While stirring for 24 h, the solution gradually turned yellow-brown. Additional chloroplatinic acid (0.100 g, 0.24 mmol) was added to the reaction mixture, which was 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 (40.5 g, 45%). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 3.78$ (q, 12H, $OC\mathbf{H}_2CH_3$, $J = 7.0$ Hz), 1.84 (m, 2H, $SiCH_2CH_2CH_2Si$), 1.15 (t, 18H, $OCH_2C\mathbf{H}_3$, $J = 7.0$ Hz), 0.85 (t, 4H, $SiC\mathbf{H}_2CH_2C\mathbf{H}_2Si$, $J = 8.2$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 58.40$ (OCH_2CH_3), 18.54 (OCH_2CH_3), 17.20 ($SiCH_2CH_2CH_2Si$), 14.99 ($SiCH_2CH_2CH_2Si$). IR (neat): $\nu = 2975$, 2928, 2884, 1484, 1444, 1391, 1366, 1341, 1295, 1229, 1168, 1078, 960, 900, 820, 774, 710 cm^{-1}. ^{29}Si NMR (99 MHz, EtOH): $\delta = -45.76$. HRMS (CI, isobutane): Calcd for $C_{15}H_{37}O_6Si_2$ $[M + H]^+$: 369.2129. Found: 369.2113.

Monomer 2.

To a solution of 4-triethoxysilylbutene (25 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%). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 3.76$ (q, 12H), 1.41 (m, 4H), 1.18 (t, 18H), 0.59 (m, 4H). ^{13}C NMR (75.48 MHz, $CDCl_3$): $\delta = 58.24$, 26.26, 18.24, 10.06. ^{29}Si NMR (99 MHz, EtOH): $\delta = -45.36$. HRMS (CI, isobutane): Calcd for $C_{16}H_{39}O_6Si_2$ $[M + H]^+$: 383.2285. Found: 383.2276.

Cyclic Disilsesquioxane 3.

To a solution of **1** (15 g, 40.7 mmol) in ethanol (150 mL) was added 1 N HCl (0.733 mL) 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 (**3**, 9.67 g, 81%). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 3.85$ (q, 8H, $OC\mathbf{H}_2CH_3$, $J = 7.0$ Hz), 1.78 (m, 2H, $SiCH_2C\mathbf{H}_2CH_2Si$), 1.23 (t, 12H, $OCH_2C\mathbf{H}_3$, $J = 7.0$ Hz), 0.71 (t, 4H, $SiC\mathbf{H}_2CH_2C\mathbf{H}_2Si$, $J = 3.8$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 58.34$ ($O\mathbf{C}H_2CH_3$), 18.23 (OCH_2CH_3), 17.17 ($SiCH_2CH_2CH_2Si$), 11.23 ($SiCH_2CH_2CH_2Si$). ^{29}Si NMR (99 MHz, EtOH): $\delta = -47.25$ (T^1_{cyclic}). IR (neat): $\nu = 2977$, 2923, 2889, 1442, 1392, 1246, 1169, 1107, 1084, 1007, 968, 899, 787, 756 cm^{-1}. HRMS (CI, ammonia): Calcd for $[C_{11}H_{26}O_5Si_2]^+$: 294.1319. Found: 294.1322.

Cyclic Disilsesquioxane 4

To a solution of **2** (15 g, 39.2 mmol) in ethanol (185 mL) was added 1 N HCl (0.705 mL) 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 (**4**, 8.22 g, 68%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.83 (q, 8H, $OC\mathbf{H}_2CH_3$, J = 7.0 Hz), 1.64 (m, 4H, $SiCH_2C\mathbf{H}_2C\mathbf{H}_2CH_2Si$), 1.16 (t, 12H, $OCH_2C\mathbf{H}_3$, J = 7.0 Hz), 0.76 (m, 4H, $SiC\mathbf{H}_2CH_2CH_2C\mathbf{H}_2Si$). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 58.39 (OCH_2CH_3), 26.67 ($SiCH_2CH_2CH_2CH_2Si$), 18.58 (OCH_2CH_3), 10.86 ($SiCH_2CH_2CH_2CH_2Si$). ^{29}Si NMR (79.5 MHz, $CDCl_3$): δ = -49.06 (T^1_{cyclic}). IR (neat): v = 2975, 2927, 2885, 1484, 1444, 1392, 1307, 1296, 1212, 1169, 1106, 1083, 1034, 961, 884, 849, 800, 762, 737, 652 cm^{-1}. HRMS (CI, isobutane): Calcd for $[C_{12}H_{28}O_5Si_2]^+$: 308.1475. Found: 308.1473.

Sol-Gel Polymerization of Cyclic Monomers.

General Procedure.

All polymerizations were performed at 0.4 M monomer concentration in ethanol. The solutions were prepared in 5 mL volumetric flasks before being transferred to polyethylene bottles. After gelation, the samples were allowed to age for 2 weeks. The gels were then fractured and washed with 3 x 100 mL of H_2O and 2 x 50 mL of ether. The materials were then dried in vacuo at 100 °C for 24 h.

Acid-Catalyzed Polymerizations of 3

To a solution of **3** (0.589 g, 2.00 mmol) in ethanol (2.0 mL) was added 1 N HCl (0.72 mL) dissolved in ethanol (2.0 mL). The volume of the solution was then brought to exactly 5.0 mL with ethanol. A rigid gel formed after 30 days. After drying, an opaque white gel was obtained (268 mg, 91%). ^{13}C CP MAS-NMR (50.20 MHz) δ = 16.5 ($SiCH_2CH_2CH_2Si$), 13.4 ($SiCH_2CH_2CH_2Si$); ^{29}Si CP MAS-NMR (39.65 MHz) δ = -49.74 (T^2_{cyclic}), -58.72 (T^3_{cyclic}); IR (KBr) 2927, 1638, 1413, 1253, 1116, 1018, 902, 754 cm^{-1}.

Base-Catalyzed Polymerizations of 3

To a solution of **3** (0.589 g, 2.00 mmol) in ethanol (2.0 mL) was added 1 N NaOH (0.144 mL) dissolved in ethanol (2.0 mL). The volume of the solution was then brought to exactly 5.0 mL with additional ethanol. Gelation occurred within 1 h. After drying, white monolithic gel fragments were obtained (303 mg, 104%). ^{29}Si CP MAS-NMR (39.65 MHz) δ = -60.78 ($T^3_{acyclic}$); IR (KBr) 2927, 1251, 1111, 1019, 903, 759 cm^{-1}.

Acid-Catalyzed Polymerizations of 4.

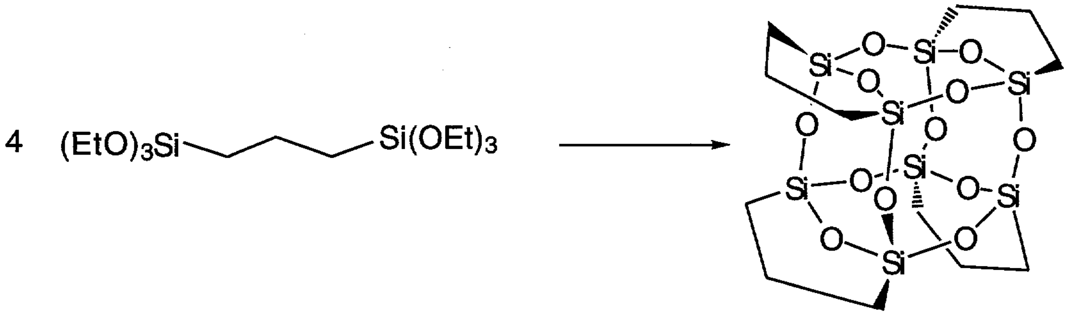
To a solution of **4** (0.617 g, 2.00 mmol) in ethanol (2.0 mL) was added 1 N HCl (0.72 mL) dissolved in ethanol (2.0 mL). Ethanol was added to bring the volume to exactly 5.0 mL. After 16 days a rigid gel formed. The final gel product was an opaque white solid (312 mg, 98%). ^{13}C CP MAS-NMR (50.20 MHz) δ = 58.0 (OCH_2CH_3), 25.0 ($SiCH_2CH_2CH_2CH_2Si$), 13.3 ($SiCH_2CH_2CH_2CH_2Si$); ^{29}Si CP MAS-NMR (39.65 MHz) δ = -58.81 (T^3_{cyclic}), -62.75 ($T^3_{acyclic}$); IR (KBr) 2931, 1655, 1638, 1459, 1407, 1029, 852, 795 cm^{-1}.

Base-Catalyzed Polymerizations of 4.

To a solution of **4** (0.617 g, 2.00 mmol) in ethanol (2.0 mL) was added 1 N NaOH (0.144 mL) dissolved in ethanol (2.0 mL). The volume of the solution was brought to 5.0 mL with ethanol. After 2 hours, a rigid gel had formed. The dried gel was an opaque white solid (344 mg, 108%). ^{29}Si CP MAS-NMR (39.65 MHz) δ = -63.74 ($T^3_{acyclic}$); IR (KBr) 2932, 1719, 1510, 1459, 1408, 1311, 1127, 1039, 853, 797 cm^{-1}.

RESULTS AND DISCUSSION

Identification of the gelation "bottleneck" generated during the acid-catalyzed hydrolysis and condensation reactions of **1** and **2** was accomplished by both solution ^{29}Si NMR spectroscopy and mass spectrometry of the of the reaction solutions. Because no significant changes in viscosity were observed over periods of weeks, we felt that the reaction was most likely forming soluble oligomeric products that would be easily characterized by these solution techniques. One possible structure proposed as the hydrolysis products of **1** (or **2**), based on the precedents for simple organotrialkoxysilanes forming polyhedral oligosilsesquioxanes [4], was the cubic tetramer (Scheme 2).



Scheme 2. A proposed, but not realized, structure for the product of the acid-catalyzed oligomerization of **1**.

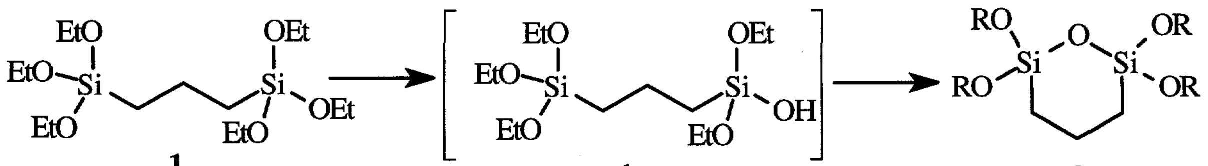
As polyhedral oligosilsesquioxanes are known to retard or prevent gelation of organotrialkoxysilanes, this fully condensed (T^3) silsesquioxane structure would easily explain anomalous polymerization chemistry of **1** and **2.** The presence of this or any other cyclic species that was preferentially formed would be readily apparent in both NMR and mass spectrometric techniques.

Solution ^{29}Si NMR Spectrscopy.

^{29}Si NMR spectra of the sol-gel reactions (1 M monomer, 1 H_2O, 1.8 mol% HCl) were collected at regular intervals to permit monitoring evolution of early hydrolysis and condensation products. The spectra obtained from the hydrolysis of the propylene- and butylene-bridged monomers were dominated by a single resonance at -47.25 ppm for **1** and -48.25 ppm for **2.** The location of these resonances was unusual in that they lie upfield of the expected ^{29}Si NMR chemical shifts of unreacted monomer (-45 ppm; T^0) and significantly downfield of a silsesquioxane with a single, *acyclic* siloxane bond (-52 ppm; T^1). The chemical shifts are *not* consistent with a cyclic (T^3) tetramer (scheme 2). As ^{29}Si NMR chemical shifts are particularly sensitive to ring strain and Si-O-Si bond angles [5], the resonances are in accord with cyclic disilsesquioxanes **3** and **4**, with single siloxane bonds (T^1) linking the silicon atoms [6]. The T^1_{cyclic} resonances persisted for hours even in the presence of excess H_2O indicating that the cyclic species were relatively stable towards ring opening. These spectra are simpler than and should be contrasted with, those normally obtained from the hydrolysis and condensation of organotrialkoxysilanes R-Si(OEt)$_3$ [7], where, within minutes of the addition of aqueous acid to propyltriethoxysilane, there were more than eight distinct T^1_{acyclic} peaks between -50 ppm and -54 ppm and T^2_{acyclic} peaks near -60 ppm.

Mass Spectrometric Analysis.

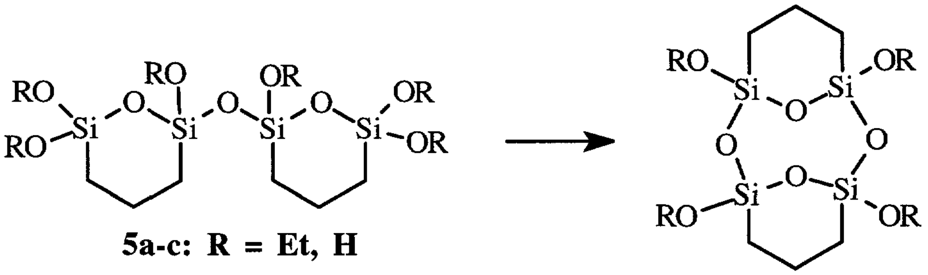
Mass spectrometric analysis of the acid-catalyzed reaction solutions obtained from **1** and **2** confirmed that the soluble products were the cyclic disilsesquioxanes **3** and **4**. For example, within one minute of the addition of aqueous HCl to **1**, the mass peaks characteristic of **1** were completely replaced by peaks at m/z 295 and m/z 312 due to $[M+H]^+$ and $[M+NH_4]^+$ ions of the cyclic disilsesquioxane **3**. As in the NMR study, none of the hydrolysis products of **1** are observed in the mass spectra suggesting that cyclization occurs rapidly relative to the rate of hydrolysis (Scheme 3).



1 **1a** **3**

Scheme 3. Hydrolysis and cyclization of 1,3-bis(triethoxysilyl)propane **1** to give six-membered cyclic disilsesquioxane **3**.

For samples that were allowed to react longer than one minute before mass spectrometric analysis, oligomers resulting from continuing condensation reactions were observed. The first oligomers to be observed were the acyclic (**5a-c**) and cyclic (**6a-c**) dimers of **3**. Presumably, two molecules of **3** hydrolyzed and condensed to form the dimer **5a** (m/z 532, $[M + NH_4]^+$) and its hydrolysis products **5b** and **5c**. Intramolecular cyclization of **5a**, driven by the formation of a tetrasiloxane ring, affords the tricyclic dimer **6a** (m/z 458, $[M + NH_4]^+$) (Scheme 4). After 29 hours of reaction time, the mass spectrum was dominated by the cyclic disilsesquioxane dimer **6a** and its hydrolysis products **6b** and **6c**.

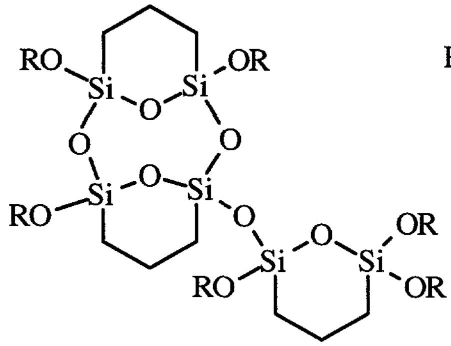


5a-c: R = Et, H

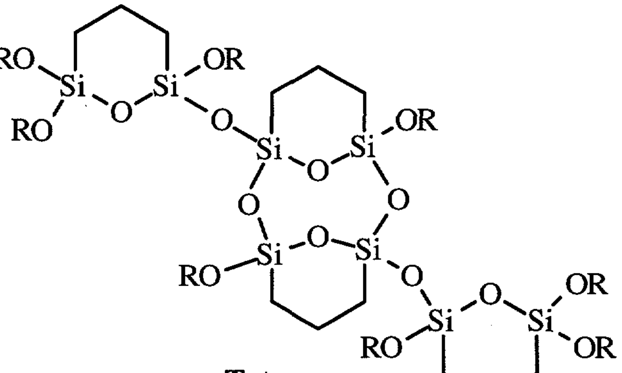
6a-c: R = Et, H

Scheme 4. Intramolecular cyclization of dimer(s) **5a-c** to give tricyclic dimer(s) **6a-c** (Note: thermodynamically favored eight-membered tetrasiloxane ring.).

Two additional groups of peaks corresponding to trimeric (m/z 532-678) and tetrameric (m/z 710-870) species were also observed, indicating that continued oligomerization *without* ring opening is possible.

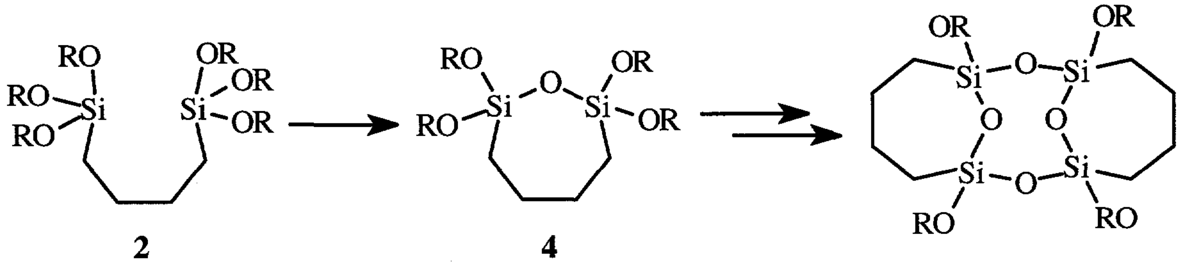


Trimer



Tetramer

Similarly, mass spectrometry revealed that hydrolysis and condensation of the butylene-bridged monomer **2** also generated cyclic disilsesquioxanes and cyclic oligomers in abundance (Scheme 5). The same pattern of cyclization followed by oligomerization seen with **1** was also observed for **2**. Hydrolysis and condensation of **2** with one equivalent of H_2O in the presence of aqueous acid led to the preferential formation of the seven membered cyclic disilsesquioxane **4**, its cyclic dimer, and trimer along with their hydrolysis products. Formation of **4** was slow compared with **3**, presumably due to greater transannular interactions in the former.



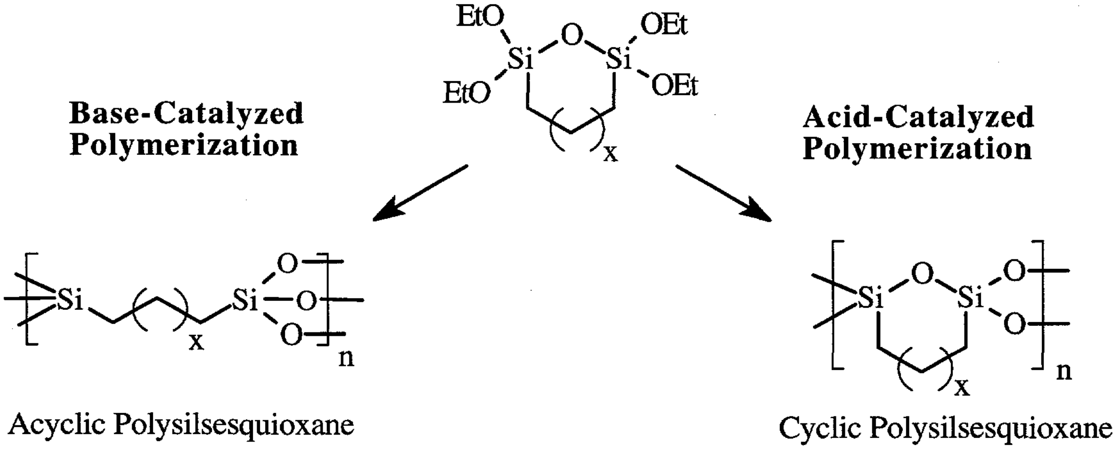
Scheme 5. Intramolecular cyclization pathway for the formation of seven-membered cyclic disilsesquioxane **4** and its dimer.

Synthesis of 3 and 4.

Conclusive proof for the existence of the cyclic disilsesquioxanes was obtained by the deliberate synthesis and isolation of gram quantities of **3** and **4**. When one equivalent of H_2O (1 N HCl) was used in the hydrolysis experiments instead of the excess needed for polymerization, **1** and **2** were *quantitatively* converted into the monocyclic disilsesquioxanes within a few hours. The cyclic monomers were isolated in excellent yields by distillation as clear colorless oils. ^{29}Si NMR spectra for **3** and **4** showed the same downfield shifted T^1 resonances observed in the reaction mixtures.

Polymerizations of Cyclic Disilsesquioxanes.

Despite their reduced reactivity under the acidic conditions normally used to polymerize bridged silsesquioxane monomers, the cyclic disilsesquioxanes are still tetrafunctional sol-gel monomers with intriguing similarities to carbohydrate building blocks (Scheme 6).



Scheme 6. Possible polymerization pathways for cyclic disilsesquioxane monomers.

Polymerizations of **3** and **4** were performed under basic and acidic conditions (Table 1). With the introduction of NaOH and excess (4 equivalents) H_2O, both monomers reacted within two hours to form transparent, colorless gels. ^{29}Si CP MAS NMR of the dried gels revealed near-quantitative ring opening to afford the acyclic propylene- and butylene-bridged polysilsesquioxanes with $T^2_{acyclic}$ resonances at -60.78 ppm and $T^3_{acyclic}$ resonances at -63.74 ppm [8]. In contrast, aqueous acid-catalyzed polymerization of **3** and **4** occurred much more slowly than under basic conditions, requiring weeks before gels were formed. ^{29}Si CP MAS NMR of the dried polymer derived from **3** revealed a single T^3_{cyclic} peak at -58.7 ppm, with a slight shoulder at -49.7 ppm assigned as the T^2_{cyclic} silicon. Clearly, hydrolysis of the four ethoxy substituents and condensation to give the cyclic polysilsesquioxane occurred faster than ring opening to the acyclic propylene-bridged polysilsesquioxane. Acid-catalyzed polymerization of **4** revealed both cyclic (-58.7 ppm) and acyclic (-62.8 ppm) T^3 resonances in the solid state ^{29}Si NMR spectrum indicating that ring opening was competitive with hydrolysis and condensation to afford the cyclic polysilsesquioxane. The impact of the cyclic disilsesquioxane building block on the properties of the resulting network polymers' physical properties can be seen by the results of nitrogen sorption porosimetry. The gels prepared under acidic conditions from the cyclic monomers were porous with high surface areas (267-969 m^2g^{-1}) and smaller mean pore diameters (2.5-2.8 nm) than observed in the acyclic polysilsesquioxanes prepared under basic conditions (4.2-5.1 nm).

Table 1. Gelation times and porosity data for acid- and base-catalyzed cyclic disilsesquioxane gels.

Monomer (catalyst)	**Gelation Times** (hours)	**BET** (m^2 g^{-1})	**Pore Diameter** (nm)
3 (acid)	720	471	2.5
3 (base)	< 2	979	4.2
4 (acid)	384	267	2.8
4 (base)	< 2	858	5.1

CONCLUSION

Intramolecular cyclizations of propylene- and butylene-bridged triethoxysilanes **1** and **2** were demonstrated to be the dominant reactions under acidic sol-gel polymerization conditions. Isolation of the six and seven membered cyclic disilsesquioxanes **3** and **4** has not only demonstrated the relative ease of the cyclization reaction, but has provided a new class of siloxane monomers with intriguing similarities to carbohydrates. We are currently investigating further the polymerization chemistry of these new molecules and are preparing new functionalized cyclic disilsesquioxanes from substituted propylene- and butylene-bridged monomers in an effort to control the resulting polymers' stereochemistries.

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[3] Sol-gel polymerizations were carried out at 0.4 M monomer concentration. It is significant to note that while bridged triethoxysilanes generally gel with a few hours at this concentration, tetraethoxysilane will not gel until the monomer concentrations is above 1.8 M.

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[6] Siloxane (Si-O-Si) bond angles were calculated to be 131.86° for **3** and 141.02° for **4** in comparison with a value of 145° for acyclic siloxanes. Calculations were performed using MM2 based models in Chemdraw 3D Plus, Cambridge Scientific Computing.

[7] Hydrolysis of organotriethoxysilanes under identical conditions gave rise to three discrete peaks *downfield* from the monomer (T^0) resonance due to the three possible hydrolysis products. Condensation reactions generate three groups of peaks *upfield* relative to T^0 representing silsesquioxanes with one (T^1), two (T^2) and three (T^3) siloxane bonds.

[8] ^{29}Si CP MAS NMR T^1-T^3 signals are broader and farther downfield than the corresponding solution ^{29}Si NMR signals due to contributions from hydrolyzed and cyclic siloxanes. See: L. W. Kelts; N. J. Effinger; S. M. Melpolder, J. Non Cryst. Solids **83**, 353 (1986).