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Intramolecular Condensation Reactions of α,ω-Bis(triethoxysilyl)alkanes. Formation of Cyclic Disilsesquioxanes

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Sol-gel polymerization of monomers with two triethoxysilyl groups, $(EtO)_3Si{-}R{-}Si(OEt)_3$, is known to give hydrocarbon-bridged polysilsesquioxanes in the form of highly cross-linked polymeric gels.[1] When α,ω-bis(triethoxysilyl)alkanes ($R = -[CH_2]_n-$, $n = 2-14$) are polymerized,[2] the flexible alkylene-bridging group provides the opportunity for *intramolecular* reactions (Scheme 1) that produce *cyclic disilsesquioxanes* to compete with the intermolecular condensations that lead directly to polymers and gels. Because of structural and reactivity differences between the acyclic and cyclic silsesquioxanes, partitioning between intermolecular and intramolecular reaction pathways would be expected to have a profound impact on the architecture of the resulting network polymers.[3] In this paper, we used mass spectrometry and ^{29}Si NMR spectroscopy to discover that the length of the alkylene-bridging groups had a pronounced effect on the competition between cyclization and polymerization of α,ω-bis(triethoxysilyl)alkanes and on the formation of polymeric gels.

Since the intramolecular pathway does not contribute to the formation of polymeric networks necessary to form gels, one manifestation of cyclization reactions would be to slow or even prevent gelation. It was, in fact, the observation of relatively long gelation times for acid-catalyzed sol-gel polymerizations of the propylene- and butylene-bridged monomers (**1** and **2**, Figure 1)[2] that led to the discovery and eventual isolation of the six- and seven-membered cyclic disilsesquioxanes **3** and **4**, respectively, described in this paper. Under basic conditions, where the rates for hydrolysis and condensation of alkoxysilanes have been shown to increase in proportion to the extent of reaction,[4] all of the α,ω-bis(triethoxysilyl)alkanes reacted to form polymeric gels within a few hours.[5a] Under acidic conditions,[5b] where the reaction rates *decrease* with extent of reaction,[4] there was a strong dependence of gelation times on the length of the alkylene group. Gelation times measured in months were observed with monomers with shorter alkylene groups ($n = 2-4$) because of cyclization to stable cyclic disilsesquioxanes ($n = 3$, 4) and cyclic dimers ($n = 2$). For monomers with longer alkylene groups ($n \geq 5$), intramolecular condensations were less productive and gelation occurred within a few hours. Interestingly, the preferred ring sizes of cyclic disilsesquioxanes formed under acidic sol-gel conditions are intermediate between the most favorable cycloalkanes (five- and six-membered rings)[6] and cyclic siloxanes (six- and eight-membered rings).[7]

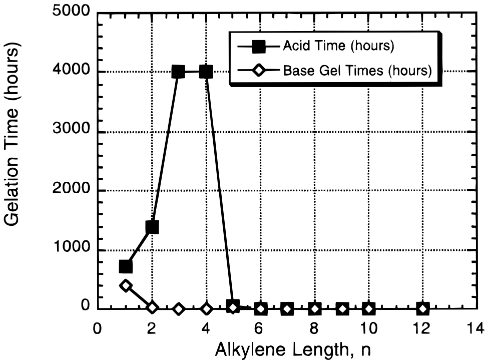
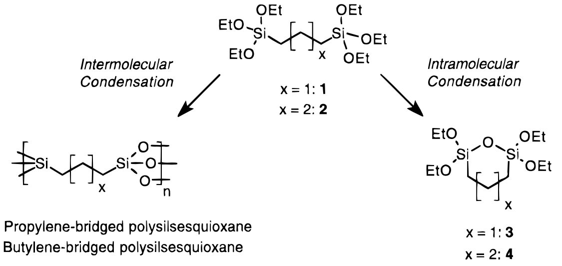


Figure 1. Gelation times for α,ω-bis(triethoxysilyl)alkanes, $(EtO)_3Si{-}(CH_2)_n{-}Si(OEt)_3$ (n 2−12). Sol-gel polymerizations were carried out at 0.4 M monomer concentration in ethanol with 6 equiv H_2O, 10.8 mol % HCl or NaOH.

Scheme 1. Intermolecular versus Intramolecular Pathways for the Hydrolysis and Condensation of 1,3-Bis(triethoxysilyl)propane (**1**) and 1,4-Bis(triethoxysilyl)butane (**2**)



In order to determine if cyclic disilsesquioxanes or some other polyhedral oligosilsesquioxanes[8] were responsible for anomolously long gelation times, the acid-catalyzed reactions of the α,ω-bis(triethoxysilyl)alkanes were monitored with solution ^{29}Si NMR.[9] In control studies, ^{29}Si spectra for monomers that underwent rapid gelation ($n \geq 5$) displayed the same pattern of resonances (T^0-T^3) and chemical shifts as those obtained for the oligomerizations of simple alkyltriethoxysilanes.[10] For example, the spectrum for 1,10-bis(triethoxysilyl)decane after 90 min was populated with eleven resonances including the following: three groups of T^0 peaks from residual monomer and its hydrolysis products ($\delta_{Si} = -40$ to -45), three distinct T^1 peaks ($\delta_{Si} = -50$ to -54) due to silicons with one siloxane bond, and a T^2 peak ($\delta_{Si} = -61$) due to a silicon with two siloxane bonds. In contrast, the spectra obtained for the hydrolysis and condensation of **1** or **2** consisted of the monomer peak and a single new T^1 peak shifted *downfield* from the typical

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[1] Review on hydrocarbon-bridged polysilsesquioxanes: Loy, D. A.; Shea, K. J. *Chem. Rev.* **1995**, *95*, 1431.

[2] (a) Small, J. H.; Shea, K. J.; Loy, D. A. *J. Non-Cryst. Solids* **1993**, *160*, 234. (b) Oviatt, H. W., Jr.; Shea, K. J.; Small, J. H. *Chem. Mater.* **1993**, *5*, 943. (c) Loy, D. A.; Jamison, G. M.; Baugher, B. M.; Russick, E. M.; Assink, R. A.; Prabakar, S.; Shea, K. J. *J. Non-Cryst. Solids* **1995**, *186*, 44.

[3] For a detailed discussion of the impact of cyclization reactions on sol-gel polymerizations see: (a) Ng, L. V.; Thompson, P.; Sanchez, J.; Macosko, C. W.; McCormick, A. V. *Macromolecules* **1995**, *28*, 6471. (b) Sharp, K. G.; Michalczyk, M. J. *J. Sol-Gel Sci. Technol.* In press.

[4] Osterholtz, F. D.; Pohl, E. R. *J. Adhes. Sci. Technol.* **1992**, *6*, 127.

[5] Sol-gel polymerizations of α,ω-bis(triethoxysilyl)alkanes (0.4 M) were carried out in freshly distilled ethanol with 6 equiv H_2O with (a) 10.8 mol % NaOH or (b) 10.8 mol % HCl as catalyst. It is significant to note that while bridged triethoxysilanes generally gel within a few hours at this concentration, organotriethoxysilanes or tetraethoxysilane will not gel until monomer concentrations exceed 1.4 M.

[6] Illuminati, G.; Mandolini, L. *Acc. Chem. Res.* **1981**, *14*, 95.

[7] (a) Rochow, E. G.; Gilliam, W. F. *J. Am. Chem. Soc.* **1941**, *63*, 798. (b) Cypryk, M.; Sigwalt, P. *Macromolecules* **1994**, *27*, 6245. (c) Sanchez, C; McCormick, A. V. *J. Non-Cryst. Solids* **1994**, *167*, 289.

[8] M. G. Voronkov, Lavrentyev, V. I. *Top. Curr. Chem.*, **1982**, *102*, 199 and references therein.

[9] Solutions of **1** in ethanol (0.4 M) were mixed with 1 equiv of water (1 N HCl, 1.8 mol %) along with 15 mM chromium acetylacetonate and immediately placed into the spectrometer. Spectra were obtained every 10 min for several hours and again after 20 h.

[10] Devreux, F.; Boilot, J. P.; Chaput, F.; Lecomte *Phys. Rev. A* **1990**, *41*, 41.

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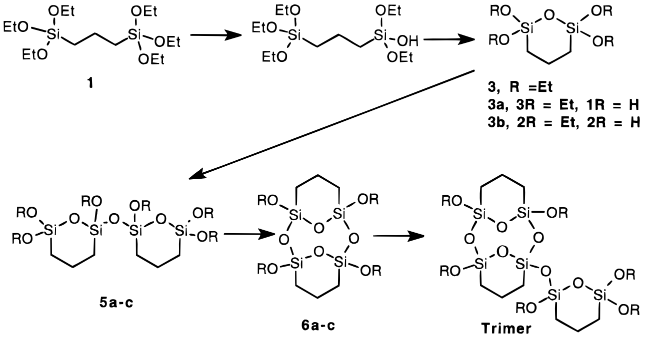
range for acyclic T^1 silicons.[10] After 90 min, the resonance due to residual **1** (T^0: $\delta_{Si} = -45.76$) had been almost entirely replaced with a single resonance (T$^1_{cyclic}$: $\delta_{Si} = -47.25$) consistent with the cyclic disilsesquioxane **3**. Similarly, a single peak (T$^1_{cyclic}$: $\delta_{Si} = -49.06$) assigned to **4** was observed during the hydrolysis and condensation of **2**. The downfield shift exhibited by the T$^1_{cyclic}$ resonances is commensurate with the bond angle distortion experienced by the silicons in six- and seven-membered rings.[11] The resonances due to **3** and **4** persisted for hours, even in the presence of sufficient H_2O (3 equiv) to form gels, indicating the cyclic species were relatively stable toward ring opening. Conclusive evidence for the formation of cyclic disilsesquioxanes **3** and **4** came from their isolation on a preparative scale under acidic hydrolysis and condensation conditions in 81 and 68% yields, respectively. Their spectroscopic properties were identical to those observed during the sol-gel reactions of **1** and **2**.

More details of the hydrolysis and condensation chemistry of the α,ω-bis(triethoxysilyl)alkanes were obtained by following the reactions by mass spectrometry.[12,13] Under alkaline conditions, only acyclic oligomers and polymers were observed. Under acidic conditions, monomers with pentylene or longer bridging groups reacted to give mostly acyclic intermediates and oligomers with only minor contributions from cyclic disilsesquioxanes. In contrast, cyclic disilsesquioxanes **3** and **4** were determined by low- and high-resolution mass spectrometry to be significant intermediates in the acid-catalyzed sol-gel polymerizations of **1** and **2**. Scheme 2 shows the reaction pathway proposed for the sol-gel chemistry of **1** based on the mass spectral data. Within 1 min of the addition of aqueous HCl, the mass spectrum revealed that **1** had completely cyclized to **3** (*m/z* 295 $[M + H]^+$ and *m/z* 312 $[M + NH_4]^+$) and its hydrolysis products **3a** and **3b**. Traces of linear dimers **5a−c** from the intermolecular condensation of **3** and/or its hydrolysis products were also detectable. At the same time, traces of cyclic dimers (**6a−c**) of **3** were detected. The latter probably arise from the intramolecular cyclization of **5a-c** driven by the formation of the thermodynamically stable tetrasiloxane ring. Mass spectra obtained after several hours revealed that these dimers had become more abundant and that traces of trimers (*m/z* 532−678) and tetramers (*m/z* 710−870) of **3** were slowly appearing. Hydrolysis and condensation of the butylene-bridged monomer **2** under acidic conditions also appeared to have a reaction profile similar to that proposed for **1** with the same sequence of cyclization and oligomerization reactions.

Scheme 2. Intramolecular Cyclization Reaction Pathway To Afford Cyclic Disilsesquioxanes **3** and **4** and Their Oligomerization to Dimeric and Oligomeric Cyclic Disilsesquioxanes



While the intramolecular reaction clearly slows gelation, the cyclic disilsesquioxanes are still tetrafunctional monomers theoretically capable of forming polymeric gels. If the ring structures, which bear a striking resemblence to carbohydrates, are preserved through the polymerization, the resulting *poly(cyclic disilsesquioxane)* gels may have structural similarities to branched or cross-linked carbohydrates, such as cellulose or chitosan. Under base-catalyzed sol-gel polymerization conditions, **3** and **4** quickly reacted to give gels with significant ring opening as determined from the ^{29}Si chemical shifts in solid-state (CP MAS) NMR spectra. However, gels prepared under acidic conditions reveal some (from **4**) or all (with **3**) of the cyclic disilsesquioxane functionality was preserved in the polymers. Future efforts will focus on kinetics of cyclization and ring opening, the complete characterization of the polymers, and evaluation of the effects of the cyclic disilsesquioxanes on the network architectures.

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Supporting Information Available: Experimental details for the preparation of **1−4** along with complete characterization data, copies of the ^{29}Si NMR spectra for the hydrolysis of **1** and **2** after 3 h, the polymerization procedures and characterization of the resulting gels, along with additional mass spectra monitoring the oligomerization and cyclization of **1** and **2** (9 pages). See any current masthead page for ordering and Internet access instructions.

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[11] (a) Englehardt, G.; Jancke, H.; Magi, M.; Pehk, T.; Lippmaa, E. *J. Organomet. Chem.* **1971**, *28*, 293. (b) Burton, D. J.; Harris, R. K.; Dodgson, K.; Pellow, C. J.; Semlyen, J. A. *Polym. Commun.* **1983**, *24*, 278−281. (c) Seyferth, D.; Robison, J. *Macromolecules* **1993**, *26*, 407.

[12] Chemical ionization mass spectrometry was performed with a VG Autospec using ammonia as the ionization gas. High-resolution mass spectra were obtained using a VG Autospec using isobutane or ammonia as the ionization gas. Solutions were prepared by dissolving monomer (0.4 M) in ethanol and adding 1 or 2 equiv of water (1 N HCl).

[13] Ten-membered cyclic disilsesquioxanes observed in mass spectrometric studies of the sol-gel polymerization reactions of tetrakis(3-(triethoxysilyl)propyl)silane were recently reported by: Sharp, K. G.; Michalczyk, M. in the Hybrid Materials Symposium of the Inorganic Divsion at the 211th ACS National Meeting, New Orleans, LA, March 24−28,1996; Michalczyk, M.; Simonsick, W. J.; Sharp, K. G. *J. Organomet. Chem.* In press.