

# A Mechanistic Investigation of Gelation. The Sol–Gel Polymerization of Precursors to Bridged Polysilsesquioxanes

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## ABSTRACT

The study of a homologous series of precursors to bridged polysilsesquioxanes has uncovered striking discontinuities in gelation behavior. An investigation of the chemistry during the early stages of the polymerization has provided a molecular basis for these observations. Monomers containing from one to four bridging carbon atoms exhibit a pronounced tendency to undergo rapid intra- or bimolecular cyclization. The cyclic and bicyclic intermediates have been characterized by <sup>29</sup>Si NMR spectroscopy, chemical ionization mass spectrometry, and isolation from the reaction solution. These carbosiloxanes are local thermodynamic sinks that produce kinetic bottlenecks in the production of high-molecular-weight silsesquioxanes. The formation of cyclic carbosiloxanes results in slowing, or in some cases completely shutting down, gelation. An additional finding is that the cyclic structures are incorporated intact into the final xerogel.

## Introduction

Hybrid materials lie at the interface of the organic and inorganic realms.<sup>1</sup> Their synthesis offers exceptional opportunities not only to combine the important properties from both worlds, but also to create entirely new compositions with truly unique properties. The size of the organic and inorganic domains can range from traditional composites prepared from physical mixtures of relatively large, micrometer-size particles to nanophase materials that include substances with organic and inorganic domains that are dispersed homogeneously at the molecular level.

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Representative of this latter group are the *bridged polysilsesquioxanes*,<sup>2–5</sup> a family of hybrid organic–inorganic materials prepared by the hydrolysis and condensation of monomers containing a variable organic bridging group with two or more trifunctional silyl groups. Trialkoxysilyl groups are the most common silyl functionality, although other groups, such as silyl chlorides, have served as precursors as well (Scheme 1).<sup>5</sup>

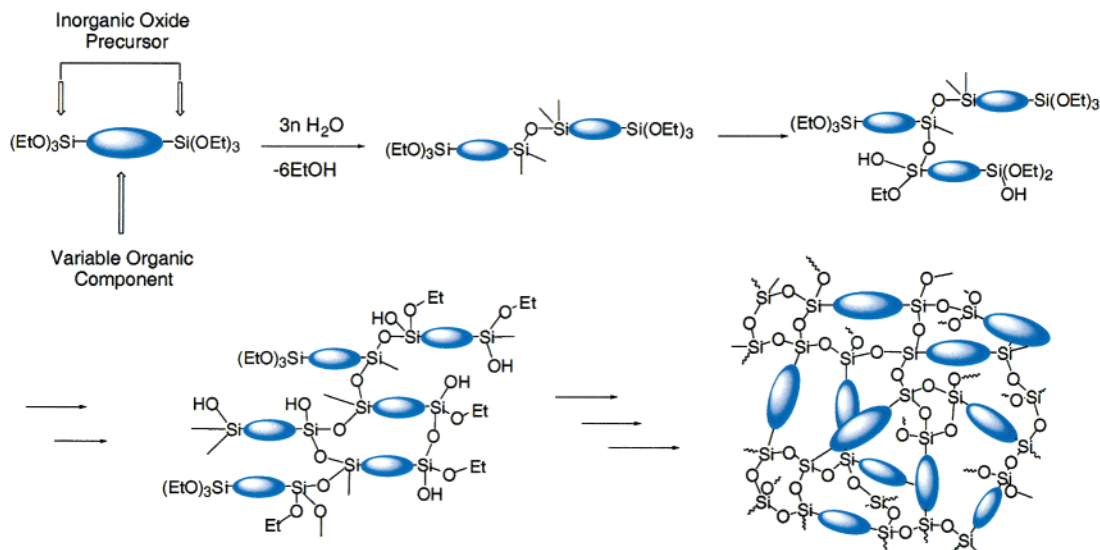
The organic group, covalently attached to the trialkoxysilyl groups through Si–C bonds, can be varied in length, rigidity, geometry of substitution, and functionality. This variability provides an opportunity to explore how the organic structural unit contributes to bulk properties such as porosity, thermal stability, optical clarity, chemical resistance, and dielectric constant. Representative monomers, divided into four groups (A–D) in Figure 1, illustrate the range of structural types that have been examined. Group A includes monomers with rigid arylene (**1–5**),<sup>5,7,8</sup> *trans*-ethenylene (**8**),<sup>10</sup> or acetylene (**6**, **7**)<sup>5,9</sup> bridging groups. Group B includes monomers with long flexible bridging groups such as alkenes (**9–13**),<sup>11,12</sup> ethers (**14**),<sup>13</sup> dialkylamines (**15**),<sup>14</sup> carbonates (**16**, **17**),<sup>13</sup> and bisaryl-imides (**18–20**)<sup>15</sup> that can permit the complete collapse of porosity during drying. Group C includes monomers with one and two carbon bridging groups such as methylene (**21**),<sup>12d</sup> vinylidene (**22**),<sup>10</sup> norbornenylene (**23**),<sup>16</sup> ethylene (**24**),<sup>12</sup> and *cis*-ethenylene (**25**).<sup>10</sup> Group D includes monomers with three and four carbon bridges such as propylene (**26**),<sup>11,12</sup> butylene (**27**),<sup>11,12</sup> and *cis*- (**28**) and *trans*- (**29**) butenylene.<sup>17</sup> Their syntheses have been recently reviewed.<sup>2b,c</sup> Each hexafunctional monomer was polymerized under a uniform set of sol–gel reaction conditions. These studies have revealed significant differences in gelation times that, in some cases, arise from only very minor differences in the organic bridging group.

Sol–gel polymerization of these “hybrid” monomers involves a series of hydrolysis reactions forming silanol-functionalized intermediates and subsequent condensation reactions that produce oligomeric silsesquioxanes and siloxanes. These species react further to produce higher molecular weight polymers that eventually form a three-dimensional infinite network which spans the dimensions of the reaction vessel. At this point the solution loses fluidity and has reached the gel point (Scheme 1). The “wet” gel is then dried to afford a xerogel (*dry gel*). During the drying process the gel undergoes significant shrinkage, resulting in partial collapse of pore structure. At first glance, the bridged polysilsesquioxane system appears to fall into the same reaction pathways observed with organotrialkoxysilanes, RSi(OR)<sub>3</sub>,<sup>19,20</sup> or tetraalkoxysilanes.<sup>21,22</sup> The sol–gel polymerization of tri- and tetrafunctional silanes is characterized by the formation of six-

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Scheme 1<sup>a</sup>

<sup>a</sup> The photograph shows dried monolithic bridged polysilsesquioxane xerogels<sup>5</sup> (clear) and aerogels<sup>6</sup> (white). At the bottom is shown a schematic of the sol-gel polymerization of monomers which, following hydrolysis and condensation, lead eventually to a network consisting of silsesquioxane and siloxane linkages that span the reaction vessel (gel point).

and, in particular, eight-membered cyclic *siloxane* rings, structures with alternating silicon and oxygen atoms.<sup>19</sup> These substructural motifs are also an integral part of the final xerogel networks from the monomers in Figure 1. However, *in addition* to the siloxane rings, selected monomers are distinguished by their pronounced tendency to rapidly form cyclic and bicyclic carbosiloxanes.<sup>12</sup> In these systems, gelation can be substantially impeded.

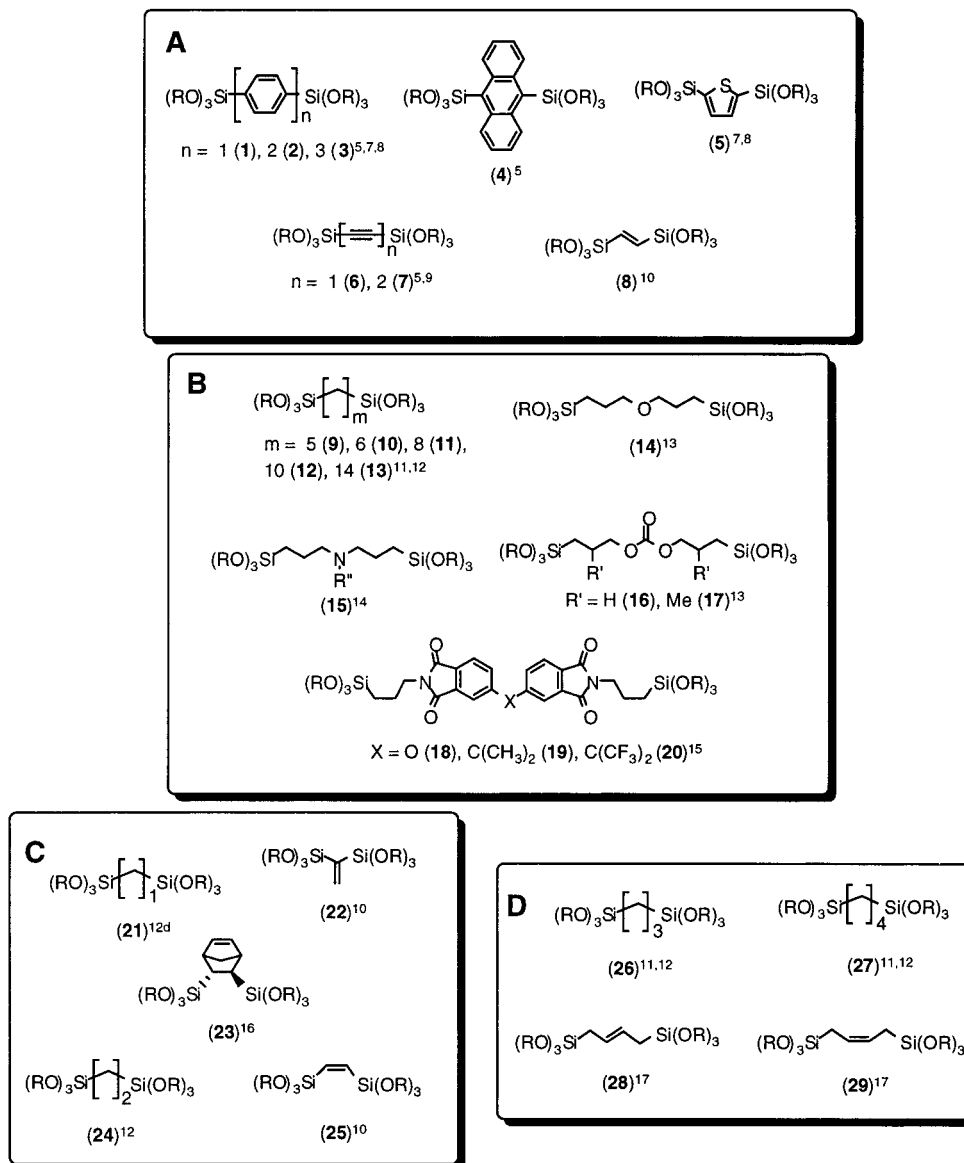
One objective of contemporary materials chemistry is to establish links between the molecular building block and the bulk properties of the resultant material. Since bulk properties of materials, such as porosity and modulus, have both chemical and physical origins, the problem is formidable. Bridged polysilsesquioxanes provide an exceptional opportunity to study relationships between the starting monomer and final xerogel morphology. There are several reasons for this. First, they readily react under a standard, uniform set of sol-gel conditions to afford gels. Second, their modular construction permits access to a wide range of monomers that allows systematic variation of the organic bridging group. Third, they have a range of interesting and highly reproducible bulk properties (such as high surface area and porosity) that are strongly coupled to the organic bridging group. Finally,

despite their amorphous nature, most have a rather simple morphology; that is, the inorganic and organic components are homogeneous to molecular length scales with no discernible phase separation between organic and inorganic domains.<sup>23</sup>

*In this Account, we discuss the influence of small, systematic perturbations of the organic fragment on the formation of bridged silsesquioxane gels.* We have focused on the early stages of the process to document the chemical events that lead up to and include gelation. These studies have produced insight into how these small perturbations affect the polymerization chemistry and, ultimately, the final xerogel structure.

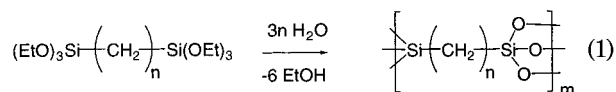
## Gelation of Monomer Precursors to Bridged Silsesquioxanes

Typical precursors to bridged polysilsesquioxanes are *hexafunctional* molecules. Experience has shown that many of these monomers (Figure 1), even as very dilute solutions (ca. 0.1 M), rapidly polymerize in the presence of water and catalyst to form gels. Our interest in the chemistry of gelation was peaked by observations of anomalous gelation times during a sol-gel polymerization



**FIGURE 1.** Monomer precursors to bridged polysilsesquioxanes with rigid (A), long, flexible (B), one- and two-carbon alkyne (C), and three- and four-carbon (D) bridging groups.

study of  $\alpha,\omega$ -alkylene-bridged bistrisethoxysilyl monomers (9–13, 21, 24, 26, 27; eq 1).<sup>11,12</sup> It was noted that, under



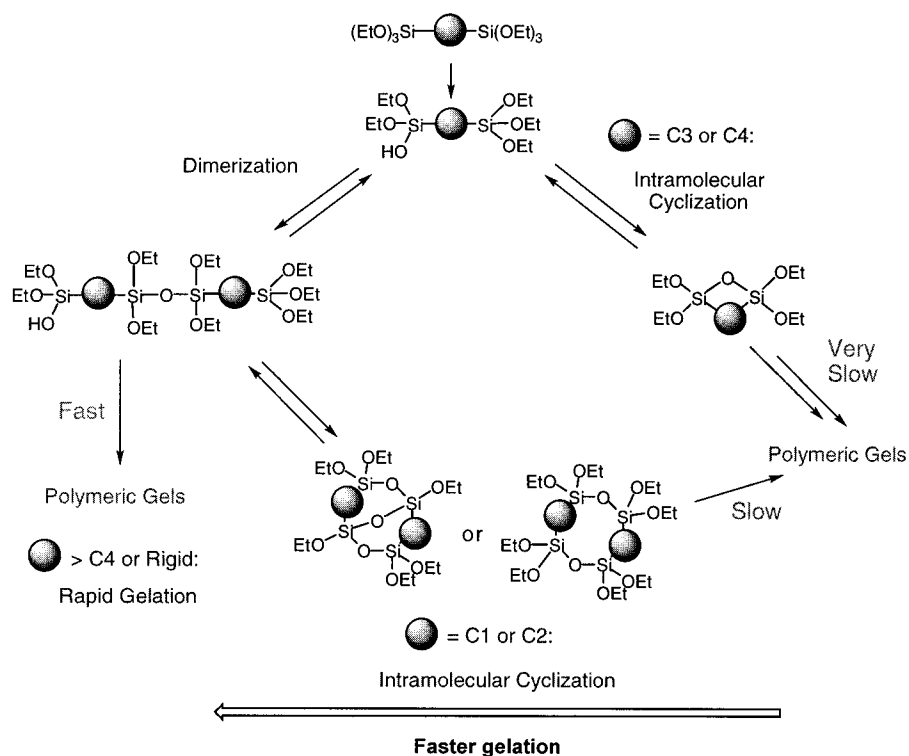
acidic conditions,<sup>24</sup> changing the length of the alkyne bridging group by a *single methylene group* could result in a change in gelation time from several hours to over 6 months!<sup>11,12</sup> Although gelation is not a primary phase transition, it was nevertheless quite reproducible under standard conditions.

The response in gel time to such small changes in the alkyne bridge is likely to have a significant influence on the network that was being produced and ultimately on the xerogel morphology. It was decided therefore to study this series in more detail.<sup>12,18</sup>

These studies have allowed grouping of hexafunctional monomers into three broad classes on the basis of their

solution chemistry and gelation behavior under acidic conditions. Scheme 2 summarizes these findings. The first group (Scheme 2, left branch) incorporates monomers that gel rapidly even as very dilute solutions. The second group of monomers is decidedly slower to gel than the first group (Scheme 2, counterclockwise path). The remaining group (Scheme 2, right branch) shows little tendency to gel under most conditions.

**Monomers That Gel Rapidly.** The first class consists of monomers that have bridging groups that are either short and stiff (Figure 1A)<sup>5,7–10</sup> or long and flexible (Figure 1B).<sup>11–15</sup> 1,4-Bis(triethoxysilyl)benzene (1), 1,6-bis(triethoxysilyl)hexane (10), and 1,10-bis(triethoxysilyl)decane (12) are representative examples. Their gelation times, together with gelation times of bridged monomers from the two other reaction pathways and TEOS ( $>2\times$  the concentration),<sup>20cd,22</sup> are summarized in Table 1. Bridged monomers in this first group rapidly form gels even at very

Scheme 2. Representation of the Oligomerization Pathways to Bridged Polysilsesquioxanes<sup>a</sup>

<sup>a</sup>The monomers are grouped into three broad categories with regard to their gel times: those that gel rapidly (left branch, e.g., groups A and B, Figure 1), those that are much slower to undergo gelation (counterclockwise path, group C, Figure 1), and those that show little tendency to gel (right branch, group D, Figure 1). The gelation behavior corresponds to a standard set of polymerization conditions (0.4 M monomer in ethanol, 6 equiv of water, 10.8 mol % HCl catalyst).

low concentrations (0.1 M), regardless of solvent or catalyst.<sup>11b,23</sup>

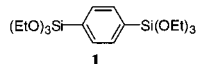
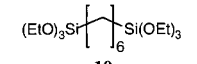
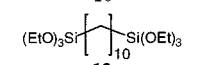
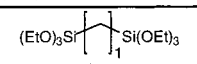
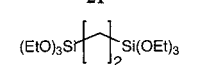
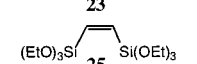
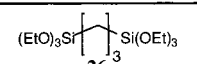
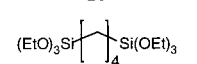
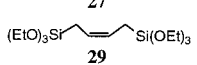
We wished to establish the pattern of oligomerization for “fast gelling” monomers to compare with related monomers with slower gelation times. However, since gelation occurs rapidly, it is difficult to follow the solution chemistry in real time. To overcome this difficulty, we developed a procedure that employs substoichiometric quantities of water for the sol–gel polymerization. These conditions permit real-time monitoring of the reaction by solution-phase <sup>29</sup>Si NMR and chemical ionization mass spectrometry.<sup>12</sup> Under the modified conditions, low-molecular-weight intermediates that are formed during the early stages of polymerization can be detected. The results of these investigations are summarized below.

Both mass spectrometry and <sup>29</sup>Si NMR studies revealed rapid accumulation of hydrolysis products (T<sup>0</sup>) and linear dimers (T<sup>1</sup>) during the very early stages of sol–gel polymerization of 1,10-bis(triethoxysilyl)decane (**12**) (Figure 2).<sup>12</sup> Their assignment was based on a systematic *downfield* shift of 2–3 ppm in the <sup>29</sup>Si NMR spectrum upon each ethoxysilane hydrolysis to a silanol and an approximate 5–8 ppm *upfield* shift for each condensation to form a siloxane bond.<sup>25</sup> The subsequent accumulation of linear and branched trimers and higher condensation oligomers proceeded rapidly even under substoichiometric reaction conditions. In a short time these higher molecular weight species exceeded the detection limits of mass spectrometry, and the rapid onset of gel formation precluded study at longer reaction times.

A similar pattern emerges with 1,4-bis(triethoxysilyl)benzene (**1**). Solution <sup>29</sup>Si NMR and chemical ionization mass spectrometry reveals a rapid burst of hydrolyzed monomer followed by dimer and trimer formation. Although the limited mass range and resolution of the analytical methods preclude following the reaction further, this process must proceed unabated with the rapid buildup of higher molecular weight branched oligomers. *Conspicuously absent in the early stages of reaction is evidence for the accumulation of significant quantities of cyclic carbosiloxanes.* Cyclization of **1** and **12** to form small carbosiloxanes is apparently entropically and/or sterically unfavorable. The xerogels produced from these polymerizations exhibit “typical” patterns of T<sup>1</sup>, T<sup>2</sup>, and T<sup>3</sup> absorptions in the <sup>29</sup>Si NMR.<sup>25</sup> The spectra were later compared with those of xerogels prepared from closely related monomers (*vide infra*).

The rapid gelation of hexafunctional monomers, such as **1** and **12**, serves as a reference point to study gelation behavior of related monomers. With this in mind, the gelation results of an extended series of alkylene-bridged monomers produced a number of surprises. Figure 3 summarizes the gelation times for the series of alkylene-bridged monomers under *acidic*<sup>24</sup> conditions (**9–13**, **21**, **24**, **26**, **27**).<sup>12</sup> There are clearly three different distinct regions on the graph delineated by gel times. The gelation times exhibit a sharp increase as the length of the bridging group increases from one to four methylenes. The extension of one additional methylene group to the five-atom bridge returns the gelation time to one that is similar to

**Table 1. Gelation Times for the Sol–Gel Polymerization of Various Monomer Precursors to Bridged Polysilsesquioxanes under “Standard” Sol–Gel Conditions (0.4 M Monomer, 6 Equiv of Water, 10.8 Mol % HCl Catalyst)<sup>a</sup>**

Monomer	EtOH/HCl Catalyst	THF/HCl Catalyst
Si(OEt) <sub>4</sub> (1.0 M)	300 days	—
<i>Rapid Gelling Monomers: Short/Stiff and Long Flexible</i>		
 1	10 minutes	1 hour
 10	24 hours	1 minute
 12	6 hours	1 minute
<i>C1 and C2 Monomers: Slower Gel Times</i>		
 21	1440 hours	50 hours
 23	720 hours	96 hours
 25	120 hours	240 hours
<i>C3 and C4 Monomers: Slowest Gel Times</i>		
 26	4000 hours	4300 hours
 27	4000 hours	—
 29	> 2000 hours	>9000 hours

<sup>a</sup> For comparison, the gelation time for tetraethoxysilane at 1.0 M concentration is also given.

the longer-chain fast-gelling monomers. What is the reason for the unusually long gelation times? By identifying the oligomers produced during the early stages of sol–gel polymerization, we have obtained insight into the anomalous gelation behavior.

**C1 and C2 Bridged Monomers.** Monomers containing short alkylene bridging groups such as the methylene- and ethylene-bridged monomers (**21** and **24**)<sup>12</sup> and the vinylidene- and (*Z*)-ethenylene-bridged monomers (**22**, **25**)<sup>10</sup> deviate significantly in gel time from their longer chain relatives (Figure 3). Using modified reaction conditions (substoichiometric water, acid catalyst), both branched and linear oligomers were observed. In addition, the solution chemistry of C1 bridging monomers (**21**, **22**) and C2 bridging monomers (**24**, **25**) included products arising from *cyclodimerization*. The formation of substantial quantities of cyclic carbosiloxane dimers marks a significant departure from what was observed with long-chain and stiff bridging groups that rapidly gelled (**1**–**19**). Indeed, monocyclic eight-membered rings and bridged bicyclics dominate the composition of the methylene-bridged monomer (**21**) (Figure 4). Monomer **22**, a 1,1-

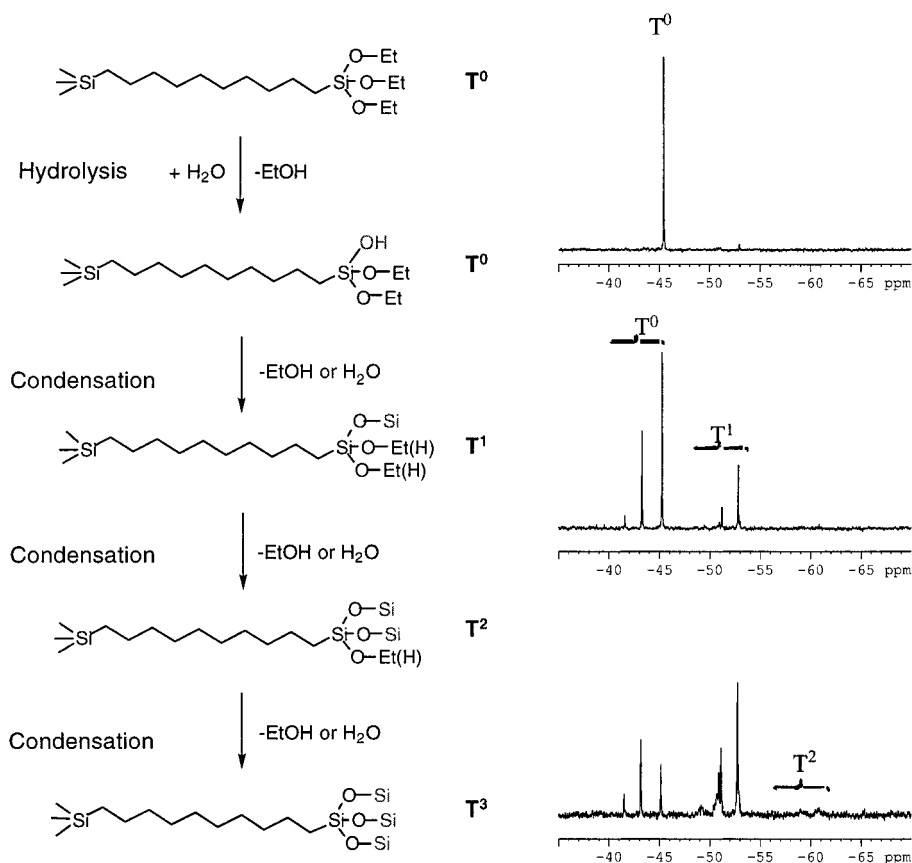
vinylidene-bridged bis(trialkoxysilane), also formed an eight-membered dimer (**30**) with two exocyclic methylene groups (Scheme 3). Carbosiloxane dimer **30** could be isolated from preparative-scale reactions and its <sup>29</sup>Si NMR and mass spectrometric signatures determined. They were consistent with the predominant species observed in the sol–gel polymerization of **22**. Gelation of **22** under these conditions has not been observed after more than two years (Table 1).

The ethylene- and ethenylene-bridged monomers (**24** and **25**), on the other hand, were found to be siphoned off to *bicyclic* dimer intermediates (Scheme 4).<sup>12d</sup> The bicyclic dimer (**31**) can be isolated in 93% yield when **24** is reacted with 2 equiv of water under acidic conditions. Comparable yields of the *unsaturated* bicyclic analogue are recoverable from the hydrolysis of **25** with 2 equiv of water. Importantly, the cyclic derivatives of **21**, **22**, **24**, and **25** formed from C1 and C2 carbon atom bridging groups have a reduced level of functionality.

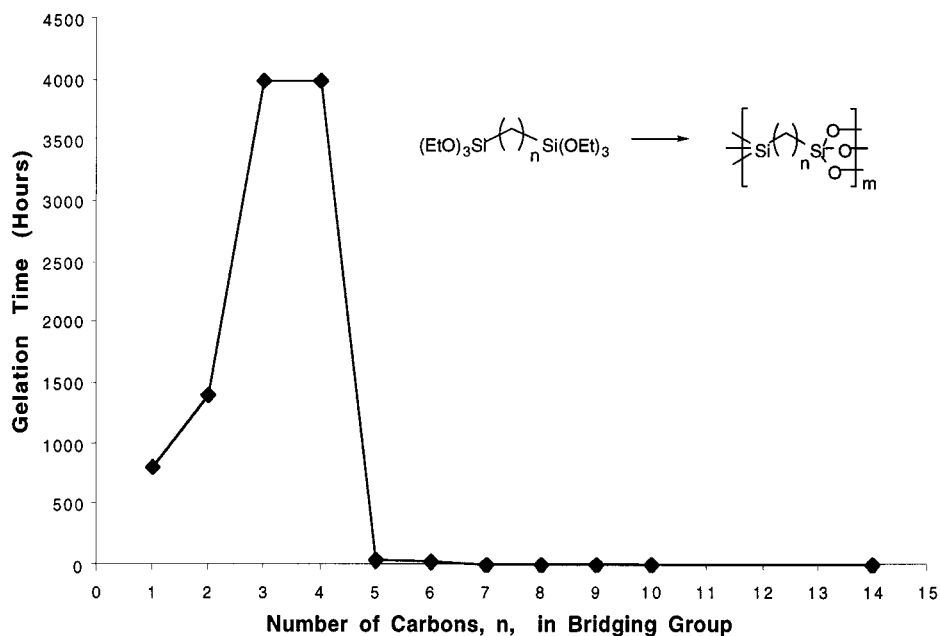
*The observation of significant populations of carbosiloxanes is an important factor in the gelation time since cyclization reduces the level of functionality and does not contribute to network formation.*<sup>21,22</sup>

In addition, some cyclics, such as the bridged bicyclic dimer (**31**) found in the ethylene-bridged system (**24**), are inherently less reactive in subsequent hydrolysis and condensation steps due to the presence of *tertiary* alkoxy-silane linkages.<sup>12d</sup> This reduced reactivity further slows the approach to gelation. Despite the reduced functionality and reactivity, gelation eventually does occur in these systems. Gelation times for the unsaturated ethenylene-bridged monomer (**25**)<sup>10</sup> are comparable to those for **24** but substantially longer than that observed for long alkylene-bridged monomers, such as **10**, under the same conditions (Table 1). The vinylidene-bridged monomer (**22**) does not gel under acidic conditions and takes 9 months to gel under basic conditions.

The observation of substantial amounts of cyclic and bicyclic carbosiloxane dimers during the early stages of polymerization is noteworthy. However, it is also important to establish the relevance of the oligomers to the final structure of the network. Substantial literature exists documenting the formation of cyclic oligomers in silica polymerization<sup>21,22</sup> and siloxane in silsesquioxane condensations. Under conditions of kinetically driven network growth, a working hypothesis is that the oligomers, including the cyclic and bicyclic structures, present during the early stages of polymerization are incorporated into the final xerogel network. In most cases this is difficult to verify since the spectroscopic “signatures” of the individual species are not unique and therefore are not resolved in the xerogel. This is a consequence of the relatively low resolution of the tools, such as solid-state NMR, for characterizing highly condensed xerogels at the chemical level. Interestingly, we have found that a number of the cyclic and bicyclic *carbosiloxane*-bridged silsesquioxane oligomers have distinct “signatures” in the <sup>29</sup>Si NMR spectrum that allow one to track the structure all the way



**FIGURE 2.** <sup>29</sup>Si NMR spectra for 1,10-bis(triethoxysilyl)decane (**12**, top) and its sol-gel solutions with 1 equiv of H<sub>2</sub>O (middle) and 2 equiv of H<sub>2</sub>O (bottom) under acidic conditions.<sup>12</sup> The two peaks downfield of the absorption from the monomer T<sup>0</sup> peak ( $\delta = -45.4$  ppm) are from hydrolysis products (silanol). Peaks from more condensed silsesquioxanes (T<sup>1</sup> and T<sup>2</sup>) appear upfield with multiple peaks due to the residual unhydrolyzed and hydrolyzed species.<sup>25</sup>

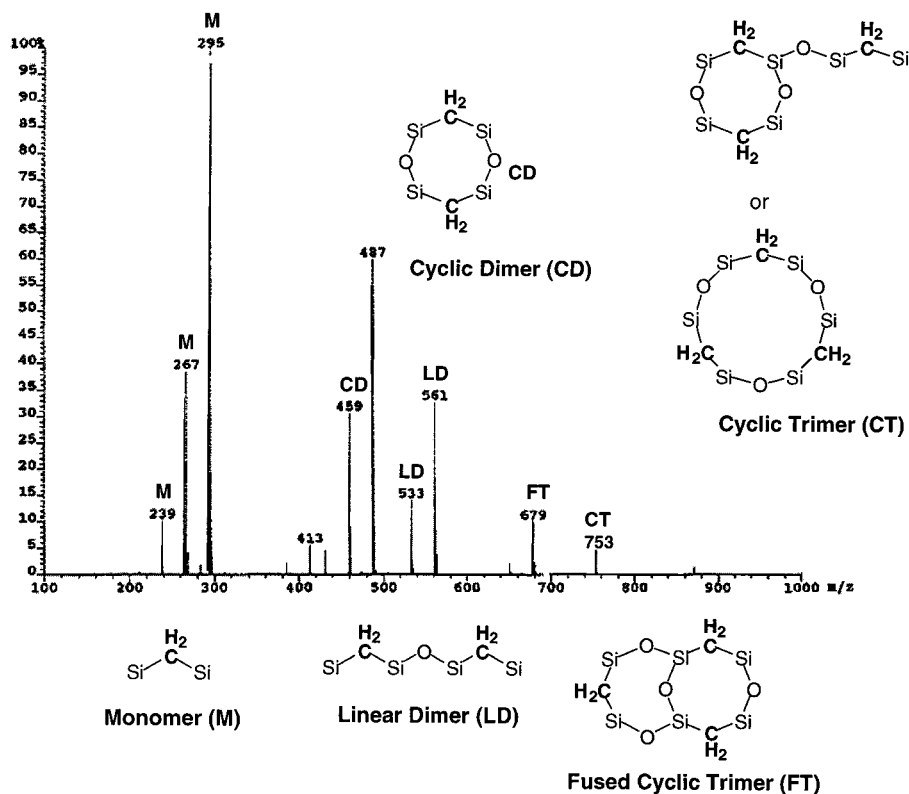


**FIGURE 3.** Graph of gelation times for alkylene-bridged polysilsesquioxanes under standard sol-gel conditions with HCl.<sup>12</sup> Under acidic conditions,<sup>24</sup> small changes in the bridging alkylene chain length produce profound changes in gel time.

through to the xerogel.<sup>12d</sup> A case in point is the bridged bicyclic silsesquioxane (**31**).

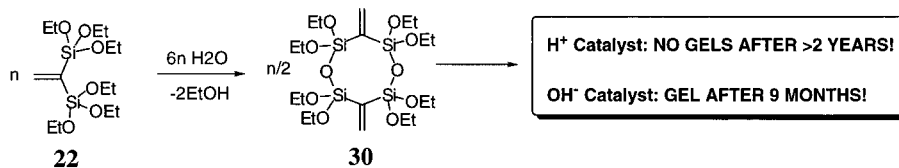
The bridged bicyclic silsesquioxane (**31**), formed from **24**, exhibits two <sup>29</sup>Si resonances at  $-50.7$  and  $-53.1$  ppm

(Figure 5). The characteristic shifts are several ppm downfield from "typical" <sup>29</sup>Si resonances found in aliphatic bridged monomers. The xerogel from the monomer (**24**) has a very atypical <sup>29</sup>Si NMR spectrum consisting of a

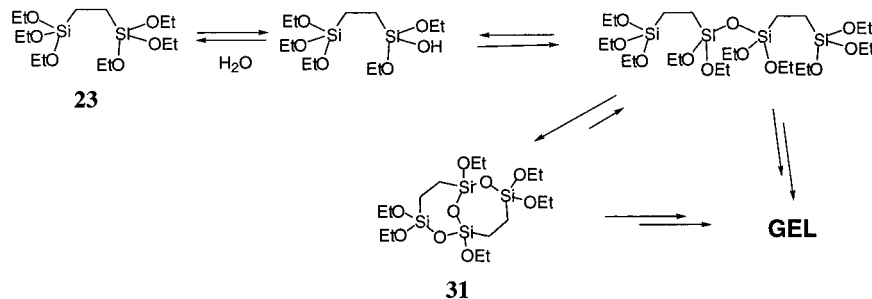


**FIGURE 4.** Chemical ionization mass spectrum of the initial stages of the acid-catalyzed sol-gel polymerization of bis(triethoxysilyl)methane (**21**). The ring size of cyclic dimers and trimers cannot be unambiguously assigned by mass spectrometry. The dominant peaks correspond to M-OEt fragmentation, a characteristic of **21** and its derivatives.

**Scheme 3.** Sol-Gel Polymerization of Vinylidene Monomer (**22**) Formed Cyclic Dimer (**30**) in Sufficient Quantities To Permit Its Isolation from Reaction Mixtures<sup>10</sup>



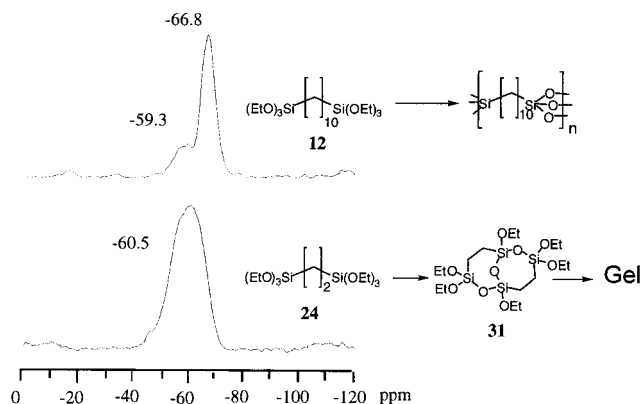
**Scheme 4.** Sol-Gel Polymerization of Monomer (**23**) Was Shown by  $^{29}Si$  NMR and Mass Spectrometry To Dimerize and Cyclize To Afford Bicyclic Dimer (**31**) as an Intermediate That Resulted in Slowing Network Growth



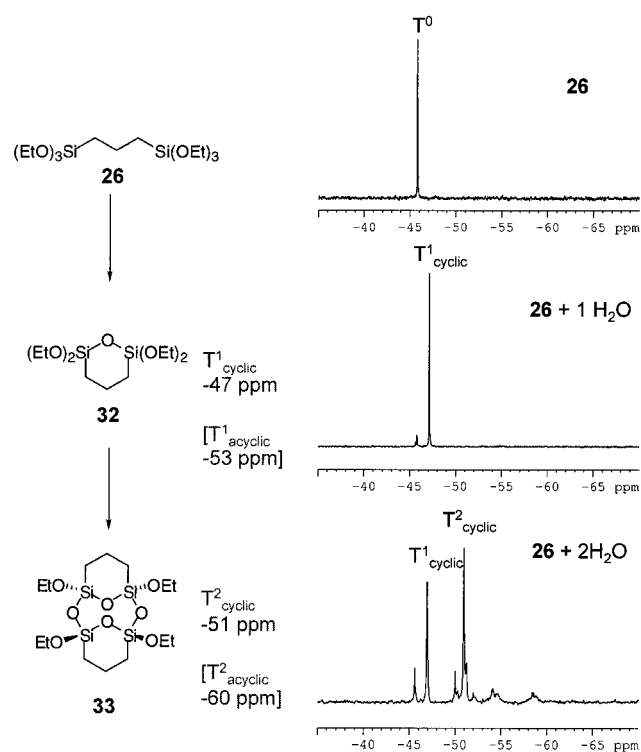
broad absorption at  $-60.5$  ppm. This peak is several ppm downfield from what would be expected for aliphatic bridged polysilsesquioxane xerogels. Compare it, for example, with the  $^{29}Si$  NMR spectrum of the xerogel from the 1,10-decylene-bridged monomer (**12**). The differences between the two spectra can be attributed to incorporation of bridged bicyclic carbosiloxane subunits into the xerogel network. Indeed, the  $^{29}Si$  NMR spectrum of a xerogel prepared from the bicyclic precursor (**31**) under basic conditions can be superimposed over that of the

spectrum obtained with the xerogel prepared from the ethylene-bridged monomer (**24**).

The spectroscopic results reveal that the early stages of the step-growth polymerization of the C1 bridged monomers (**21**, **22**) and the C2 bridged monomers (**24**, **25**) are dominated by *bimolecular* dimerization reactions to form carbosiloxanes. These cyclic dimers have reduced reactivity, slowing, but not stopping, progress toward gelation. In the case of the ethylene-bridged and the ethylene-bridged monomers, the "signature" of bridged



**FIGURE 5.**  $^{29}\text{Si}$  solid-state NMR of the dried xerogel formed from the acid-catalyzed polymerization of monomer **12** (top) and a spectrum of the dried xerogel from monomer **24** (bottom).<sup>12d</sup> The difference in the lower spectrum is attributed to incorporation of the bicyclic structure (**31**) in the dried xerogel.

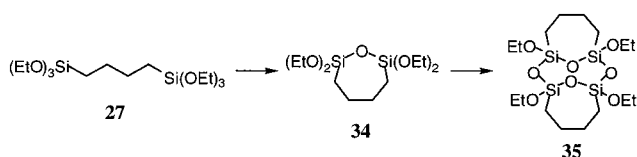


**FIGURE 6.** Solution  $^{29}\text{Si}$  NMR of monomer **26** (top) in the presence of 1 (middle) and 2 equiv (bottom) of water and acid catalyst.<sup>12d</sup> The spectra consist of almost exclusively monocyclic and bicyclic products.

bicyclics present in the dried xerogels provides evidence that the oligomers formed in the early stages of polymerization are being incorporated in the network.

**C3 and C4 Monomers.** A more dramatic effect is observed when the bridging group consists of three or four bridging methylenes. Under the standard acidic sol-gel conditions, these monomers fail to gel after 6 months!<sup>11,12</sup> This is truly remarkable when compared to a gelation time of 1 min for the 1,6-hexylene- (**10**) and 1,10-decylene- (**12**) bridged monomers (HCl/THF). How can such a small change in the monomer result in such a profound change in gelation time? The answer is in the chemistry of the sol-gel polymerization. In the presence of 1 equiv of

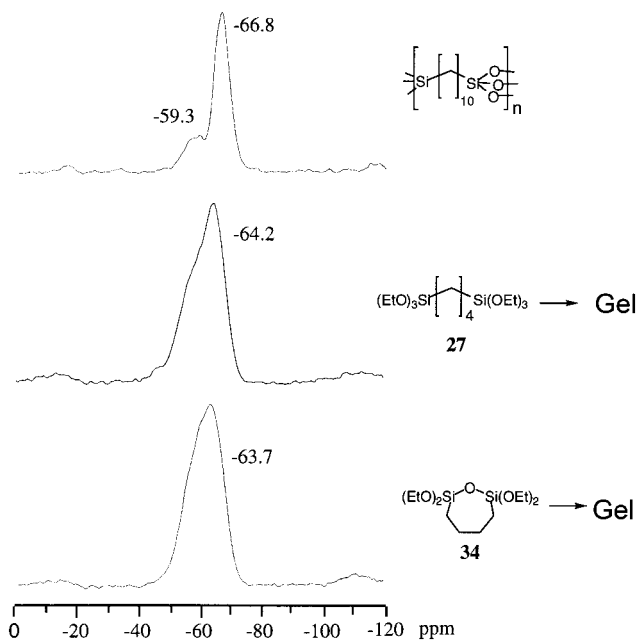
**Scheme 5.** Cyclization of **27** To Afford Seven-Membered Cyclic (**34**) and Tricyclic (**35**)



water, both the C3 and C4 monomers are rapidly siphoned off to *intramolecular* cyclization products. Indeed, both cyclization products can be prepared and isolated in >80% yield by the addition of 1 equiv of water. The mass spectra and  $^{29}\text{Si}$  NMR of these reactions are remarkably simple (Figure 6). Upon addition of a single equivalent of water to the propylene-bridged monomer (**26**), the monocyclic silsesquioxane (**32**) is formed quantitatively. Furthermore, no higher molecular weight condensation products are observed; the polymerization reaction runs into a wall.

The failure of these monomers to gel reflects the reduction in number of functional groups (6  $\rightarrow$  4) of the cyclic product and its intrinsic lower reactivity toward subsequent condensation reactions. Indeed, when a second equivalent of water is added, the sole product is the bicyclic dimer (**33**) and its hydrolysis products (Figure 6). Crystalline bicyclic dimer (**33**) can readily be isolated, and its structure has been confirmed by X-ray crystallography.<sup>12a</sup> It is important to note that these conditions (2 equiv of water) are sufficient to gel monomers with longer alkylene bridging groups (**9–13**).<sup>12d</sup>

A very similar pattern of reactivity is observed for the four-carbon-bridged monomer (**27**) (Scheme 5). Rapid and



**FIGURE 7.**  $^{29}\text{Si}$  solid-state NMR of the dried xerogel formed by the acid-catalyzed polymerization of monomer **12** (top spectra), the dried xerogel prepared by the base-catalyzed polymerization of **27** (middle spectrum), and the xerogel prepared from the base-catalyzed polymerization of the cyclic monomer (**34**) (bottom spectra).<sup>12d</sup> See text for an explanation of the differences.



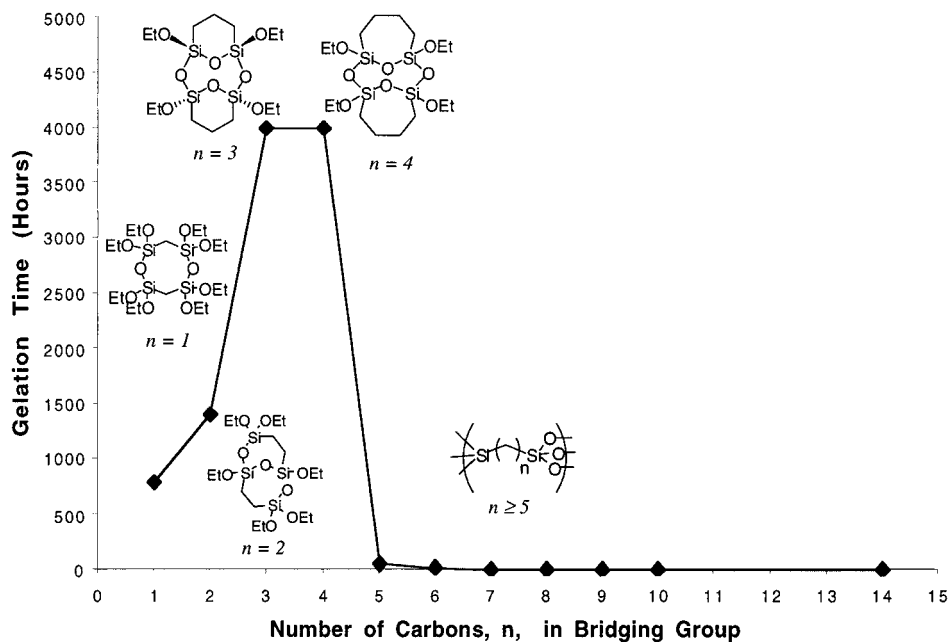


FIGURE 8. Plot of gel time of the alkylene-bridged silsesquioxane series as a function of chain length. Structures refer to the dominant species present in the polymerization reaction shortly after initiation.

almost quantitative intramolecular cyclization to produce the seven-membered cyclic carbosiloxane (**34**) is observed. This is followed by slower formation of a bridged bicyclic dimer (**35**) when the second equivalent of water is added (Scheme 5). Similarly, the (*Z*)-2-butenylene-bridged monomer (**29**) also readily cyclizes to afford the analogous unsaturated cyclic monomer and tricyclic dimer. Gelation of both butylene<sup>12</sup> and 2-butenylene systems,<sup>17</sup> when it eventually occurs (ca. 6 months or more!), produced xerogels that bear the “signature” of a bridged bicyclic. This is illustrated in Figure 7. A <sup>29</sup>Si NMR spectrum of a “typical” silsesquioxane xerogel (decylene-bridged) is shown as a reference at the top of the stacked plot. The butylene-bridged xerogel is shown immediately below, and the <sup>29</sup>Si NMR of a xerogel prepared from base-catalyzed condensation of the cyclic carbosiloxane monomer (**33**) is shown at the bottom (base catalysis was used so that experiments could be completed in reasonable amounts of time). The absorptions at approximately -60 ppm in the spectra of the xerogels derived from **27** and **34** are very similar to what would be predicted for a network comprised of bridged bicyclic units. These results provide additional support for the concept that cyclic oligomers are incorporated in the growing network.

With the identification of these cyclic and bicyclic carbosiloxane structures, it is now possible to explain the trends in gelation behavior (Figure 8). The formation of stable mono- and bicyclic carbosiloxane intermediates not only results in reduced functionality of the monomers but also lowers reactivity in subsequent condensations, particularly under acidic conditions. Shortly after the reaction begins, the structure of the monomer has been funneled to a more stable and less reactive species.

## Conclusion

The study of a homologous series of monomer precursors to bridged silsesquioxanes has uncovered striking discontinuities in gelation behavior. An investigation of the chemistry during the early stages of the polymerization has provided a molecular basis for these observations. Monomers containing from one to four carbon atoms exhibit a pronounced tendency to undergo inter- or intramolecular cyclization to form carbosiloxanes. The cyclic intermediates have been characterized by <sup>29</sup>Si NMR, chemical ionization mass spectrometry, and isolation from the reaction solution. These carbosiloxanes are local thermodynamic sinks that produce kinetic bottlenecks in the production of high-molecular-weight silsesquioxanes. The formation of cyclic carbosiloxanes results in slowing or in some cases completely shutting down gelation. An additional finding is that the cyclic structures are incorporated intact into the final xerogel. Since cyclization alters the structure of the building block that eventually makes up the xerogel network, it is expected that this will contribute importantly to the bulk properties of the xerogel as well.

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- (24) During acid-catalyzed sol–gel polymerizations, the rate of condensation becomes slower with higher degrees of condensation.<sup>21,22</sup> Thus, cyclics formed early in the sol–gel polymerization can slow gelation. Under base-catalyzed conditions, the rate remains the same or increases with condensation. Even when cyclics form, they will be incorporated into the network.
- (25)  $^{29}\text{Si}$  NMR is used to evaluate the degree of hydrolysis and condensation of silsesquioxanes.<sup>2–4</sup> The chemical environment of the silicon is succinctly described by a modified  $Q^n$  notation. In this representation (Figure 2), silsesquioxanes with one siloxane bond are denoted as  $T^1$ , those with two siloxane bonds,  $T^2$ , and those with three (not shown) as  $T^3$ . A silsesquioxane with no siloxane linkages is denoted as  $T^0$ .

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