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Formation of Cagelike Intermediates from Nonrandom Cyclization during Acid-Catalyzed Sol–Gel Polymerization of Tetraethyl Orthosilicate

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ABSTRACT: In the sol–gel synthesis of silica by the acid-catalyzed hydrolysis and condensation of tetraethyl orthosilicate (TEOS), the fractal dimension, density, and homogeneity of the gel depend strongly on reaction conditions such as the acid and water concentrations. However, ^{29}Si nuclear magnetic resonance shows that gel conversions of at least 80% are observed over a wide range of initial acid (10^{-5}–10^{-1} mol/L), water (4–22 mol/L), and TEOS (1.3–2.5 mol/L) concentrations. This is very high compared to the value predicted by random branching theory even under the worst possible negative first-shell substitution effect. Moreover, nonrandom cyclization is commonly evidenced in these systems by ^{29}Si NMR, Raman spectroscopy, and gas chromatography with mass spectroscopy. The gel conversions suggest that nonrandom cyclization reactions are strongly favored, and the development of conversions with time is consistent with the formation of compact three-dimensional cagelike intermediates. These are probably the same nanometer-scale objects shown by recent scattering and microscopy observations.

Introduction

For organic condensation polymerization, Flory's random branching theory (RBT) has been successful in predicting the gel conversion and molecular size distribution.[1-3] The inorganic condensation polymerization processes in sol–gel reactions, however, are highly nonideal. For example, RBT fails to predict gel structures of different fractal dimension (from weakly branched polymeric networks to colloidal particles) that are produced (with different acid and water concentrations) from the hydrolysis and condensation of tetraethoxysilane (TEOS) and tetramethoxysilane (TMOS).[4-7] Results from small-angle X-ray scattering (SAXS)[7] show that the fractal dimension of the gels decreases with decreasing starting water concentration and solution pH (for pH values less than 2).

A deficiency of RBT is its exclusion of cyclization, which is common in the alkoxide (silicon and alkyl-modified silicon alkoxide) systems. Four-membered rings (and, in some cases, three-membered rings) are commonly found by ^{29}Si NMR,[8-13] Raman spectroscopy,[14,15] and gas chromatography with mass spectroscopy[16,17] in sols and gels. Moreover, since even slightly larger rings would not be distinguished from other sites by these methods, probably many fairly small rings remain undetected. Note, though, that Kelts and Armstrong[10] used results from alkaline aqueous systems[18,19] to assign certain peaks in their acid-catalyzed TMOS and TEOS systems to five- and six-membered rings; they also attributed the delay in gel time in the TEOS systems to the abundance of various rings. Ling[13] speculated that the formation of the cyclic species is energetically favored[20] and the polymeric structural development occurs through the formation and subsequent connection of these species. Brunet and Cabane,[8] Himmel and co-workers,[7] and Devreux and co-workers[21] have proposed the presence of "cages", "characteristic polyhedrons", or "highly condensed primary units" in the TMOS and TEOS systems they studied. Devreux and co-workers went further to suggest that the highly condensed primary units are formed from nonrandom assembly of the TEOS monomers early in reaction. The existence of such primary units has also been suggested based on SAXS[7] and cryogenic transmission electron microscopy (TEM)[22] results. Consistent with these results, a kinetic study on the trimeric chain precursor has found that ring closure can be much faster than chain extension,[23] suggesting that cyclization is kinetically favored. Bailey and co-workers attributed to cyclization the failure in modeling the gelation of silicon alkoxides.[24]

In short, experimental results show the abundance of small rings and that ring closure is kinetically favored over chain extension in conditions typical of acid-catalyzed hydrolysis and condensation of TEOS. So, cyclization is nonrandom—there is preferred reaction between the silicon sites separated by only several siloxane bridges. This should be a short-range effect and is due to siloxane bond stability and solvent interaction.[20,25-27] This type of cyclization kinetics will deviate from RBT more severely than the random cyclization assumed in statistical models such as the percolation theory (e.g., refs 28 and 29), where loops of various sizes are formed randomly.

In this paper, we investigate how nonrandom cyclization in sol–gel polymerization can explain gelation conversion under different reaction conditions by examining conversions using ^{29}Si NMR. We attempt to bridge polymerization theory with sol–gel science, exploring the challenges to sol–gel modeling posed by selective direction of molecular architecture.

Experiments

Absolute ethanol (containing 1% by weight of paramagnetic relaxing agent chromium(III) acetylacetonate) was added to TEOS, followed by aqueous HCl solution of desired pH. TEOS and chromium(III) acetylacetonate were purchased from Aldrich, while ethanol was from Minnesota Grain Products. Deionized and distilled water was used. The samples were capped in polypropylene tubes and kept at room temperature. ^{29}Si NMR spectra were acquired on a Varian VXR500 or a GE 500 spectrometer at 99.3 MHz at room temperature. For each spectrum, 32 or 128 scans were acquired with a delay time of

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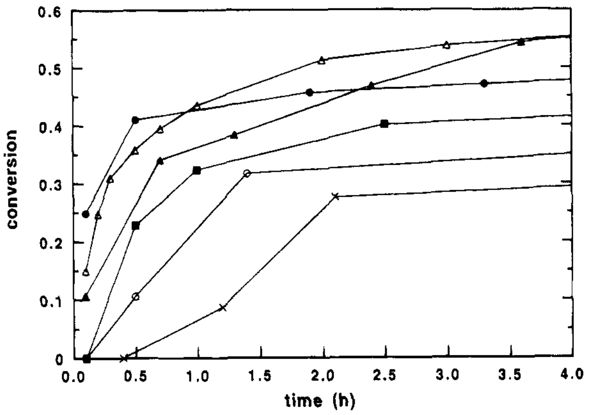

Figure 1. Hydrolysis and condensation of TEOS: early in the reaction, conversion rate varies with acid and water concentrations. Compositions (TEOS/EtOH/H_2O/HCl) are in mole/liter: (●) (a1) 2.02 / 8.11 / 4.04 / 0.012; (■) (a2) 2.02 / 8.11 / 4.04 / 0.003; (×) (a3) 2.02 / 8.11 / 4.04 / 0.001; ▲ (b1) 1.89 / 7.56 / 7.54 / 0.006; (○) (b2) 1.89 / 7.56 / 7.54 / 0.002; (△) (c1) 1.32 / 7.94 / 13.24 / 0.001 (data extracted from ref 21). (The same legends are used in Figures 2 and 3).

10 s. The background glass signal, obtained from an equal-volume sample of absolute ethanol with dissolved Cr(III), was subtracted. The ethanol sample was used to minimize change in magnetic environment which may affect the probe tuning.

Results and Discussion

1. Failure of RBT. Random branching theory (RBT) assumes that the reactivity of any functional group is independent of its neighbors and the size of its host polymer and that only intermolecular reactions are possible. Although the underlying assumptions are highly ideal, RBT works remarkably well for most organic step polymerizations to predict the average degree of polymerization and the molecular size distribution as a function of the extent of reaction and the functionality of the monomeric unit.[1-3]

For sol–gel inorganic step polymerization, however, the experimental results deviate significantly from the values predicted by random branching theory even during the initial period of reaction. An explanation that has been presumed by several groups[8,13,24,30,31] takes the form of a negative first-shell substitution effect (FSSE), which is most clearly evidenced in the following way.

According to RBT, at any extent of reaction, the monomer should always be the most abundant molecule, and the molecular size number distribution decreases monotonically with increasing size.

Unlike the prediction of RBT, though, results obtained from gas chromatography on an acid-catalyzed TEOS polymerization[8,32] show a nonmonotonic decrease in the mole fraction of x-mer. The functional groups on a monomer seem more reactive than on the larger molecules, causing monomers to be depleted more quickly than larger oligomers. This phenomenon can be explained by a negative first-shell substitution effect, whereby, for instance, the hydroxyl group on a more branched silicon is less likely to take part in condensation. By negative FSSE, we are referring to a phenomenological condition; we do not attempt to speculate the chemical or physical cause of this condition. Attempts to model the gelation (not merely early reactions[13,30,33,34]) of silicon alkoxides incorporating a negative FSSE kinetic scheme have not been successful, and cyclization was proposed as a cause for deviation.[24]

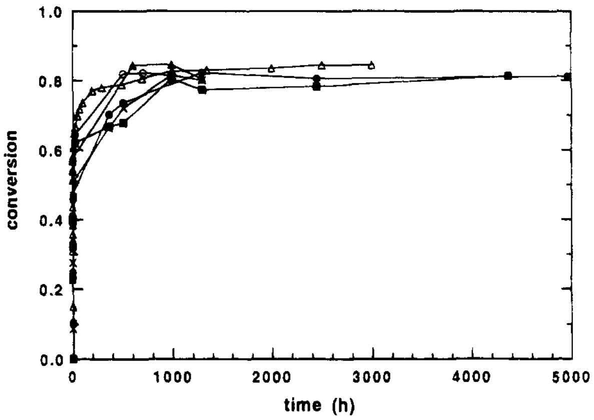

Figure 2. Hydrolysis and condensation of TEOS: later in the reaction, conversions all slow down and converge to 83%. Gel times: (a1) 5064 h; (a2) 4392 h; (a3) ≈1700 h; (b1) ≈ 1500 h; (b2) 1020 h; (c1) 1200 h.

Another nonideality in sol–gel reactions is of course that the monomers have to be hydrolyzed before they can condense, so they may have different degrees of functionality over the time of reaction, depending on the rate of hydrolysis relative to condensation. This effect will also be discussed.

2. Conversion. TEOS polymerization occurs by the formation of a siloxane bridge between two silicon atoms of valency 4, represented by

$$\mathrm{Si{-}OH} + \mathrm{XO{-}Si} \rightarrow \mathrm{Si{-}O{-}Si} + \mathrm{XOH} \qquad (1)$$

where X can be H or CH_3CH_2. The silanol groups are formed from hydrolysis of ethoxy groups. Regardless of which reaction or combination of them is responsible for producing condensation, the conversion (α) of the polymerization process, defined as the fraction of the maximum possible number of siloxane bridges (e.g., for SiO_2), can be determined from ^{29}Si NMR:

$$\alpha = \frac{1}{4}\sum_{i=0}^{4} i[Q_i] \qquad (2)$$

where $[Q_i]$ is the fraction of the silicon sites with i siloxanes bridges.

In Figure 1, we show the conversion over time for collections of systems with different initial acid, water, and TEOS concentrations. Within each collection of system (a's and b's) the initial acid concentration varies, while the water and TEOS concentrations vary over different collections of systems (a's, b's, and c's). Early in the reaction, the conversion rate is dependent on both acid and water concentrations. This is possibly a manifestation of different intermediates being formed. The overall conversion is a result of simultaneous hydrolysis, branching, and cyclization reactions, which are each influenced, to different degrees, by solution conditions. Depending on the relative rates of these reactions, which certainly vary with reaction time, the initial reactions proceed on different combination of kinetic paths, so the silicon monomeric precursor may be constructed into collections of intermediates with different architecture. For example, if cyclization is rapid compared to branching, small rings can be formed. Work is underway to investigate the kinetic paths on intermediate formation.

It is striking, though, that beyond a conversion of 60–70%, conversions of all systems slow down and converge to 83%, as shown in Figure 2. This gel conversion at

Table 1. Gelation Occurs Consistently at 83% (±2%) over a Wide Range of Initial TEOS, Water, and Acid Concentration (mol/L), Which Spans the Miscibility Region

[TEOS]	[H_2O]	[HCl]	α_g (%)[a]
2.46	9.83	0.4589	84
2.46	9.83	0.0274	83
2.46	9.83	0.0027	83
2.02	4.04	0.0035	81
1.93	7.72	0.0430	84
1.89	7.55	0.0005	81[i]
1.80	10.82	0.0020	82
1.46	8.78	0.0006	81[i]
1.43	5.72	0.0012	83
1.34	21.44	0.0134	84[iii]
1.32	13.24	0.0009	81[ii]
1.32	13.24	0.00005	82[ii]

[a] The pH of water was adjusted to (i) 2.5[21] and (ii) 4.3[35] using relaxation agents. An effective HCl concentration was calculated for each case. Data set iii: the gel was prepared at 80 °C under reflux, followed by the removal of solvents by vacuum.[36]

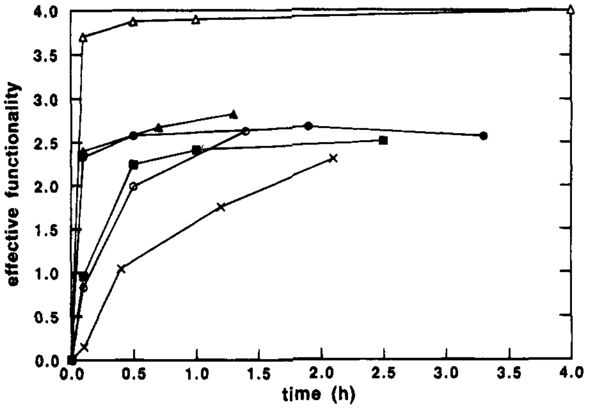

Figure 3. Concurrent hydrolysis and condensation: even if hydrolysis is incomplete initially, it continues to occur with condensation, bringing up the effective functionality to a value determined by equilibrium. Systems a2 and c1, though they differ in effective functionality (2.5 compared with 4.0), gel at 83%.

83% is observed over a wide range of reaction conditions, consistent with results analyzed from literature data,[21,35,36] as shown in Table 1. These gel conversions (α_g) are estimated to each have a deviation $\pm 0.03\alpha_g$ (based on the scattering in data set a2, $\alpha > 0.6$, shown in Figure 2) and so lie in the range of 80–85%. For the conversion measured in our group, series of spectra were obtained prior to gelation, showing insignificant changes in conversion as the liquid was approaching the gel point. The conversion at gelation (α_g) is measured for a near-gelling sol and is checked with ^{29}Si magic angle spinning (MAS) experiments. Consistent with common practice, the gel point was determined as the time at which the fluid no longer flows upon tilting of the sample tube. Since change in conversion is extremely slow near gelation, this method of determination should not affect the gel conversion measured.

As shown in Table 1, 83% gel conversion is observed for acid concentration ranges from 10^{-5} to 10^{-1} mol/L. This range of composition was studied by Klein,[37] who observed different gel times and final gel structures. Dilution (TEOS concentration ranging from 1.3 to 2.5 mol/L) and water concentration (4–22 mol/L) also have little effect on the gel conversion. This is consistent with the results obtained by Devreux and co-workers[21] showing identical distribution of silicon site connectivities at the gel point over a range of water concentration. Moveover, Vega and Scherer[36] prepared their gels at 80 °C under reflux, followed by the removal of solvents by vacuum, and still observed a gel conversion of 83%!

The consistently high 83% conversion at gelation for these gels is astonishing. First of all, this value is much higher than the 33% predicted by RBT for a monomeric unit which is capable of forming 4 linkages.[1-3]

Under negative FSSE, gelation should be delayed, but only up to a maximum of 50% conversion. Since severe negative FSSE prevents the formation of Q_3 and Q_4, gelation at worst occurs when an infinitely long chain is formed, i.e., $[Q_2] = 1$. So, gel conversion is then at worst 50%, as demonstrated by kinetic and Monte Carlo computer simulations.[24,34,38,39] Moreover, even though the FSSE condition is expected to change as the acid, water, and TEOS concentrations change, the 83% gel conversion is consistently observed for quite a wide range of these values (Table 1).

It is worth commenting that we have addressed FSSE for a four-functional monomer. It is possible that gel conversion increases due to incomplete hydrolysis so that conversion involves only low-functional monomeric unit until gelation. However, in general, the rate of acid-catalyzed hydrolysis of alkoxysilanes depends only mildly on the silicon site substituents.[40-42] Given a stoichiometric amount of water, hydrolysis tends to go to equilibrium. Hydrolysis occurs concurrently with condensation, producing a distribution of sites of different functionality. The effective functionality of the monomeric units, which can be represented by the average number of silanol groups and siloxane bridges connected to the silicon site, evolves with reaction time, as shown in Figure 3. The plateau in effective functionality indicates that hydrolysis equilibrium has been reached. It is apparent then that even if hydrolysis is incomplete initially, it continues to occur with condensation, bringing up the effective functionality to a value determined by equilibrium. Since hydrolysis equilibrium should change with reactant concentrations and temperature, the consistently observed 83% gel conversions, shown in Table 1, indicate that it plays only a minor role for the systems studied. This is supported by the observation that even though systems a2 and c1 differ in effective functionality (2.5 compared with 4.0), they both gel at 83%. Thus, initial differences in effective functionality seem to have no effect on the gel conversion. This result is supported by computer simulations which demonstrate that gel conversion is insensitive to the relative rate of hydrolysis to condensation.[34,39] Thus, although the rate of hydrolysis relative to condensation decreases with changing acid and water concentrations, as indicated by numerous ^{29}Si NMR results in the literature, it does not explain the observed high 83% gel conversion.

It might be argued that merely random cyclization might explain this universal conversion, but such an argument would be quantitatively incorrect. The argument would suggest that although monomeric units of higher effective functionality are more likely to form branch points, they are also more likely to randomly form cycles. The random cyclization effect might balance out the branching effect, and so these high-functional units might gel at similar conversion as those of lower effective functionality. However, percolation theory, which allows both statistical branching and statistical cyclization, is in qualitative agreement with RBT, predicting lower gel conversions (percolation threshold) for higher effective functionality (coordination number).[29,43,44] Random cyclization cannot have a

Table 2. Random Cyclization Leads to Slight Increase in Gel Conversion

	gel conversion from random growth	
eff functionality, f	α_g(PT) (branching and cyclization)	α_g(RBT) (branching)
3	0.5	0.5
4	0.375	0.333
5	0.3	0.25
6	0.25	0.2

strong enough effect to reverse the branching effect. Table 2 compares the gel conversion predictions from percolation theory (α_g(PT)) with those from RBT (α_g(RBT)), showing that gel conversion depends on f in the same way, being only slightly underrepresented by RBT for high f. Moreover, experimental and theoretical studies collected by Heiba[29] indicate that a three-dimensional lattice network topology can even be approximated by a Bethe lattice (an infinite tree). Monte Carlo simulation of mean-field gelation also shows only a minor effect of random cyclization.[45]

Thus, evaluations of various possible explanations for the observed 83% gel conversion point to a strong indication of preferred nonrandom cyclization occurring in the acid-catalyzed TEOS polymerization, which is supported by experimental observation of small rings and favorable ring closure kinetics. There is preferred reaction between the silicon sites beyond their first-shell neighbor over several siloxane bridge separation. Nonrandom cyclization (or selective kinetics) seems to occur early in reaction, explaining the initial rapid rise in conversion. Further reactions involve connection of these cycles, which should require a lower fraction of siloxane bridges, and can explain why conversion slows down. Strongly favorable nonrandom cyclization has been shown by the kinetics of trimeric chain closure versus chain extension.[23] As dilution is usually used to promote random cyclization, the 83% gel conversion observed over different TEOS concentrations is another indication that cyclization kinetics must be preferred.

3. Nonrandom Cyclization. A variety of ring and compact cagelike precursors have been identified by ^{29}Si NMR in aqueous potassium silicate solutions which make zeolites.[18,19,46] Thus, it is reasonable that intermediates of similar or related architecture can be formed in the acidic sol–gel systems from preferred intramolecular reactions. These intermediates are formed from different extents of cyclization, and it is instructive to examine how gel conversion is affected.

Existing polymerization models can, at best, give only a crude estimate of the effect of preferred intramolecular reactions.[1–3,34] Nevertheless, the gelation conversion can be estimated by treating different proposed ring or cagelike intermediates as f-functional random branching "monomeric" units. Nonrandom, ordered cyclization occurs early in reaction, resulting in the formation of f-functional intermediates, which then connect with each other, without further cyclization, to form a gel. After these intermediates are fomed, no more preferred cyclization is expected since this phenomenon is thought to be a two- to three-bond effect,[20,25–27] and RBT should be quite accurate even with random cyclization. Surely, this situation is idealized since clearly a variety of intermediates are formed. Nevertheless, it is instructive to test if this model can approximate the effect of nonrandom cyclization suggested by experimental observations. In the following set of calculations, a cyclic intermediate is considered an f-functional "monomeric" unit, T_0 (see Figure 4), for random branching. In general, the conversion from random branching of f-functional "monomeric" units, T_0, is given by

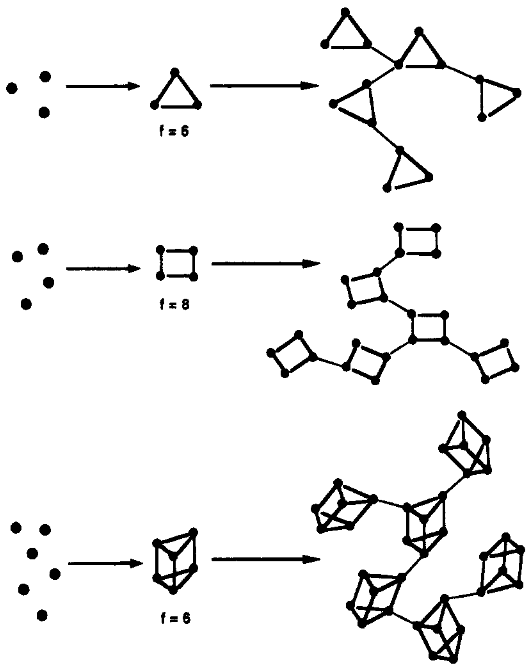

Figure 4. Nonrandom cyclizations arrange initial monomers into cyclic intermediates which then connect with each other as new precursors of functionality f.

$$\alpha_{(T)} = \frac{1}{f}\sum_{i=0}^{f} i[T_i] \tag{3}$$

where $[T_i]$ is the fraction of T-unit with i interprecursor bridges. The total fraction of siloxane bridges, which includes the intramolecular bonds within the cyclic precursor, is

$$\alpha = \frac{1}{2}\left\{\frac{f\alpha_{(T)}}{2S} + \frac{C}{S}\right\} \tag{4}$$

where S = number of Si sites per T-unit and C = number of intramolecular bonds per T-unit. Gelation conversion from random branching of the T-units is given by RBT to be (note: contribution of random interprecursor cyclization is neglected)

$$\alpha_{(T)g} = \frac{1}{f-1} \tag{5}$$

Thus, the total fraction of siloxane bridges at gelation, including bonds formed in the creation of the cyclic precursors from silicon monomers, is

$$\alpha_g = \frac{1}{2}\left\{\frac{f}{2S(f-1)} + \frac{C}{S}\right\} \tag{6}$$

Figure 5 shows the calculated gel conversion for intermediates varying in extent of cyclization. All of these intermediates have been detected in aqueous potassium silicate solutions.[18,19,46] As one moves from planar to cagelike intermediates, one increases the number of bonds involved in cycles, so gelation occurs at higher conversion merely because of an increase in C/S. Among the cagelike intermediates, smaller (more compact) ones tend to gel at higher conversion merely

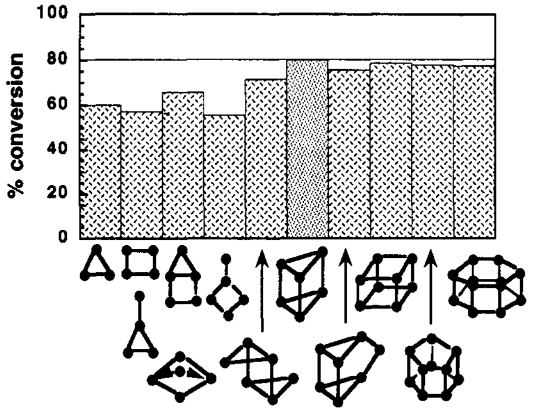

Figure 5. Gel conversion from random branching of cyclic precursors: 80% conversion can only be reached starting from the most compact cagelike precursor.

because of lower functionality. Comparing the larger double rings (D4R, D5R, D6R, using the symbol in zeolite science) with the double three-membered ring (D3R), the functionality of the intermediate decreases as the size shrinks, increasing the gel conversion. This result suggests that gel conversion reaches a maximum value as the intermediate becomes more compact. Equation 6 shows that a "compact" cyclic intermediate is one which contains (a) more intramolecular bonds per silicon site, maximum C/S, and (b) lower functionality per silicon site for branching, maximum ($f/[S(f-1)]$).

Notice that the observed 83% gel conversion is high even with nonrandom cyclization and that only the most compact structure considered here (with lowest functionality for branching), the D3R intermediate, gels at 80% conversion. Should we consider even more compact cyclic precursors? No. The only structure that might be more compact than D3R is if four silicons are involved in a three-dimensional framework, e.g., a tetrahedron. However, the experimentally observed O−Si−O bond angle ranges from 98 to 122°, while the more flexible Si−O−Si bond angle can range from 120 to 180°.[26] Even with the most strained O−Si−O and Si−O−Si bonds, the four-silicon, three-dimensional framework should be impossible to build and has never been observed.

We proposed only that the D3R structure is a typical intermediate. It is expected that other cagelike intermediates are also present in the solutions. Recall that we have postulated random branching among the typical intermediates. Normally, relaxing this assumption (allowing a minor role of random cyclization and possible steric effects) would allow somewhat less compact, of higher functionality, typical intermediates to play a role as well. Note that if a D3R intermediate exists, we have underestimated the gelation conversion. A silicon Q_3 site that is involved in the D3R precursor will, because of bond strain, produce a peak close to the region for planar Q_2 sites.[19] It is possible that the 83% measured gel conversion was actually a lower limit.

The Si−O bond length has been measured in silicate structures to be between 1.57 and 1.72 Å.[26] This gives the longest dimension in the D3R structure to be about 4.5 Å. Including the alkoxy or silanol groups, the longest dimension should be around 10 Å. This length scale is of the same order of magnitude as that of the "primary particles" detected in a collection of acid-catalyzed TEOS sol−gel polymerization systems by SAXS and TEM.[7,22]

Conclusions

In the acid-catalyzed hydrolysis and condensation of tetraethyl orthosilicate (TEOS), gelation is observed by ^{29}Si NMR to occur at 83% conversion over a wide range of initial reaction conditions which should yield gels of various fractal dimension, density, and homogeneity. Initial reaction conditions seem to have little effect on the final gel conversion. Moreover, the 83% conversion is much higher than the 33% predicted by random branching theory and the 50% even under the worst negative first-shell substitution effect. Initial differences in effective functionality have no effect on the gel conversion, consistent with results from kinetic and Monte Carlo simulations. Dilution and elevation of temperature have shown no effect on the final gel conversion, suggesting very favorable cyclization kinetics, consistent with the literature results on trimeric chain closure kinetics. Merely random cyclization cannot explain the observed 83% gel conversion. Moreover, abundant literature results show the presence of small rings in these systems. These results indicate that cyclization is nonrandom—there is preferred reaction between the silicon sites separated by only several siloxane bridges. Nonrandom cyclization (or selective kinetics) seems to occur early in reaction, explaining the initial rapid rise in conversion. Results from gel conversion calculation based on a collection of typical intermediates varying in the extent of cyclization lead us to speculate the formation of a typical cagelike intermediate with diameter around 10 Å, consistent with results from SAXS and TEM.

We conjecture, in agreement with other researchers,[7,21,22] that primary units of nanometer length scale are formed by nonrandom cyclization and further polymerize with each other to form a gel. These primary units are compact cagelike intermediates and exist over a wide range of acid (10^{-5}−10^{-1} mol/L), water (4−22 mol/L), and TEOS (1.3−2.5 mol/L) initial concentrations. On a micron scale, these reaction conditions have been observed to result in different polymer growth patterns.

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