Self-Diffusion Coefficients of Sol-Gel Intermediates

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Sol-gel techniques have shown great potential for producing ceramic materials of designed composition and properties. A typical sol-gel process involves the hydrolysis and polymerization of one or more metal alkoxides in an alcohol solution in a batch reactor to form a homogeneous gel, which is then further treated to provide the type of ceramic desired (such as aerogel, glass, crystal, and coating). Several authors have suggested that diffusion effects may influence the development of the gel microstructure. We investigate what governs the diffusivity of the precursors using the pulsed-gradient-spin-echo NMR technique. This initial report focuses on the early stages of the batch reaction.

The system chosen is the acid catalyzed hydrolysis and condensation of tetraethyl orthosilicate in ethanol. ^1H *PGSE NMR and* ^{29}Si *NMR show that the diffusivities of the silicate precursors are strong functions both of the molecular weight and of hydrogen bonding between the polar functional groups and the solvent. Moreover, since hydrolysis increases and polymerization reduces the concentration of these polar groups, the mobility of the reactive oligomers changes in a complex manner. Combining our results from PGSE NMR and gas chromatography, we estimate the extent of hydrogen bonding effect on the mobility of various oligomers, providing a model to predict diffusivity trends throughout the batch reaction.*

Introduction

The hydrolysis and condensation of TEOS in alcohol constitute one of the most extensively studied systems in sol-gel synthesis. Previous work has focused on the reaction mechanisms, the kinetics, the structure and mechanism of growth, and the effects of processing parameters (for an excellent review, see Brinker and Scherer, 1990). Typical reactions are:

Hydrolysis

$$(EtO)_3Si\text{-}OEt + H_2O \rightarrow (EtO)_3Si\text{-}OH + EtOH \qquad (1)$$

Condensation

$$(EtO)_3Si\text{-}OEt + HO\text{-}Si(OEt)_3 \rightarrow (EtO)_3Si\text{-}O\text{-}Si(OEt)_3 + EtOH \qquad (2)$$

$$(EtO)_3Si\text{-}OH + HO\text{-}Si(OEt)_3 \rightarrow (EtO)_3Si\text{-}O\text{-}Si(OEt)_3 + H_2O \qquad (3)$$

where Et represents CH_2CH_3. The reactions above represent only a few generic reactions. The entire sol-gel synthesis process involves many reactants and products ranging from monomers to large polymers, each with various degrees of hydrolysis.

X-ray scattering studies (Brinker et al., 1984; Himmel et al., 1990; Schaefer and Keefer, 1984, 1986) have shown that, depending on processing conditions (such as type of catalyst and water concentration), the condensation reactions can lead to radically different gel structures—from colloidal particles to weakly branched polymeric networks. Results obtained by Himmel and coworkers (1990) show that the fractal dimension of the gels decreases with decreasing starting water concentration and solution pH (for pH values less than 2). Consistent with other results (Brinker et al., 1984; Schaefer and Keefer,

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1984), gels produced with low water concentration at low pH were found to be weakly branched.

Computer simulations (see references in Brinker and Scherer, 1990; Himmel et al., 1990; Schaefer and Keefer, 1986) on the growth of fractal objects have shown that the fractal dimension can depend on the nature of the growth process (such as particle-cluster vs. cluster-cluster growth) and the rate-determining step (such as reaction-limited vs. diffusion-limited). Comparing their results with computer simulations, Himmel and others suggest that the weakly branched gel produced from the hydrolysis and condensation of TEOS (tetraethyl orthosilicate) with low water concentration and solution pH is a result of a diffusion-limited growth process.

Pouxviel and Boilot (1987) have found that even though initially the system with water-to-silicon molar ratio (r_W) of 10 showed faster hydrolysis rate and higher degree of condensation than the system with $r_W = 4$, the former takes about twice as long to gel. To explain this apparent inconsistency in kinetic behavior, they speculate that the growth process changes from kinetic- to diffusion-controlled as the polymers become sufficiently large, at which point the diffusion-controlled growth is then faster for the system with smaller polymers ($r_W = 4$). Colby and coworkers (1988) compared the gel time of an HCl-catalyzed TEOS system with a similar TMOS (tetramethyl orthosilicate) system and found that the apparent activation energy for gelation was higher for the TEOS system. The difference was attributed by these workers to the effects of diffusion.

The origin of different gel structures is still not well understood. In particular, it is not clear how diffusion limitations can play a role in the microstructural development of the gels. By understanding factors controlling diffusion, it is possible to engineer the properties of sol-gel-derived materials. In this work, we investigate the factors that govern the mobility of intermediates. It is to be expected that changes in diffusivity might be more complicated than in ordinary polymer solutions since molecular weight, solvent polarity, and polymer group polarity are changing simultaneously in a batch reactor.

Experiments

Preparation of the TEOS reaction mixture

TEOS and absolute ethanol (both used as purchased from Aldrich and Minnesota Grain Products, respectively) were mixed slowly for 20 s. Aqueous acid solution was added, with vigorous stirring, for 1 min to yield a solution with the molar composition TEOS:EtOH:H_2O:HCl = 1:4:0.8:0.0008 (the selection of this system will be discussed later). The sample was kept at room temperature and remained clear over the reaction times studied (from 1 h to 27 d). Samples were prepared with a range of reaction times and were analyzed together on the same day so that signal intensities could be compared quantitatively between spectra without variations introduced by probe tuning, magnet shimming, and so on. Three separate sets of data were obtained to estimate the reproducibility of the diffusion results.

^1H and ^{29}Si NMR

^{1}H spectra were obtained on a Nicolet NT300 at 300 MHz and ^{29}Si spectra on a Varian VXR500 at 99.3 MHz. Chromium (III) acetylacetonate was used as a paramagnetic relaxing agent to reduce the T_1 of ^{29}Si to about 2.5 s. For each ^{29}Si spectrum, a total of 1,024 scans separated by a relaxing delay of 3 s and a line-broadening of 1.0 Hz were employed. To check if the fast relaxation delay affects the quantitative nature of the spectra, we compared the integrated peak intensities of these spectra with those where an ample relaxation delay of 12 s was used; we have found no significant difference.

PGSE NMR experiment

The pulsed-gradient-spin-echo NMR technique is used to determine the self-diffusion coefficient of intermediate oligomers. The technique involves labeling the positions of nuclei by applying a magnetic field with a spatial gradient. It is a nonintrusive method and ideal for probing the thermal motion of chemical species. The technique is standard for studies in polymer solutions and melts (Blum, 1986; Boss et al., 1967; McCall et al., 1963; von Meerwall, 1983) and emulsions (Stilbs, 1987). Detailed descriptions of the PGSE NMR technique can be found in several sources (Blum, 1986; Callaghan, 1984; Stilbs, 1987; von Meerwall, 1983), which explain that the self-diffusion coefficient, D, of a chemical species is related to its NMR signal intensity, S, by the following equation (Blum, 1986):

$$S = S_o \exp(-2\Delta/T_2) \exp(-\gamma^2 G^2 \beta D) \tag{4}$$

where

$\beta = \delta^2(\Delta - \delta/3)$,
T_2 = spin-spin relaxation time constant
G = field gradient strength, Tesla·cm^{-1}
Δ = diffusion observation time
δ = duration of the pulsed gradient
γ = nucleus gyromagnetic radio, rad·Tesla^{-1}·s^{-1}

Since NMR signal is additive, the signal intensity contributed by n type of oligomers of different diffusivity D_j becomes (von Meerwall, 1982):

$$S = S_o \sum_{j=1}^{n} f_j \exp(-2\Delta/T_{2,j}) \exp(-\gamma^2 G^2 D_j \beta) \tag{5}$$

where f_j is the mole fraction of the resonating nuclei.

PGSE experiments were performed on a Nicolet 300 MHz NMR spectrometer with parameters:

Δ = 100 ms
δ = 0.4 to 5.4 ms
$G \approx 15$ Gauss/cm = 0.15 Tesla/m

For self-diffusion coefficients in the order of 10^{-5} cm^2/s, an observation time of $\Delta = 100$ ms is recommended (*Nicolet NMC 1180 Manual*, 1987). This corresponds to a root-mean-square displacement of:

$$\sqrt{\langle (\mathbf{r} - \mathbf{r}_0)^2 \rangle} = \sqrt{6D\Delta} \approx 20\mu \tag{6}$$

The field gradient strength was calibrated using benzene at 25°C (2.28×10^{-5} cm^2/s). For each self-diffusion measurement, 10 to 26 values of δ were used, holding Δ constant. The signal intensity, S, corresponding to the lowest β value was normalized to 100. The self-diffusion coefficients D_j of the silicate oligomers were found by combining results from PGSE NMR and gas chromatography which give the mole fractions f_j.

Gas Chromatography

An experimental study of molecular motion in a multicomponent system must include the identification of various molecules and the determination of their concentrations. These molecules are the various silicate oligomers (such as monomers, dimers, and trimers), the distribution of which cannot be accurately determined solely by NMR. Combining data from gas chromatography and ^{29}Si NMR, though, we were able to separate and identify the silicate oligomers. These techniques have been used by other investigators (Klemperer et al., 1988; Klemperer and Ramamurthi, 1988; Wheeler, 1988) for studies on the hydrolysis and condensation of TMOS.

Flame ionization detection was effective in detecting and quantifying hydrocarbon-containing molecules (David, 1974). It has been referred to as a carbon-counting device since the response factor for a molecule is approximately proportional to the number of carbon it contains (comparison of GC-FID peak intensities with ^{29}Si NMR results showed that the approximation is reasonable). We were able to quantify the molecular size distribution using this technique since our system does not contain completely hydrolyzed silicates, as verified by ^{29}Si NMR.

The GC-FID used was a Hewlett Packard HP 5890 series II. A 10 m × 0.53 mm ID fused silica capillary column bonded with 50% phenyl and 50% methyl-polysiloxane, film thickness 2.0 μm (Hewlett Packard model HP-17), is employed using helium as carrier gas. The operating conditions following (Klemperer et al., 1988) were:

Injector temperature = 300°C
Detector temperature = 300°C
Oven temperature program:
  60°C for 1 min
  15°C/min to 150°C
  5°C/min to 260°C
  260°C for 1 min
Column flow rate = 22 mL/min

Results and Discussions

Selection of composition

A typical proton NMR spectrum for the reaction mixture is shown in Figure 1a. Note that because of fast chemical exchange, the (-OH) peak is a mole-weighted average of the signals from the protons of water, the hydroxyl groups on ethanol and silanols. The phenomenon of fast chemical exchange occurs because the nuclei are rapidly exchanging between various molecular sites, with respect to the NMR detection time. As the exchange slows down, the individual peaks will be resolved. This effect can be seen on a ^{1}H spectrum of a mixture of TEOS, ethanol and water (Figure 1b). The exchange slows down without the acid, which catalyzes proton exchange (Becker, 1969). Note that a ^{1}H spectrum (Figure 1c) with higher water concentration confirms the water peak identification. High water concentration promotes proton exchanges, as shown by the collapse of ethanol hydroxyl triplet.

Another feature of the ^{1}H spectra is that protons on all silicon-bonded ethoxy groups resonate at virtually the same frequency. This means that various silicate species, such as monomers and dimers cannot be differentiated through the proton signals on the NT300 (a 300 MHz spectrometer). [Overlapping of the signals on a 270 MHz spectrometer had been reported by McGrath and coworkers (1988) (our experience with a 500 MHz spectrometer is also similar). Results of previous workers and ours are inconsistent with those reported by Turner and Franklin (1987) who used a 90 MHz Bruker.] Moreover, the methyl signal on the silicate overlaps with that on the ethanol. Since the (-SiO-CH_2) signal is the only one available for the labeling of various silicate species, the self-diffusion coefficient measured is an average of all ethoxy-containing silicates. To preserve this signal for the PGSE experiments, we are restricted to systems with low concentration of water because, when present in high concentration, water promotes hydrolysis which replaces the ethoxy groups, as shown

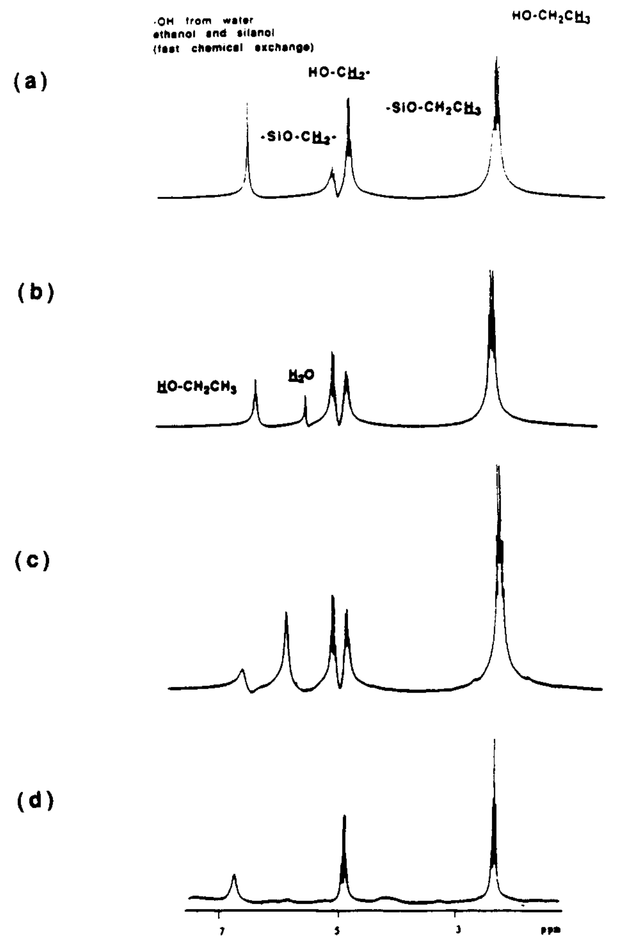


Figure 1. ^{1}H NMR spectra (ref. TMS).

(a) Molar ratio TEOS: EtOH:H_2O:HCl = 1:4:0.8:0.0008; reaction time = 655 h. (b) Molar ratio TEOS:EtOH:H_2O = 1:4:0.8; the spectrum was obtained within about 0.5 h; no reaction could have occurred appreciably. (c) Molar ratio TEOS:EtOH:H_2O = 1:4:4; the spectrum was obtained within about 1 h; no reaction could have occurred appreciably. (d) Molar ratio TEOS:EtOH:H_2O:HCl = 1:4:4:0.0005; reaction time = 26 h; high water concentration results in significant extent of hydrolysis, and thus the disappearance of silicon-bonded ethoxy signals.

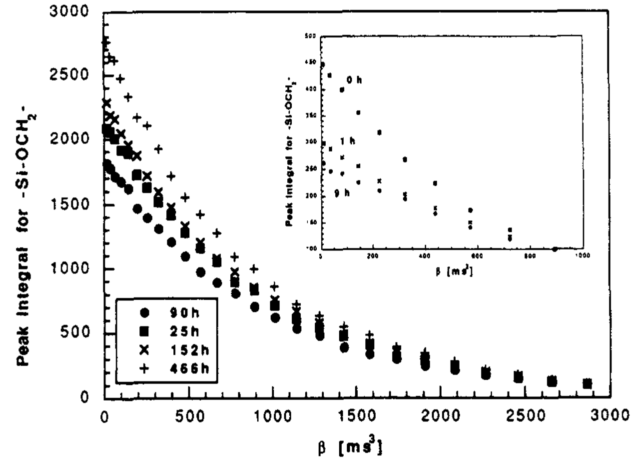


Figure 2. ^{1}H PGSE NMR results showing the decay of the NMR peak intensity of (-Si-OCH$_2$-) with β at different reaction times.

Molar ratio TEOS:EtOH:H$_2$O:HCl = 1:4:0.8:0.0008. For comparison ($t = 0$ h), measurement was also made on a system with composition TEOS:EtOH:H$_2$O = 1:4:0.8. No reaction could have occurred since diffusion measurement was taken within 0.5-1.0 h after mixing.

in Figure 1d. These systems also tend to yield weakly-branched polymers which, simulations suggest, are formed by a diffusion-limited process. Further work is underway using "tagging" silylation technique.

Self-diffusion of silicate intermediates

As TEOS undergoes condensation polymerization, the fraction of silicon-bonded ethoxy groups belonging to large molecules increases. Thus, the NMR peak intensity of the ethoxy groups (S) should decay slower with β as reaction progresses, provided if the oligomer diffusivity is a function of molecular weight only. Repeated PGSE NMR experiments have shown that the decay rate drops initially. However, rather than continuing to decrease, the decay rate stays constant, and, late in reaction, increases! Figure 2 shows a few typical decay curves of S vs. β. This anomaly suggests that there are factors other than the molecular weight which determine the silicate oligomers diffusivity.

Effect of molecular weight

^{29}Si NMR. To reveal other factors affecting the mobility

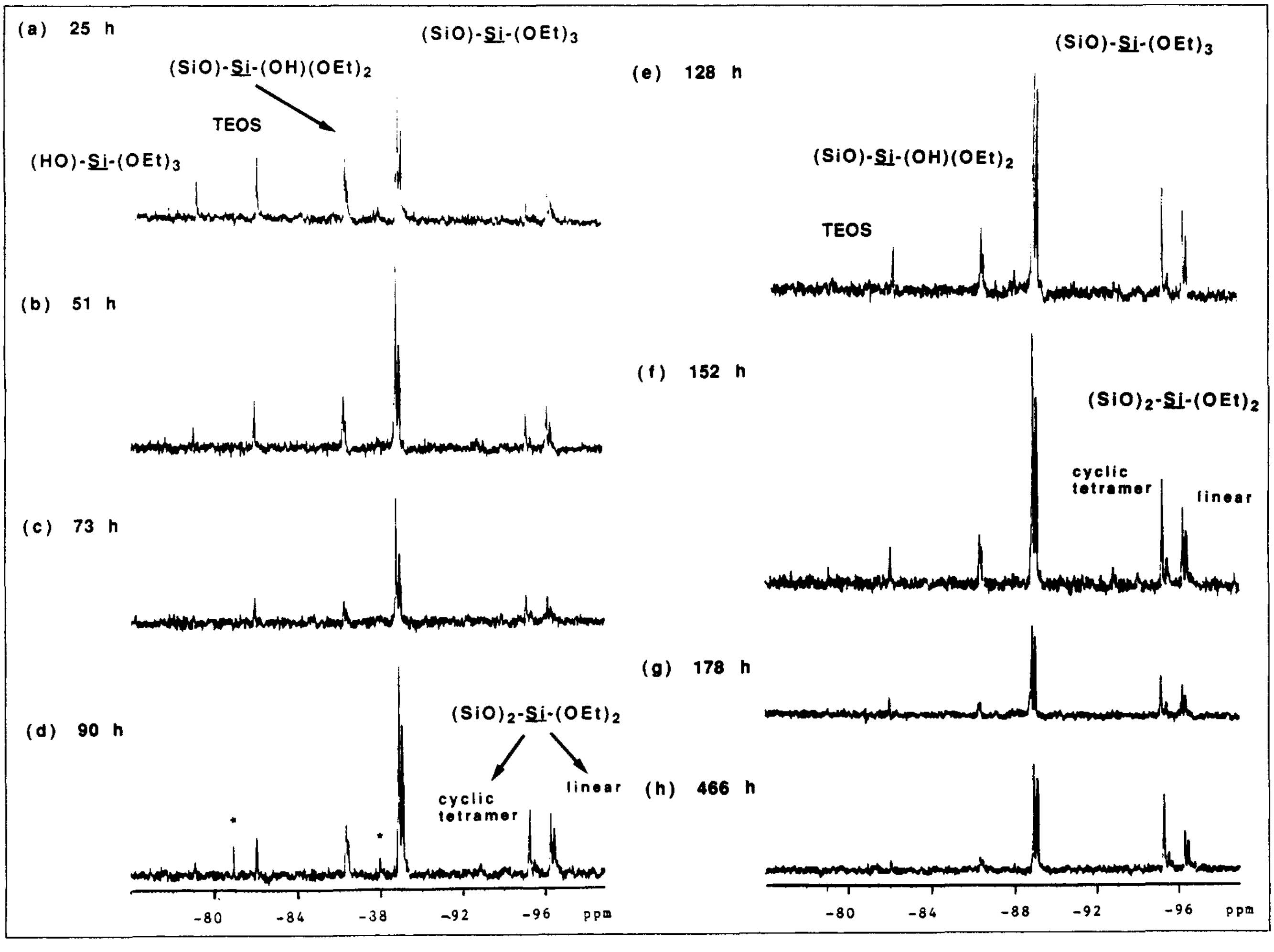
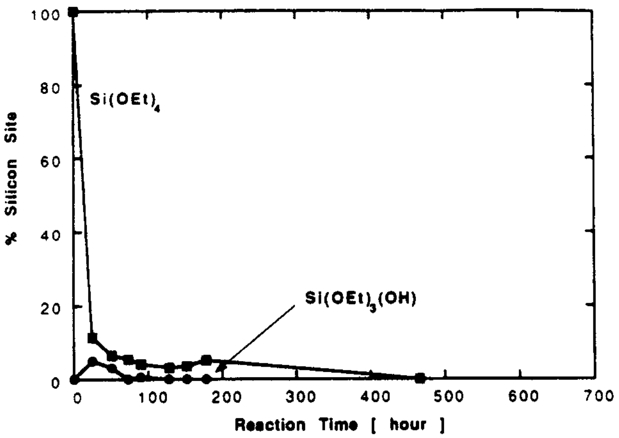


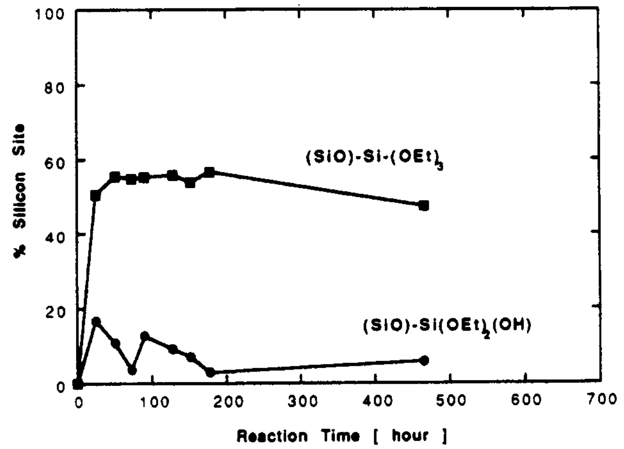
Figure 3. ^{29}Si NMR spectra (ref. TMS) for TEOS reaction mixture.

Molar ratio for this and the following systems, unless stated otherwise, is TEOS:EtOH:H$_2$O:HCl = 1:4:0.8:0.0008.
(d) Resonances at −81 and −88 ppm each are comprised by one data point in the nonlinebroadened spectrum and so are artifacts (indicated by asterisks).

(a) unsubstituted silicon



(b) monosubstituted silicon



(c) disubstituted silicon

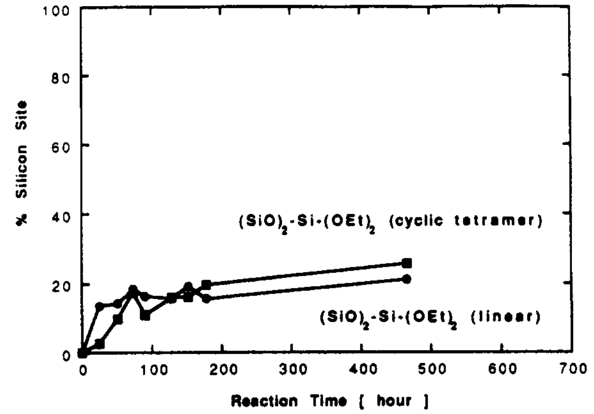


Figure 4. Time evolution of silicon species as detected by ^{29}Si NMR.

of the silicates, ^{29}Si NMR is used. The peak assignments for the ^{29}Si NMR spectra in Figure 3 follow those reported in the literature (Kelts and Armstrong, 1989; Pouxviel et al., 1987; Turner and Franklin, 1987). The chemical shifts of commercial products TEOS and ethyl polysilicates are known. The latter exhibits three lines corresponding to the end, middle and trisubstituted groups. In addition, since a hydroxyl substituent on the silicon nucleus is more electron-withdrawing than an ethoxy substituent, a shift of +2.5 ppm for each replacement of an ethoxy group by a hydroxyl group has been shown (Turner and Franklin, 1987). The assignments of the unhydrolyzed middle-group silicon in a cyclic tetramer (approximately −95 ppm) and a linear oligomer (approximately −96 ppm) follow the results obtained by Marsmann and coworkers (1983). The strained bond-angle in a cyclic tetramer causes a slight deshielding effect. This trend is also observed by Harris and Knight (1983) who identified the ^{29}Si chemical shifts of the silicate ions in alkaline aqueous potassium silicate solutions. The multiplets for (SiO)-$\underline{\text{Si}}$-(OH)(OEt)$_2$, (SiO)-$\underline{\text{Si}}$-(OEt)$_3$ and linear (SiO)$_2$-Si-(OEt)$_2$ sites are due to the variety of different environments of the adjacent silicon. Hydrolysis of the adjacent silicon causes deshielding, while substitution on this silicon causes shielding (Kelts and Armstrong, 1989).

It can be seen from the ^{29}Si NMR spectra (Figure 3) that all the silicons are linked to ethoxy groups, so that they are accounted for in the diffusion and GC-FID measurements. To examine the evolution of different silicon sites, the peaks are integrated and the intensities plotted against reaction time in Figure 4.

From Figure 4, it appears that, between 0 and 20 hours, a high concentration of the monohydrolyzed monomers [Si(OEt)$_3$OH)] is formed and quickly condensed, resulting in high concentration of endgroups (SiO)-Si(OEt)$_3$. A combination of hydrolysis and condensation also results in (SiO)-Si(OEt)$_2$(OH). These hydrolyzed endgroups undergo further condensation, leading to the disubstituted silicons [(SiO)$_2$-Si(OEt)$_2$]. The liberated water hydrolyzes the remaining endgroups, resulting in further condensation. The reactions can be represented as (R can be Et or H):

$$\text{Si(OEt)}_4 + \text{H}_2\text{O} \rightarrow \text{(HO)-Si-(OEt)}_3 + \text{EtOH} \quad (7)$$

$$\equiv\text{Si-OR} + \text{HO-Si-(OEt)}_3 \rightarrow \equiv\text{Si-O-Si(OEt)}_3 + \text{ROH} \quad (8)$$

$$\equiv\text{Si-OR} + \text{(HO)}_2\text{-Si-(OEt)}_2 \rightarrow \equiv\text{Si-O-Si(OH)(OEt)}_2 + \text{ROH} \quad (9)$$

$$\equiv\text{Si-O-Si(OH)(OEt)}_2 + \text{RO-Si}\equiv \rightarrow (\equiv\text{Si-O})_2\text{-Si(OEt)}_2 + \text{ROH} \quad (10)$$

When the concentration of water and silanols drop (time > 200 h), the rates of hydrolysis and condensation should become comparable. Consequently, as shown by the following equations, the concentration of silanol decreases only slowly:

$$\equiv\text{Si-OH} + \text{HO-Si}\equiv \rightarrow \equiv\text{Si-O-Si}\equiv + \text{H}_2\text{O} \quad (11)$$

$$\equiv\text{Si-OEt} + \text{H}_2\text{O} \rightarrow \equiv\text{Si-OH} + \text{EtOH} \quad (12)$$

It is clear from Figure 4 that condensation continues throughout the experiments, as shown by the increase in concentration of the disubstituted silicon groups and by the decreasing proportion of (SiO)-$\underline{\text{Si}}$(OEt)$_2$(OH). Since the (SiO)-$\underline{\text{Si}}$(OEt)$_3$ sites are present in much higher concentration than the (SiO)-$\underline{\text{Si}}$(OEt)$_2$(OH) sites, the condensation observed here will most likely result in short chain oligomers (chances of

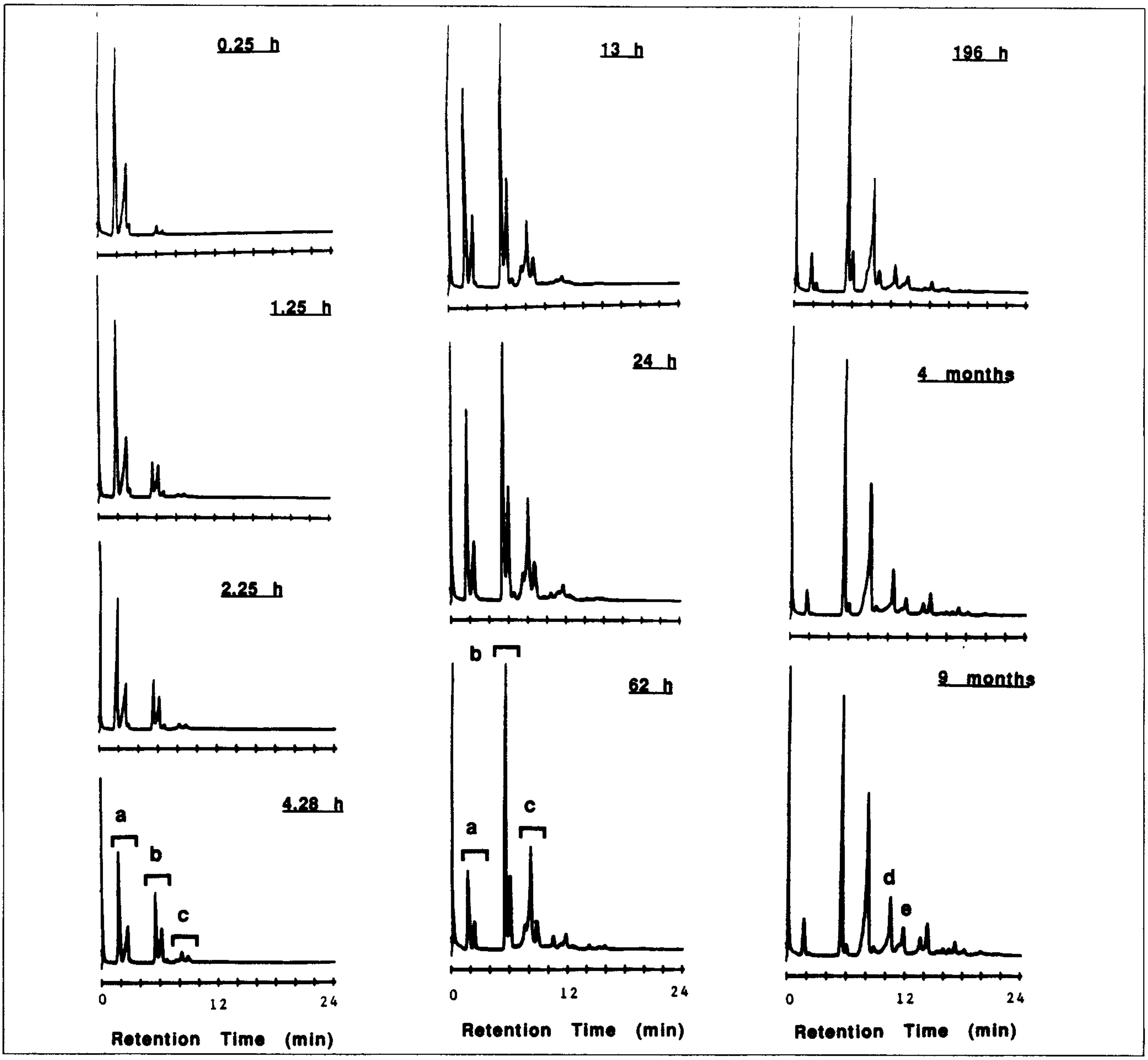


Figure 5. Gas chromatograms for TEOS reaction mixtures.

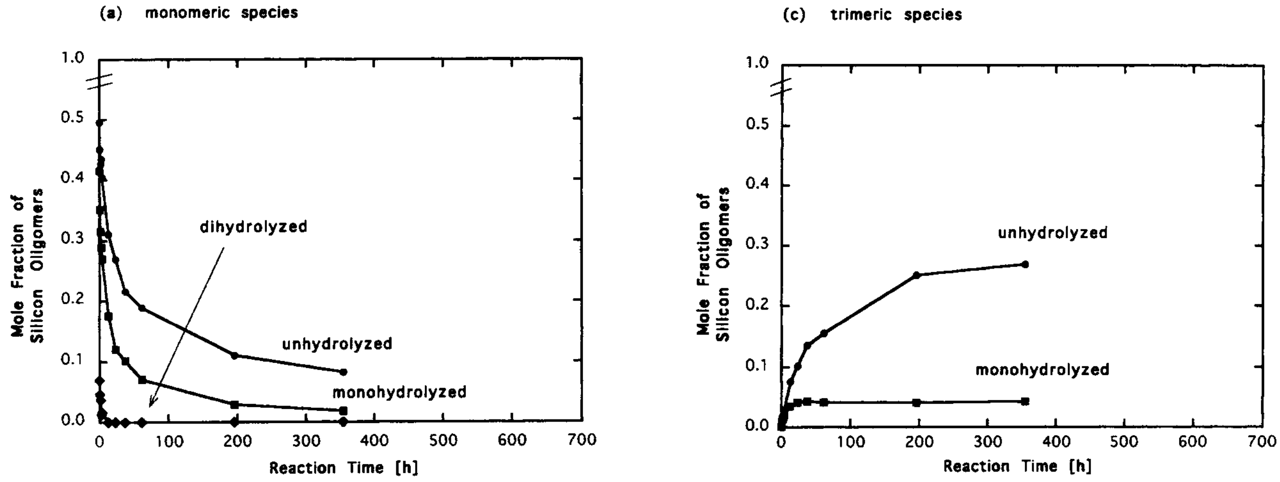
termination is high). Moreover, since the degree of hydrolysis is low, the oligomers are probably linear. These observations are supported by the results of GC-FID.

Gas Chromatography. Gas chromatograms are shown in Figure 5, where the peak assignments are aided by the results of Klemperer and Ramamurthi (1987) and coworkers (1988), as well as the ^{29}Si NMR results. Similar oligomers have been detected for systems with the same range of water-to-silicon ratio (Mulder and Damen, 1987). Klemperer and Ramamurthi (1987) found that the presence of hydroxyl groups on an oligomer increases the species retention time slightly. This is understandable since the hydroxyl groups promote hydrogen bonding which will lower the vapor pressure.

The mole fractions of the silicate oligomers are calculated from the peak intensities, as shown in Figure 6. These results show that reactions are occurring rapidly within the first few hours after mixing, leading to the sequential formation of hydrolyzed monomers, dimers and trimers. The reaction rates slow markedly after 24 h, but condensation is still occurring. Note that beyond a certain point, all reactions have ceased, so that there is no observable change between the gas chromatograms for the 4-month and 9-month samples. These results also show that the molecular size distributions are not monotonic as predicted by Flory's random branching theory (Odian, 1981), indicating that the polymerization process is not random even for low extent of reaction.

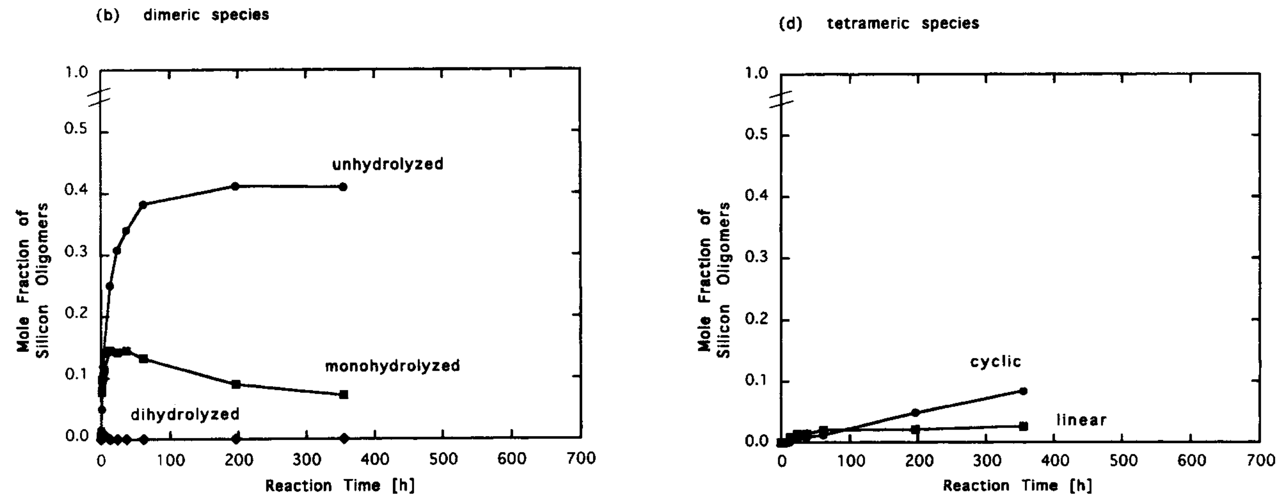
Hydrogen bonding

It is clear that some factor other than molecular weight is decreasing the average mobility of the silicates. The solvent is a mixture of water and ethanol, containing polar hydrogen atoms which are ready to form hydrogen bonds with the hydroxyl groups of the silanols. The mobility of these solutes



(a) monomeric species

(c) trimeric species



(b) dimeric species

(d) tetrameric species

Figure 6. Molecular size distribution of silicate oligomers as determined by GC-FID.

will consequently decrease (Erdey-Gruz, 1974; Pimentel and McClellan, 1960; Vinogradov and Linnell, 1971). The effect of hydrogen bonding on the solute mobility has been reported for some polymeric systems (Mokrys et al., 1979).

One indication of the H-bonding effect is the drastic drop in the silicate mobility 1 h after mixing, when chromatograms show that low-molecular-weight silanols are present in high concentrations. After 24 h, GC-FID and ^{29}Si NMR (Figure 4) both show that the reaction mixture still contains a high concentration of silanols, so the silicate mobility stays rather constant owing to the solute-solvent associations effect. Eventually, when the silanols are consumed completely, a rise in silicate mobility is observed. The loss in silicon hydroxyl groups is also coincidental with the complete consumption of water (Figure 7). Without any water, reactions stop at this point, leaving predominantly dimers and trimers (Figure 5).

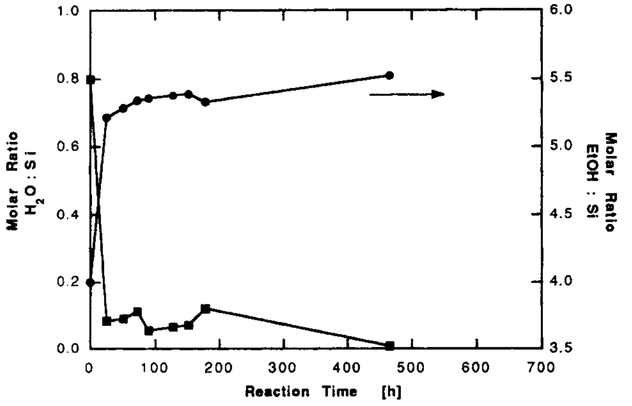


Figure 7. Hydrolysis and condensation of TEOS: water and ethanol content, calculated from ^{29}Si NMR results.

The consumption of water is a net result of the hydrolysis and condensation of TEOS, as shown by the following stoichiometric relations:

$$2(EtO)_3Si\text{-}OEt + 2H_2O \rightarrow 2(EtO)_3Si\text{-}OH + 2EtOH \quad (13a)$$

$$2(EtO)_3Si\text{-}OH \rightarrow (EtO)_3Si\text{-}O\text{-}Si(OEt)_3 + H_2O \quad (13b)$$

The equation above indicates that water is gradually consumed and ethanol produced as reactions progress. The system starts with low water concentration (a substoichiometric water-to-silicon molar ratio, W/Si, of 0.8), so that the water supply for the reactions vanishes before an appreciable degree of polymerization is achieved. It is shown in Appendix A how the water and ethanol content of the system can be calculated from the ^{29}Si NMR results using molar balances.

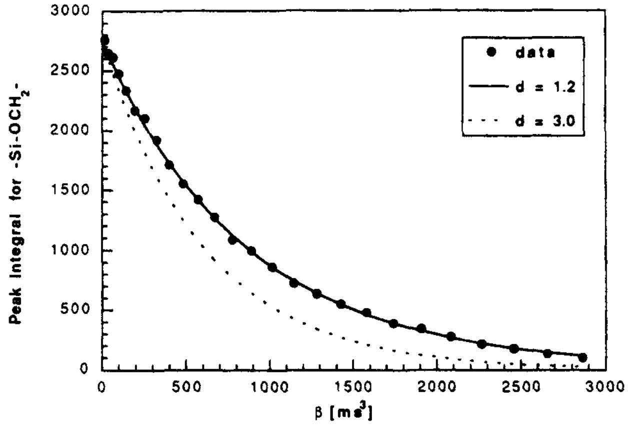


Figure 8. Determination of the diffusivity of unhydrolyzed silicon oligomers from ^{1}H PGSE NMR result obtained at the virtual completion of reaction (t = 466 h).

Diffusivity of hydrolyzed and nonhydrolyzed oligomers

The NMR signal intensity contributed by n type of oligomers of different diffusivity, D_j, is given by (von Meerwall, 1982):

$$S = S_o \sum_{j=1}^{n} f_j \exp\left(-2\Delta/T_{2,j}\right) \exp\left(-\gamma^2 G^2 D_j \beta\right) \tag{14}$$

where f_j is the mole fraction of the resonating nuclei, which is equivalent to the mole fraction of the silicon-bonded ethoxy group and can be obtained from the gas chromatograms as the fraction of the integrated peak area. For low molecular weight oligomers, T_2 is independent of molecular weight (von Meerwall, 1982), and the equation above becomes:

$$S = S_o' \sum_{j=1}^{n} f_j \exp\left(-\gamma^2 G^2 D_j \beta\right) \tag{15}$$

To predict the dependence of solute diffusivity, D_j, on molecular weight the Stokes-Einstein equation is used:

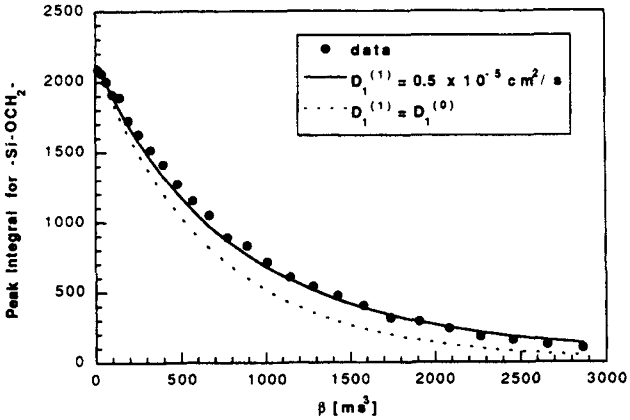


Figure 9. Determination of the diffusivity of monohydrolyzed silicon oligomers from ^{1}H PGSE NMR result obtained at t = 25 h.

Table 1. Diffusivity of Silicon Oligomers

	Diffusivity* [10^{-5} cm^2/s]	
Oligomer	Unhydrolyzed	Monohydrolyzed
Monomer	1.08	0.50
Dimer	0.71	0.31
Trimer	0.54	0.23
Cyclic tetramer	0.49	
Linear tetramer	0.44	

*In pure ethanol of viscosity 1.1 cp (Erdey-Gruz, 1974).

$$D_j = \frac{kT}{6\pi\eta_o R_j} \tag{16}$$

where η_o is the solvent viscosity and R_j is the solute hydrodynamic radius. The diffusivity of a j-mer is related to the monomer diffusivity by:

$$D_j = D_1 \left(\frac{R_1}{R_j}\right) \tag{17}$$

As the molecular weight increases, the size of the oligomer is expected to increase. If the oligomer increases in size as a dense sphere, then its radius, R, is proportional to $M^{1/3}$ (where M is its molecular weight). In general, though, we must allow for a less dense configuration, so,

$$R \sim M^{1/d} \tag{18}$$

where $d \leq 3$. Thus,

$$D_j^{(k)} = D_1^{(k)} \left(\frac{M_1}{M_j}\right)^{1/d} \tag{19}$$

where the index k indicates the degree of hydrolysis.

The diffusivities of the unhydrolyzed oligomers are first determined from the PGSE measurements at the virtual completion of reaction (t = 466 h) using Eqs. 15 and 19. The monomer diffusivity is obtained from measurements before the start of reactions to be 0.9×10^{-5}cm^2/s. To correct for the difference in solvent viscosity due to the loss of water, the

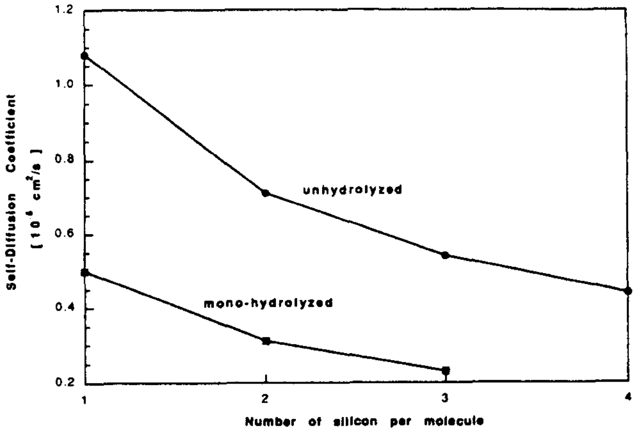


Figure 10. Self-diffusion coefficients of unhydrolyzed and monohydrolyzed small silicon oligomers.

monomer diffusivity, $D_1^{(0)}$, is estimated to be 1.08×10^{-5} cm^2/s based on the Stokes-Einstein equation and viscosity data from the literature (Erdey-Gruz, 1974). The experimental data are consistent with a dimensionality (d) of 1.20 ± 0.02, as shown in Figure 8. This implies, and reasonably so, that these small oligomers are slightly bent chains. Larger oligomers, though, will not necessarily have such a low dimensionality. Equations 15 and 19 are applied to the PGSE data early in reaction ($t = 25$ h) to obtain the monohydrolyzed monomer diffusivity, $D_1^{(1)}$ to be $(0.50 \pm 0.02) \times 10^{-5}$ cm^2/s (Figure 9). Results are listed in Table 1 and plotted in Figure 10.

The hydrogen bonding effect in reducing the mobility of the silicon species has been demonstrated. Nevertheless, the consequences of H-bonding are far-reaching. The effects of H-bonding on chemical reaction rates have been observed (Amis and Hinton, 1973). Moreover, according to the absolute reaction rate theory (Laidler, 1965), H-bonding can reduce the condensation reaction rate constant by increasing the heat of activation. This effect suggests that condensation is more favorable in aprotic solvents. It also suggests that alcohol-producing condensation reaction is thermodynamically more favorable than water-producing condensation since the latter involves two water-complexed reactants. The effects of hydrogen bonding on the condensation process in sol-gel reactions have been discussed (Artaki et al., 1986).

Comparing our diffusion results with the kinetic studies performed separately in our group, the Smoluchowski equation (Cussler, 1984) predicts that the early stages of condensation reactions (when the Brownian motion of the reactants is not hindered) are reaction-limited. However, when the polymers become sufficiently large, diffusion effects can be important. The influence of diffusion on the overall reaction rate and the polymer microstructural development is presently being examined.

Summary

It has been suggested in the sol-gel literature that diffusion effects may influence the development of the gel microstructure. To investigate if diffusion effects are important, we begin by determining what governs the diffusivity of the precursors.

This work focuses on the early stages of the sol-gel reaction by studying the acid-catalyzed hydrolysis and condensation of TEOS with starting molar ratio TEOS:ethanol:H_2O:HCl = 1:4:0.8:0.0008 using ^1H, ^{29}Si and ^1H-PGSE NMR, and gas chromatography with flame ionization detector. Low-molecular-weight, partially hydrolyzed oligomers (mainly dimers) are formed rapidly, and the average mobility of these silicates decreases. As condensation continues, shown by ^{29}Si NMR and GC-FID, the average mobility remains constant and then goes up late in reaction. Our results show that the mobility of the silicon precursors is reduced with increasing molecular weight and the extent of hydrolysis. Complexation with the water molecules reduces the diffusivities of the hydrolyzed species by increasing the effective hydrodynamic radii. At early stage of the reaction, molecular weight plays a lesser role in determining the diffusivity of the oligomers. We attribute the late rise in mobility to the loss in hydrogen bonding as silanols and water are consumed completely. Reactions have stopped without water so that our system produces only low-molecular-weight oligomers, the largest detected in significant amount being the linear tetramers. Although the early stages of reactions are clearly not diffusion-limited, our results suggest that hydroden bonding may be important in slowing the motion of intermediates in the presence of high water concentration.

These results have demonstrated that unlike ordinary polymer solutions, the diffusivity of sol-gel intermediates depends on a combination of molecular weight, solvent polarity, and polymer group polarity, the contribution of each of these factors changing with the extent of reaction.

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Appendix A: Water and Ethanol Content

From Eqs. 1, 2 and 3, we observe that, in the hydrolysis and condensation of TEOS, the proton (H) and ethyl (Et) groups are neither created nor destroyed. Hence, the total concentration of each of these groups is conserved. A molar balance on (Et-) shows that the ethanol concentration at any time (expressed in molar ratio of ethanol-to-silicon) is related to the concentrations of various silicon-groups as determined from the ^{29}Si NMR spectra in Figure 4 (all quantities, in bold letters, are expressed as ratios to the total concentration of silicons, subscript zero indicates initial value):

$$\mathbf{Et\text{-}OH} + \mathbf{EtO\text{-}Si} = \mathbf{(Et\text{-})_0} \qquad (\mathrm{A1})$$

$$\begin{aligned}\mathbf{EtO\text{-}Si} = {} & 3[\mathbf{(EtO)_3\text{-}Si\text{-}OH}] + 4[\mathbf{(EtO)_4\text{-}Si}] \\ & + 2[\mathbf{(EtO)_2(OH)\text{-}Si\text{-}(OSi)}] + 3[\mathbf{(EtO)_3\text{-}Si\text{-}(OSi)}] \\ & + 2[\mathbf{(EtO)_2\text{-}Si\text{-}(OSi)_2}] \qquad (\mathrm{A2})\end{aligned}$$

$$\begin{aligned}\mathbf{EtO\text{-}Si} = {} & 3[\mathbf{(EtO)_3\text{-}Si\text{-}OH}] + 4[\mathbf{(EtO)_4\text{-}Si}] \\ & + 2[\mathbf{(EtO)_2(OH)\text{-}Si\text{-}(OSi)}] + 3[\mathbf{(EtO)_3\text{-}Si\text{-}(OSi)}] \\ & + [2\mathbf{(EtO)_2\text{-}Si\text{-}(OSi)_2}] \qquad (\mathrm{A2})\end{aligned}$$

From the starting composition, the initial concentration of the ethyl group is 8. Similarly, the water concentration at any time can be determined from a molar balance of (H-), as shown below:

$$\mathbf{H_2O} + \mathbf{EtOH} + \mathbf{Si\text{-}OH} = \mathbf{(H\text{-})_0} \qquad (\mathrm{A3})$$

$$\mathbf{Si\text{-}OH} = [\mathbf{(EtO)_3\text{-}Si\text{-}OH}] + [\mathbf{(EtO)_2(OH)\text{-}Si\text{-}(OSi)}] \qquad (\mathrm{A4})$$

The value of **EtOH** in Eq. A3 can be obtained from Eqs. A1 and A2, while the initial concentration of (H-) is 5.6. The concentration of water is then equal to 1/2 [$\mathbf{H_2O}$]. Figure 7 shows the calculated results.

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