

SPINNABILITY OF SILICA SOLS

Structural and rheological criteria

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Received 16 February 1989

Revised manuscript received 8 May 1989

²⁹Si NMR spectroscopy of concentrated silicate sols, prepared by acid-catalyzed hydrolysis of TEOS in ethanol with H₂O/Si ratios, $r \approx 1.5$ or 1.7 , followed by alcohol evaporation, shows that the polysilicate species responsible for spinnability are not simple rigid-rod, ladder polymers or linear polymers. Instead a distribution of silicate species is observed consistent with the products of a statistical (random) growth process. The primary criterion for spinnability is high viscosity without premature gelation. This is accomplished under acid-catalyzed conditions with low values of r .

1. Introduction

A fluid is spinnable if it is capable of assuming large irreversible deformations when subjected to uniaxial stress, a measure of spinnability being the maximum attainable elongation [1]. Experimental data show that spinnability is exhibited by materials differing greatly in structure and composition. Long fluid threads can be obtained from mineral oils, soap solutions, and honey as well as from polymer melts and inorganic sols. The maximum length of the fluid thread, x^* , depends on the material involved and the processing conditions. Generally for low viscosities, η , and low elongational velocities, V , x^* increases with the product, ηV , while a decrease in x^* is observed at very high values of ηV [1]. Two mechanisms are proposed to account for the breakage of fluid threads, cohesive failure and capillary wave instability (droplet formation). The former mechanism is most important at high ηV , conditions where viscoelastic fluids behave elastically. Capillary wave instability is most important at low viscosity, and is exacerbated by high surface tensions [1].

Several groups have investigated the rheological behavior of silicate sols prepared from tetraethylorthosilicate (TEOS) in order to establish the criteria for spinnability. Sacks and Sheu [2] ob-

served that for acid-catalyzed systems prepared with H₂O/Si ratios, $r = 1$ or 2 , the best spinnability occurred in viscous systems ($\eta > 100$ mPa-s) that were highly shear thinning but not thixotropic. Sakka et al. [3–6] evaluated acid- and base-catalyzed systems prepared with r values ranging from 1 to 20 by determining the concentration dependence of the reduced viscosity, η_{sp}/C :

$$\eta_{sp}/C = k_1/\rho \quad (1)$$

or

$$\eta_{sp}/C = [\eta] + k_2[\eta]^2 C, \quad (2)$$

where η_{sp} is the specific viscosity, C is concentration, k_1 and k_2 are constants, and ρ is density, and the molecular weight dependence of the intrinsic viscosity, $[\eta]$:

$$[\eta] = k_3 M_n^\alpha, \quad (3)$$

where M_n is the number average molecular weight, k_3 is a constant that depends on the polymer, solvent, and temperature, and α is an exponent that ranges from 0 to 2 depending on polymer structure.

Equation (1), which shows no concentration dependence of the reduced viscosity, pertains to systems composed of discrete, non-interacting

polymers or particles [7]. Equation (2) pertains to extended, chain-like or linear polymers that exhibit a concentration dependence of η_{sp}/C [8]. Sakka and Kamiya [3] observed that, for an acid-catalyzed system prepared with $r = 1$, aging in open containers caused a progressively greater dependence of η_{sp}/C on C and eventually resulted in spinnability. This suggests that, for these conditions, solvent evaporation accompanied by continued hydrolysis and condensation causes a gradual progression of the silicate structure from small non-interacting species to extended, weakly-branched polymers responsible for spinnability. Base-catalyzed conditions as well as acid-catalyzed conditions with $r = 20$ exhibited no concentration dependence of η_{sp}/C and no evidence of spinnability [3].

It is postulated that the value of α in eq. (3) depends on the polymer or particle structure: $\alpha = 0$ for rigid, spherical particles, $\alpha = 0.5$ to 1.0 for flexible, chain-like or linear polymers, and $\alpha = 1.0$ to 2.0 for non-flexible or rigid rod polymers [9]. For example, $\alpha = 0.5$ for linear polydimethylsiloxane, $\alpha = 0.21$ to 0.28 for branched or crosslinked polymethylsiloxane, and $\alpha = 0.3$ for spherical polysilicates [8]. Sakka et al. observed that for acid-catalyzed silicate systems prepared with r values ranging from 1 to 20, α decreased with r (see table 1). Spinnability was observed only for α values above 0.5 corresponding to linear or perhaps rigid rod polymers [10].

In a subsequent study Sakka et al. explored fiber formation in silicate systems prepared from

methyltriethoxysilane (MTES) or dimethyldiethoxysilane (DMES) [11]. They observed that the hydrolysis of DMES resulted preferentially in the formation of cyclic tetramers. Based on this observation it was suggested that rigid rod polymers, such as ladder polymers, are necessary for spinnability since linear polymers would tend to cyclize [11]. Ladder polymers have also been associated with the inflection in the viscosity versus time behavior observed in spinnable systems hydrolyzed with $r = 1.7$, which is close to the theoretical value required to form ladder polymers, viz 1.666. Various linear or ladder-like structures proposed by Kamiya et al. [12] to account for spinnability are shown below:

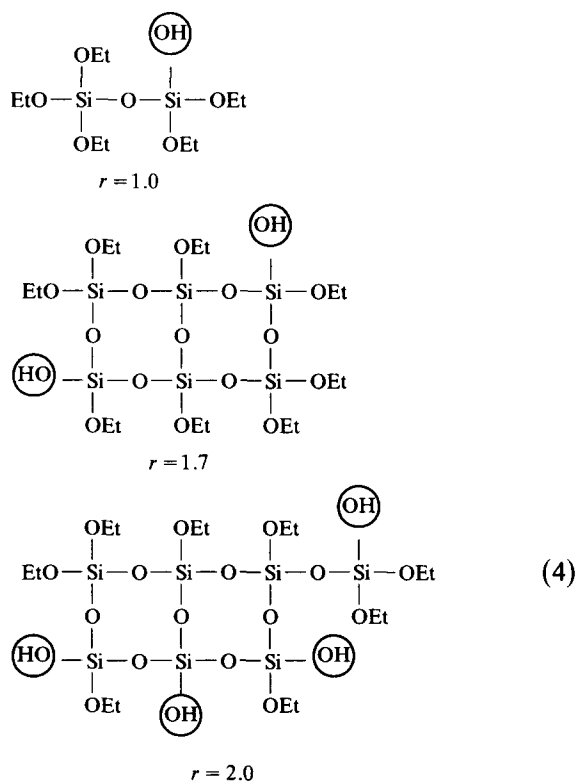


Table 1
The exponents α 's for the alkoxide polymers and properties of $\text{Si}(\text{OC}_2\text{H}_5)_4$ solution

Solution	H_2O (r)	α	Type of polymer	Spinnability
1	1.0	0.75	linear	yes
2	2.0	0.64	linear	yes
3	5.0	0.5	branched	no
4	20.0	0.34	three-dimensional spherical	no

In an attempt to understand the relationship between polymer structure and spinnability, we have used ^{29}Si NMR to examine the local chemical environment of Si in spinnable silicate systems. At least for the relatively high molecular weight systems used for fiber formation, knowledge of the average number of bridging and termi-

nal groups surrounding the central silicon¹ allows us to distinguish between several of the structures proposed to account for spinnability: linear polymers (Q^2), double chain ladder polymers (Q^3) and triple chain ladder polymers ($Q^3 : Q^4 = 2 : 1$).

2. Experimental

2.1. Materials

Spinnable silicate sols were prepared by two methods: (1) acid-catalyzed hydrolysis of TEOS in ethanol under reflux (mole ratios of TEOS : ethanol : H₂O : HCl = 1 : 3 : 1.5 : 0.0007) followed by ethanol distillation at 85 °C under Ar and exposure to 100% RH water vapor at 80 °C for 2–3 h, or (2) acid-catalyzed hydrolysis of TEOS in ethanol ($r = 1.7$) at 30 °C followed by solvent evaporation at 80 °C in an uncovered vessel according to the procedure of Sakka and co-workers [5–7].

Although in the first procedure virtually all the added alcohol and alcohol produced by hydrolysis and condensation was removed by distillation under Ar, spinnability² was not observed at the end of the distillation process. Therefore some additional hydrolysis appears necessary.

2.2. Instrumentation

The ²⁹Si NMR spectra were recorded at 39.6 MHz on a spectrometer described previously [13]. Broadband ¹H decoupling was applied only during acquisition in order to suppress the nuclear Overhauser effect and the RIDE pulse sequence [14] was used to reduce baseline roll. The pulse delay time was 45 s. Quantitatively similar spectra were obtained when chromium acetylacetonate, a spin relaxation agent, was added to the solution.

Preliminary small-angle X-ray scattering data were obtained on the spinnable system at full

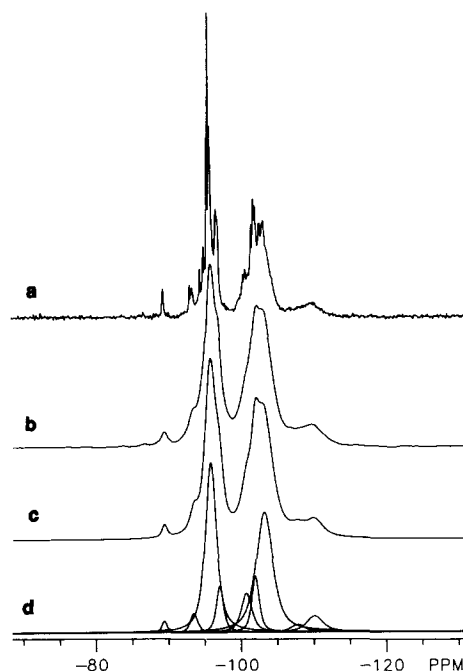


Fig. 1. Experimental and simulated ²⁹Si NMR spectra of the H₂O = Si = 1.5 spinnable sol-gel solution: (a) experimental, 1.0 Hz exponential line broadening; (b) experimental, 30 Hz exponential line broadening; (c) computer simulation; (d) resonance components of computer simulation.

concentration and after dilutions by factors of 10, 100, or 1000 with anhydrous ethanol.

3. Results and discussion

3.1. ²⁹Si NMR

The ²⁹Si NMR spectra of the spinnable sol-gel solutions are shown in figs. 1(a) and 2(a). The spectra exhibit resonances in four regions: Q^1 species, -82 to -90 ppm; Q^2 species, -91 to -99 ppm; Q^3 species, -99 to -106 ppm; and Q^4 species -106 to -112 ppm. The presence of Q^0 species (monomers as TEOS or in a hydrolyzed state) at or downfield from -82 ppm could not be detected. The assignment of sol-gel silicates into these regions has been discussed previously [16], and should be quite exact except for the downfield shift of resonances of highly strained species such as tricyclics. Significant quantities of

¹ In Q^n terminology, the n refers to the number of bridging oxygens (0–4) surrounding the central silicon atom.

² Spinnability was evaluated qualitatively by determining whether fibers could be drawn from the sol using a glass rod.

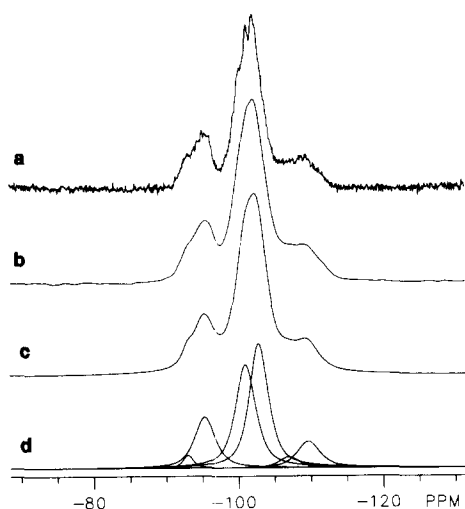


Fig. 2. Experimental and simulated ^{29}Si NMR spectra of the $\text{H}_2\text{O} = \text{Si} = 1.7$ spinnable sol-gel solution: (a) experimental, 1.0 Hz exponential line broadening; (b) experimental, 30 Hz exponential line broadening; (c) computer simulation; (d) resonance components of computer simulation.

such highly strained species are not expected to form under the present reaction conditions [17].

The spectra could not be accurately integrated into their resonance components directly because of the amount of overlap between resonances, particularly the Q^3 and Q^4 resonances. Therefore, simulation of the spectra by the General Electric 1280 software was used to determine the relative intensities of the resonances. The free induction decay was multiplied by a 30 Hz exponential function before Fourier transformation. The broadened spectra, shown in figs. 1(b) and 2(b), contain substantially fewer resonances which simplifies the simulation procedure without affecting the resultant areas of the various regions. Figures 1(c) and 2(c) show the simulated spectra while figs. 1(d) and 2(d) show the component resonances of the simulated spectra, for the two samples. The component resonances contain 70% Lorentzian and 30% Gaussian character. The simulation parameters were varied by trial and error to give the best visual fit of the experimental spectra. The relative areas of the simulated Q^n regions were reproducible to within $\pm 1.0\%$.

The relative areas of each of the Q^n regions determined by the simulation procedure are shown

in the first column of table 2. The broad distribution of silicon functionalities indicates that the silicate polymers are not composed of any one of the simple repeat units shown in, (4): linear polymers (Q^2) or ladder polymers (Q^3 or $2Q^3:1Q^4$). The presence of significant amounts of Q^2 , Q^3 , and Q^4 species, and the many resonances evident within each of these spectral regions (figs. 1(a) and 2(a)) indicate that the polymers are very complex and highly branched.

The distributions shown in table 2 are reminiscent of the distributions seen for the equilibrium structure of tetramethoxysilane (TMOS) reacted with limited amounts of water [18]. These experimental distributions could be predicted quite accurately by a statistical reaction model [15] that assumes that all the hydrolysis and condensation rate constants depend only on the functional group reactivity, not the local silicon environment. The predictions of this model for $r = 1.5$ and $r = 1.7$ are shown in column 2 of table 2. The distributions predicted by the statistical reaction model differ qualitatively from the experimental distributions in two respects. First, the distributions predicted by the statistical reaction model are biased to higher functionalities compared to the

Table 2

The experimental and theoretical function distributions for the sol-gel silicon atom

Speciation	Experimental distribution	Theoretical distribution		
		$\text{H}_2\text{O} = 1.5$	$\text{H}_2\text{O} = 1.31$	$\text{H}_2\text{O} = 1.31$ $R = 0.35$
Q^0	0.0	0.4	1.4	0.0
Q^1	1.0	4.7	10.8	0.8
Q^2	41.9	21.1	30.6	41.5
Q^3	50.3	42.2	38.8	52.5
Q^4	6.8	31.6	18.4	5.2
Standard deviation		7.5	4.9	0.6
		$\text{H}_2\text{O} = 1.7$	$\text{H}_2\text{O} = 1.47$	$\text{H}_2\text{O} = 1.47$ $R = 0.35$
Q^0	0.0	0.0	0.5	0.0
Q^1	0.0	1.1	5.4	0.0
Q^2	18.3	9.7	22.8	19.5
Q^3	69.0	36.9	42.2	67.0
Q^4	12.7	52.2	29.2	13.5
Standard deviation		11.5	7.2	0.6

experimental distributions. Second, the distribution of the Q^n species predicted by the statistical reaction model are broader than the experimental distributions.

The bias to higher functionalities predicted by the statistical reaction model is a consequence of the incomplete reaction of the sol-gel system at the time when the NMR spectra were recorded. The moles of H_2O per mole of silicon consumed by condensation reactions can be calculated as follows:

$$\text{moles } H_2O = \frac{1}{2}Q^1 + Q^2 + \frac{3}{2}Q^3 + 2Q^4. \quad (5)$$

From the experimentally determined Q^n distributions of the sol-gel silicons, the moles of H_2O per mole of silicon that were consumed by condensation reactions are calculated to be 1.31 and 1.47 for the two samples. The remaining moles of H_2O per mole of silicon (0.19 for the first sample and 0.23 for the second plus any additional water supplied by the subsequent exposure to water vapor) were probably used to hydrolyze ethoxy groups, but the resultant silanols had not yet undergone condensation reactions. If the values of 1.31 and 1.47 moles of H_2O per mole of silicon are used in the statistical reaction model, the distributions shown in column 3 of table 2 are obtained. The calculated distributions now reflect the same degree of overall condensation as the sol-gel, but are still broader than the experimental distribution.

A trend to a narrower distribution can be explained if the early reactions are faster than average and the late reactions are slower than average. For example, suppose that the Q^0 to Q^1 reaction is very fast and that the Q^3 to Q^4 reaction is very slow. Then, the concentrations of both the Q^0 and Q^4 species will be diminished. Column 4 of table 2 shows the distribution calculated by a model which incorporates these ideas. The rate of the Q^0 to Q^1 was set equal to 1 and the rate of each successive reaction was then multiplied by a factor R , where R is less than 1. Thus the relative rate of Q^1 to Q^2 is R , the relative rate of Q^2 to Q^3 is R^2 and the relative rate of reaction of Q^3 to Q^4 is R^3 . The value of R was then adjusted to minimize the standard deviation between the theoretical and experimental distributions. The best agreement

between theory and experimental for the samples was obtained for $R = 0.35$. The standard deviations between the experimental distribution and the various model distributions are also shown in table 2. Obviously, the best prediction is generated by the model incorporating R , whose fit is well within the uncertainty of the experimentally determined distribution. A decreasing rate of condensation of a silicon atom as its state of condensation increases is reasonable on the basis of steric and inductive considerations [6]. Experiments have also shown that the condensation rate of dimeric species is much slower than the condensation rate of monomeric species in the TMOS sol-gel system [19].

Based on the above discussion, the sol-gel polymer in its spinnable state is a combination of silicon atoms forming linear segments, trifunctional branching points, and tetrafunctional branching points. It does not consist of simple, high molecular weight linear polymers (Q^2), double-chain ladder polymers (Q^3), or triple-chain ladder polymers ($Q^3:Q^4 = 2:1$). Instead the distribution of silicon atoms among these various functionalities can be explained by very simple statistical arguments implying random, not ordered, growth processes.

3.2. Rheology and scattering

In addition to the local chemical structure, several other factors argue against the presence of rigid rod polymers in spinnable silicate sols. According to eq. (3), the exponent, α , is required to be 1–2 for rigid polymers, yet the largest value observed was 0.75. In order to give structural significance to the value of α , eq. (3) may be re-expressed in terms of a mass fractal dimension, D [20]:

$$\eta \sim R_g^3/M_n \sim k_4 M_n^{(3/D)-1}, \quad (6)$$

where R_g is the radius of gyration and k_4 is a constant. Since the mass fractal dimension of a rod is 1, eq. (6) predicts that for rigid-rod polymers $\alpha = (3/1) - 1 = 2$. According to eq. (6), $\alpha = 0.75$ corresponds to $D = 1.83$, a value in between that of a linear swollen polymer (self-avoiding random walk), $D = 5/3$, and either an ideal (ran-

dom walk) linear polymer or swollen branched polymer or reaction-limited cluster–cluster aggregate, $D \approx 2$ [21].

Although it is often possible to determine the value of D from small-angle scattering according to

$$I(K) \sim K^{-D} \quad (7)$$

a preliminary SAXS investigation of the spinnable system did not show a linear dependence of I on K . Instead the slit-smear slopes increased progressively from $< 1/3$ to > 1 (corresponding approximately to $D < 1.33$ to $D > 2$) over the range $K = 0.01$ to 1 . These curvature effects are generally attributed to strong polydispersity disallowing an interpretation of the slope according to eq. (7). Even though a fractal dimension describing the spinnable system has not been obtained, the preliminary SAXS data do not support $D = 1$, as expected for rigid-rod polymers.

3.3. Criterion for spinnability

From the combined results summarized above, we see that the criterion for spinnability is high viscosity of the sol without premature gelation. This criterion is achieved using acid catalysts and low values of r (generally < 2).

As discussed in the Introduction, for low elongational velocities, V (normally case for laboratory experiments), high viscosity is necessary to stabilize the fiber from capillary wave instabilities (droplet formation). Equations (2, 3, 6) indicate that for any particular concentration or extent of condensation (M_n), less-highly branched “extended” structures, e.g., chains or randomly branched polymers ($D \ll 3$), are more efficient than compact structures, e.g. discrete particles ($D = 3$), at increasing the viscosity. Extended structures interact at low concentrations and at low extents of condensation which explains the concentration and molecular weight dependence of the reduced and intrinsic viscosities, respectively. Although rigid-rod polymers ($D = 1$) confer the greatest effect on the viscosity per unit concentration or molecular weight, our NMR results clearly show that neither rod polymers nor linear polymers are necessary for spinnability.

However, high viscosity alone is not a sufficient condition for fiber formation. All gel forming systems by definition attain high viscosities, but most often the spinnable state is too short-lived to be of any practical consequence. Acid catalysts and low r values facilitate high viscosity without premature gelation.

Acid catalysts generally lead to extended structures as opposed to compact structures by promoting random (statistical) cluster–cluster growth that proceeds more or less irreversibly, i.e., without much rearrangement [22]. In addition sufficient acid concentrations to yield an effective pH near 2 minimize the condensation rate. This allows the viscosity to be increased by increasing the concentration (eq. 2) without causing immediate gelation. Kozuka et al. [23] found that for an acid-catalyzed TEOS system prepared with $r = 2$ spinnability was observed only when the viscosity was increased by solvent removal in an open container. In closed containers equivalent viscosities can be achieved only by continued condensation reactions leading to network formation and premature gelation.

Because ether (ROR) forming condensation reactions do not occur at low temperature, low H_2O/Si ratios, r , effectively reduce the functionality of Si, thereby promoting the formation of extended rather than compact structures. In addition, since OR terminated polymers do not react, the viscosity can increase via solvent removal as opposed to network formation leading to spinnability as described above.

An r value of 1 is theoretically sufficient to produce infinite chains, while r values of 1.66 and 2 are theoretically sufficient to produce double chain ladder polymers and fully condensed silica, respectively. However, in this study ($r = 1.5$ or 1.7) even reflux conditions followed by distillation of ethanol at $85^\circ C$ did not drive the reaction to completion. Thus the system retains some uncondensed OH groups that may be important with regard to spinnability. Clearly in our experiments some hydrolysis of the terminal groups appears necessary, since solvent removal alone at $85^\circ C$ in the absence of water vapor ($r = 1.5$) did not result in spinnable systems, whereas spinnability was observed after subsequent exposure of the sol to

100% RH water vapor at 80°C (conditions under which little further evaporation occurs). In all of the referenced work cited in this paper spinnability was achieved by aging the sols uncovered in uncontrolled environments, so that some amount of additional hydrolysis occurs during the concentration step. These hydrolyzed groups as well as additional silanol groups formed during fiber formation may be necessary to stabilize the drawn fiber. Sacks and Sheu for example found that although a sol prepared with $r = 1$ was spinnable, the drawn fibers were unstable toward droplet formation [2].

4. Conclusions

^{29}Si NMR of silicate sols prepared by acid-catalyzed hydrolysis and condensation of TEOS with $r \approx 1.5$ or 1.7 and fractal analysis of rheology data reveal that polysilicate species comprising spinnable sols are not simple rigid-rod ladder polymers or strictly linear polymers. Instead we observe a distribution of Q species consistent with the product of a statistical (random) growth process (suitably modified to take into account steric and inductive effects) and a mass fractal dimension $\gg 1$ indicating that rigid rods are not present on intermediate length scales (1–20 nm). The primary criterion for spinnability is high viscosity without premature gelation. This is accomplished by acid-catalyzed conditions employing low values of r , which produce extended rather than compact structures consistent with the conclusions of Sakka and coworkers based on rheological investigations. In order to achieve stable fibers a second criterion appears to be some additional condensation during fiber formation. This topic will be addressed in a future publication.

The technical assistance of D.A. Schneider and C.S. Ashley is gratefully acknowledged.

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