SPINNABILITY OF SILICA SOLS: THE ROLE OF ALKOXY GROUP EXCHANGE

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ABSTRACT

The exchange and spinnability of several systems with the general form $\text{Si}(\text{OR})_4$ (where $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$) in ethanol, propanol and butanol were investigated. We have followed the alkoxy group exchange, the hydrolysis and condensation reactions and the Q distributions of these systems using ^{29}Si and ^{17}O NMR. The observed differences in spinnability of the various sol-gel systems are attributed to the effect of the bulkiness of the alkoxy group on its reactivity.

INTRODUCTION

The sol-gel process provides a low temperature route for preparing glass fibers. The nature of the polymeric species strongly influences spinnability. Previous studies have indicated that a spinnable sol has a high viscosity without premature gelation [1-3]. These conditions appear to be controlled by two parameters. First, the sols were found to have an extent of reaction on the order of 0.7. Second, the sols were found to have a greater than expected number of Q^2 and Q^3 species where the Q indicates that the silicon is tetrafunctional and the superscript refers to the number of bridging oxygens surrounding the silicon. These conditions were measured for an acid-catalyzed tetraethoxysilane (TEOS)- H_2O - $\text{C}_2\text{H}_5\text{OH}$ by ^{29}Si NMR spectroscopy. The requirement for a preponderance of Q^2 and Q^3 species is supported by the observation that TMOS sols, which react statistically and hence contain a lower fraction of Q^2 and Q^3 species, do not exhibit spinnability while TEOS sols, which react non statistically, do exhibit spinnability [3-5].

In order to have practical utility, a sol must be spinnable for an extended period of time. In this study we explore methods by which a non statistical distribution of Q species can be introduced into the sol, an appropriate extent of reaction reached quickly and then the reaction slowed so that the duration of spinnability can be extended. We investigated several systems with the general form $\text{Si}(\text{OR})_4$ where $\text{R} = \text{CH}_3$ or C_2H_5 in ethanol, propanol and butanol. In an acid catalyzed sol, the alkoxides and alcohols undergo rapid exchange. If tetramethoxysilane (TMOS) is mixed with butanol, an equilibrium distribution of methoxy and butoxy groups is quickly reached. We expect that this distribution will be non statistical because of the different sizes of the alkoxides. When these species undergo hydrolysis and subsequent condensation, the number of bridging oxygens surrounding the silicon will also be non statistical. The methoxy groups are expected to react rapidly so that the spinnability stage is quickly reached, while the remaining butoxy groups are expected to react more slowly so that length of the spinnability stage is extended.

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MASTER

EXPERIMENTAL

The alkoxy group exchange reactions of TMOS in ethanol, propanol and butanol were carried out by mixing TMOS in the appropriate alcohol in the molar ratio of 1:4 (equal molar ratios of alkoxy groups) keeping the total volume constant at approximately 25 ml. The exchange reaction was initiated by adding 20 μ l of 1 N aqueous HCl. The spinnable sol-gels were prepared by the hydrolysis of TMOS or TEOS in the appropriate alcohol (ethanol, propanol or butanol) with a $\text{H}_2\text{O}/\text{Si}$ ratio of 1.7 followed by solvent evaporation at 80°C in an uncovered vessel according to the procedure by Sakka *et al* [6]. Spinnability was evaluated qualitatively by pulling fibers from the sol using a glass rod.

The ^{29}Si NMR spectra were recorded at 39.6 MHz on a Chemagnetics console interfaced to a GE-1280 data station and pulse programmer. A silicon free probe and 20mm quartz tubes were employed. Chromium acetylacetonate was used as a relaxation agent. The ^{17}O NMR spectra were recorded at 54.2 MHz on a Bruker AMX spectrometer using a 5 mm probe.

RESULTS AND DISCUSSION

The ^{29}Si NMR spectrum of a TMOS/ethanol solution is shown in Figure 1(a). The spectrum consists of a single resonance at -78.5 ppm due to TMOS. When a small amount of 1 N HCl is added to the solution, the spectrum exhibits five resonances ranging from -78.5 to -82.0 ppm as shown in Fig 1(b). The additional resonances correspond to various numbers of methoxy groups having been replaced by ethoxy groups. For example, the resonance at -82.0 ppm corresponds to a silicon surrounded by four ethoxy groups. Similar experiments were performed with TMOS/propanol, and TMOS/butanol solution.

Figure 1. The ^{29}Si NMR spectra of (a) TMOS and ethanol, and (b) TMOS and ethanol and a small amount of 1 N HCl.

The resonances of the alkoxy exchanged solutions were integrated and their relative intensities reported in Table I along with the distribution expected for a totally statistical arrangement of alkoxyes. The TMOS/ethanol solution exhibits a reasonably statistical distribution of species. The TMOS/propanol and TMOS/butanol solutions, however, are markedly non statistical. Neither solution has a resonance corresponding to complete exchange of the methoxy group by 4 propoxy or 4 butoxy groups. Presumably, these species are difficult to form because of the bulkiness of the propoxy and butoxy groups compared to that of the methoxy group. This behavior causes an increase in the number of silicons surrounded by 2 or 3 methoxy groups. We believe that the non statistical distribution of alkoxy groups can be exploited to increase the spinnability of these solutions.

Table I. Alkoxy group distributions in acid-catalyzed TMOS/alcohol sols.

Alcohol (R)	Si(OCH ₃) _x (OR) _{4-x}				
	x = 4	x = 3	x = 2	x = 1	x = 0
Ethanol	0.05	0.20	0.35	0.28	0.13
Propanol	0.09	0.33	0.40	0.17	0.00
Butanol	0.09	0.27	0.41	0.22	0.00
Statistical	0.06	0.25	0.37	0.25	0.06

If the alkoxy groups have different reactivities, then their non statistical distribution will result in a non statistical distribution of bridging oxygens. The hydrolytic reactivities of the various functional groups are reflected by the rate at which they consume water in an acid-catalyzed sol. This rate can be conveniently measured by ¹⁷O NMR when ¹⁷O enriched water is used to prepare the sols. The H₂¹⁷O resonates at 0 ppm, while silanols resonate at 9-14 ppm and bridged oxygens resonate at 25 ppm. Figure 2 shows the consumption of water by acid-catalyzed sols of TEOS, TPOS and TBOS where TPOS represents tetrapropoxysilane and TBOS represents tetrabutoxysilane. The TMOS sol is not shown because nearly all of the water had been consumed before the first measurement could be completed. Thus, the hydrolysis rate slows substantially as the size of the alkoxy group increases [7,8]. If a limited amount of water is used, then the water will be consumed primarily by the smaller substituents (methoxy and ethoxy) while the large substituents (propoxy and butoxy) will be largely unreacted. Thus, the distribution of bridging oxygens will be a function of the distribution of alkoxy groups.

Figure 2. The consumption of water as a function of time for TEOS, TPOS and TBOS as determined by ¹⁷O NMR spectroscopy. The intensity of the initial water resonance has been normalized to 1.0.

A spinnable sol was prepared from a TMOS/butanol solution as described in the experimental section. The sol remained spinnable for 74 days at room temperature, see Table II. The Q^n distributions were measured by high resolution ^{29}Si NMR [9,10]. The total number of Q^2 and Q^3 silicons equaled 79 %, while the statistical number for a sol with an extent of reaction of 0.67 is only 69 %. The times for which various TEOS/alcohol sols were spinnable are also shown in Table II along with the extent of reactions and Q^2 plus Q^3 percents for day one, an intermediate day, and the day in which the material was observed to have gelled.

A couple of features are common to the spinnable sols. First, with the lone exception of day one of the TMOS/butanol sol, all of the sols had an extent of reaction ranging from 0.63 to 0.70 during the times they were spinnable. This is a fairly narrow range for the extent of reaction and demonstrates that the $\text{H}_2\text{O}/\text{Silicon}$ ratio as well as the reaction conditions must be carefully controlled. Second, the experimentally determined ($Q^2 + Q^3$) percentages were higher than the percentages predicted statistically from the extents of reaction of the sols. Ten of the twelve sols had ($Q^2 + Q^3$) ranging from 78 to 90 %. Each sum is significantly higher than that predicted by a statistical distribution from the corresponding extent of reaction. In fact, the sum of Q^2 and Q^3 , calculated for a statistical distribution, reaches a maximum value of less than 70% corresponding to an extent of reaction of 0.63.

Table II. Spinnability duration, extent of reaction, and Q distributions for various sols.

Sol Composition	Spinnability Duration (Days)	Analysis Time (days)	Extent of Reaction (fraction)	$Q^2 + Q^3$ (%)	
				Exp.	Statistical
TMOS/Butanol	74	1	0.57	84	68
		50	0.67	79	69
		75	0.67	78	69
TEOS/Ethanol	6	1	0.63	87	70
		4	0.66	88	69
		7	0.67	87	69
TEOS/Propanol	11	1	0.64	88	70
		7	0.65	70	70
		12	0.70	66	68
TEOS/Butanol	60	1	0.64	90	70
		21	0.65	86	70

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CONCLUSIONS

In an acid-catalyzed TMOS/alcohol sol, the alkoxies quickly rearrange to reach a distribution which is dependent on their bulkiness. These distributions can be used to prepare non statistical sols which are spinnable for extended periods of time. The spinnable sols are characterized by an extent of reaction ranging from 0.63 to 0.70 and by a significantly higher Q^2 plus Q^3 content than that predicted by a statistical model.

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