

## Spinnability and Rheological Properties of Sols Derived from $\text{Si}(\text{OC}_2\text{H}_5)_4$ and $\text{Zr}(\text{O}-n\text{C}_3\text{H}_7)_4$ Solutions

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### Abstract

The shape of the polymers in the mixed alkoxide solutions of  $\text{Si}(\text{OC}_2\text{H}_5)_4$  and  $\text{Zr}(n-\text{OC}_3\text{H}_7)_4$  with various water contents (1, 2, 4, and 8 in molar ratio to alkoxide,  $r$ ) and catalysts was examined by rheological measurements, and its relation with fiber drawing behavior of the solutions was described. It was found that fibers could be drawn in the viscosity range 1~100 P from the acid-catalyzed solutions with lower water contents of the molar ratio  $\text{H}_2\text{O}/\text{alkoxide}$ ,  $r \leq 2$ . On the other hand, no fiber could be drawn from the acid-catalyzed solutions including a large amount of water ( $r \geq 4$ ) and the base-catalyzed solutions.

The relation between the intrinsic viscosity  $[\eta]$  and number average molecular weight  $\bar{M}_n$ , namely  $[\eta] = K\bar{M}_n^\alpha$ , has shown that the acid-catalyzed spinnable solution ( $r = 1$  and  $2$ ) had linear polymers where the exponent  $\alpha$ 's were about 0.56 and 0.81, whereas non-spinnable solutions ( $r = 4$  and  $8$ ) had three dimensional network polymers or spherical particles where the exponent  $\alpha$ 's were 0.41-0.51 and 0.35.

키워드 : 졸-겔법, 방사성, 섬유, 점성, 분자량

Keywords: sol-gel method, spinnability, fiber, viscosity, molecular weight

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### 1. Introduction

Introduction of zirconia into the glass increases the chemical durability of the glass [1]. The glass containing zirconia, however, is very difficult to prepare by the traditional melting method because zirconia has a high melting temperature and is liable to crystallize [2]. Sol-gel method enables formation of oxide glass by heating gels to temperature lower than that required in the conventional melting method [3]. Using this method, some glasses with high zirconia content have been prepared. Kamiya et al. produced glass fibers containing zirconia up to

33wt% [1]. Nogami and Moriya prepared glass film in the  $\text{ZrO}_2 \cdot \text{SiO}_2$ [4].

In order to obtain fibers by the sol-gel method, it is required that the alkoxides primarily form chain-like or linear metalloxane polymers in solutions through hydrolysis and polycondensation reactions [5].

It has been found in the case of  $\text{Si}(\text{OC}_2\text{H}_5)_4$  solutions that the formation of chain-like polymers is achieved under acidic conditions when the molar ratio of the added water to the alkoxide is relatively small. In other words, when the molar ratio of water to  $\text{Si}(\text{OC}_2\text{H}_5)_4$  is less than 2, linear polymers having some branches are formed. Gel fibers can be converted to glass fibers by heating to  $800^\circ\text{C}$  [6].

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Table 1. Composition and properties of the mixed alkoxide solutions

Solution	Composition of solution			Gelation time		Spinnability	
	Si(OC <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> : Zr(O-nC <sub>3</sub> H <sub>7</sub> ) <sub>4</sub> : H <sub>2</sub> O : C <sub>2</sub> H <sub>5</sub> OH : HCl(NH <sub>4</sub> OH)			(h)			
1	0.8	0.2	1	1	0.3	4.5	Yes
					0.03	11.3	"
					0.003	24.5	"
2			2	1	0.3	3.4	Yes
					0.03	8.7	"
					0.003	12.6	"
3			4	1	0.3	2.3	No
					0.03	3.3	"
	0.003	4.5			"		
4	8	1	0.3	0.2	No		
			0.03	1.3	"		
			0.003	2.9	"		
5	1	1	(0.3)	185	No		
6	2	1	(0.3)	245	No		
7	4	1	(0.3)	450	No		
8	8	1	(0.3)	850	No		

H<sub>2</sub>O:C<sub>2</sub>H<sub>5</sub>OH:HCl(NH<sub>4</sub>OH) ; the molar ratio of the total alkoxide.

In the previous reports we discussed the effect of various processing conditions of sol-to-gel and gel-to-glass transitions of Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> and Zr(O-nC<sub>3</sub>H<sub>7</sub>)<sub>4</sub> [7-10]. ZrO<sub>2</sub> • SiO<sub>2</sub> fibers have been drawn from mixed solutions of Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> and Zr(O-nC<sub>3</sub>H<sub>7</sub>)<sub>4</sub>. However, the nature of the polymeric particles in the mixed solutions of Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> and Zr(O-nC<sub>3</sub>H<sub>7</sub>)<sub>4</sub> has been not completely known. A number of questions remain unsolved, so further investigation is necessary.

In this work, rheological properties of the sols and diluted solutions of the trimethylsilylated sol polymers were studied, and the number average molecular weight  $\bar{M}_n$  was determined for the mixed alkoxide solutions in order to investigate the shape of polymers and the spinnability of the sols.

## 2. Experimental Procedure

### 2.1 Preparation of the Mixed Alkoxide Solution and Fiber Drawing

Table 1 shows the molar compositions of the starting solution, and Fig. 1 shows the procedure for preparing the 20ZrO<sub>2</sub> • 80SiO<sub>2</sub> gel fibers. Several alkoxide-H<sub>2</sub>O-C<sub>2</sub>H<sub>5</sub>OH-HCl(or NH<sub>4</sub>OH) solutions with the molar ratios of H<sub>2</sub>O/total alkoxides(r) ranging from 1.0 to 8.0 were prepared by the method described in the previous work[10]. Molar ratios of C<sub>2</sub>H<sub>5</sub>OH/total alkoxides and HCl(NH<sub>4</sub>OH)/total alkoxides were 1.0 and 0.003-0.3(NH<sub>4</sub>OH=0.3), respectively. The solutions were kept standing at room temperature without cover.

Spinnability of the sol was examined by immersing a glass rod of about 3 mm in diameter into the sol and pulling it up by hand. This step was repeated until the sol gelled into a jelly-like mass.

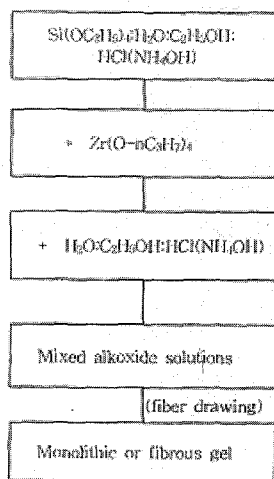


Fig. 1. The procedure for the preparation of the gel fiber

## 2.2 Trimethylsilylation (TMS) of the Metalloxoane Polymers

The metalloxoane polymers in the  $20\text{ZrO}_2 \cdot 80\text{SiO}_2$  solution were trimethylsilylated by trimethylchlorosilane  $[(\text{CH}_3)_3\text{SiCl}]$  in order to cap the reactive  $-\text{OH}$  and  $-\text{OR}$  ( $\text{R} = \text{alkyl}$ ) side group [11], dissolved in benzene, and then subjected to molecular weight and viscosity measurements.

## 2.3 Measurement of the Molecular Weight of the Metalloxoane Polymers

The number average molecular weight ( $\bar{M}_n$ ) of the metalloxoane polymers was estimated from freezing point depression ( $\Delta T_f$ ) of the benzene solution by using the following formula:

$$\bar{M}_n = K_f \cdot 1000 \cdot g / (G \cdot \Delta T_f)$$

where,  $g$  is the weight of trimethylsilylated polymer,  $G$  is the weight of benzene, and  $K_f$  is 5.12, the freezing point depression constant of benzene[12].

## 2.4 Measurement of Viscosity of the Mixed Alkoxide Solutions

The viscosity of the benzene solution of the trimethylsilylated metalloxoane polymers was measured by an Ostwald viscometer as a function of the concentration  $C$  in the range  $1 \sim 10\text{g/dl}$  at  $25^\circ\text{C}$ . The values of  $\eta_{\text{rel}}$  can be converted to specific viscosities  $\eta_{\text{sp}} = (\eta_{\text{rel}} - 1)$  and to reduced viscosities  $\eta_{\text{sp}}/C$  against  $C$  give the intrinsic viscosity  $[\eta]$ .  $C$  was a proportionality constant, and the concentration of the polymer is defined usually as gram in dl solutions.

## 3. Results and Discussion

### 3.1 The Properties and the Spinnability of the Mixed Alkoxied Solutions

The mixed alkoxide solutions became viscous and sticky with increasing reaction time as a result of polymerization of alkoxides. Some of the solutions showed spinnability just before gelation.

The time required for gelation and the result on the examination of spinnability of the alkoxide solutions are shown in Table 1. The gelation time was dependent on the amount of water and the kind of catalyst. Larger amounts of water accelerated the gelation of sol, when  $\text{HCl}$  was used as a catalyst. The gelation time decreased with the  $\text{HCl}$  concentration. On the other hand, the gelation time increased with  $\text{NH}_4\text{OH}$ .

Acid-catalyzed solutions 1 and 2, with the relatively small amounts of water  $\text{H}_2\text{O}/\text{alkoxide} = 1$  and 2, exhibited spinnability just before gelation. Acid-catalyzed solutions 3 and 4, with the larger amount of water of  $\text{H}_2\text{O}/\text{alkoxide} = 4$  and 8, and base-catalyzed solutions 5-8 showed no spinnability before gelation.

### 3.2 The viscosity of the Mixed Alkoxide Solutions and the Molecular Weight of the Polymers

Fig. 2 presents the time dependence of viscosity on the different water contents of the

acid catalyzed (the molar ratios HCl/alkoxide = 0.3) alkoxide solutions of various H<sub>2</sub>O/alkoxide molar ratios *r*. The viscosity increases with time during the hydrolysis-condensation reaction. When the viscosity reaches about 10 P, the solution becomes sticky and spinnable.

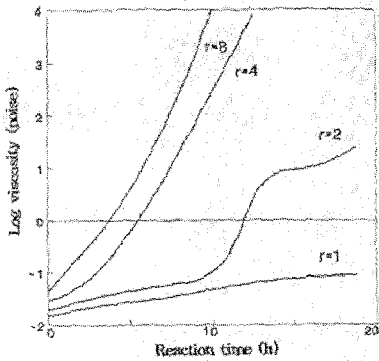


Fig. 2. Dependence of the viscosity on the reaction time for the mixed alkoxide solutions of various H<sub>2</sub>O/alkoxide molar ratios, *r*. The molar ratios HCl/alkoxide = 0.3.

Solutions 1 and 2, which are catalyzed with 0.3 mol of HCl and characterized by the lower water content, become spinnable at viscosities higher than about 10 P. No drastic change in viscosity with reaction time is observed in solution 1. In solution 2 (*r* = 2), the increasing rate of the viscosity decreases remarkably after the viscosity reaches about 10 P, which makes it possible to draw fiber for a long time without gelation of the sol. The decrease in the rate of viscosity can be attributed to the exhaustion of the water in the solution required for the hydrolysis reaction. The viscosity of the solution, however, continues to increase at lower rates, which is thought to be caused via absorption of moisture from the air[13].

Solutions 3 and 4, which are catalyzed with acid and characterized by higher water contents, are not spinnable. The viscosity increases sharply from the beginning of reaction time in comparison

with solution 2. It has been known that a solution is generally spinnable only when long-shaped particles are contained [11]. The reduced viscosity ( $\eta_{sp}/C$ ) of the polymer solution can be expressed by the following Huggins' equation, if the polymer dissolved in the solution is chain-like or linear,

$$\eta_{sp}/C = [\eta] + K[\eta]^2C$$

where  $\eta_{sp}$  is the specific viscosity defined as  $\eta_{sp} = \eta_{rel}(\text{relative viscosity}) - 1$ ,  $[\eta]$  is the intrinsic viscosity, *K* is a proportionality constant, and *C* is the concentration of the polymer, defined usually as g/dl solution. This formula indicates that for linear polymer, the ( $\eta_{sp}/C$ ) vs. *C* plot is a straight line with the slope of  $K[\eta]$  [6]. On the other hand, the reduced viscosity ( $\eta_{sp}/C$ ) of the solution containing spherical particles is expressed by Einstein's equation,

$$\eta_{sp}/C = K/\rho,$$

where *K* is a constant and  $\rho$  is the density of the particles. This formula indicates that  $\eta_{sp}/C$  is not dependent on *C* for spherical particles and is expressed by a straight line parallel to the *C* axis [6].

Fig. 3 shows the ( $\eta_{sp}/C$ ) vs *C* plots of the reduced viscosity of the benzene solutions of trimethylsilylated polymers obtained from solutions 2 and 4 with the molar ratios HCl/alkoxide = 0.3 mol. It is shown that the plots for the polymers in solution 2 are straight lines with various values for slope, indicating that long-shaped particles are included in the solution, causing spinnability. In the case of polymers in solution 4, no slope was seen for the plots, indicating that the particles in this solution are round-shaped; this is the reason for the absence of spinnability in solution 4.

Fig. 4 shows the reaction time dependence of  $\bar{M}_n$  of the polymers in the acid-catalyzed solutions of HCl/alkoxide = 0.3 for different water contents ( $t/t_g$  is the relative gelation time).

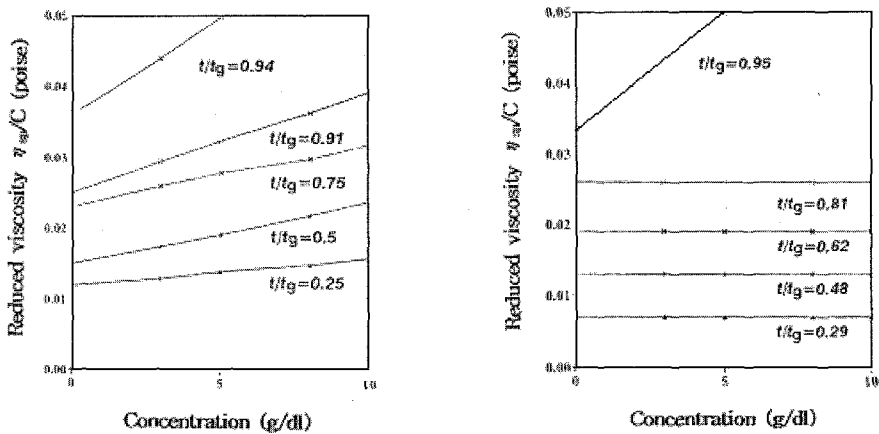


Fig. 3. The relationship between the reduced viscosity ( $\eta_{sp}/C$ ) and the concentration of the trimethylsilylated polymers for (a) solution 2 and (b) solution 4 with molar ratios of HCl/alkoxide = 0.3

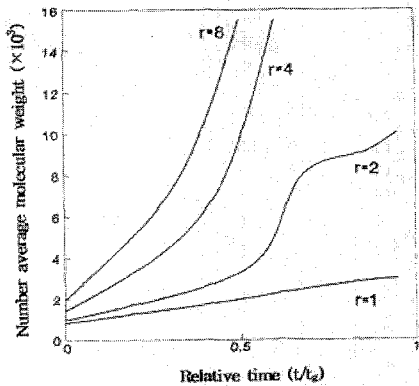


Fig. 4. Dependence of the number average molecular weight ( $\bar{M}_n$ ) of the polymers on the relative time ( $t/t_g$ ) for the acid-catalyzed (the molar ratios of HCl/alkoxide = 0.3) solutions with different  $r$ 's

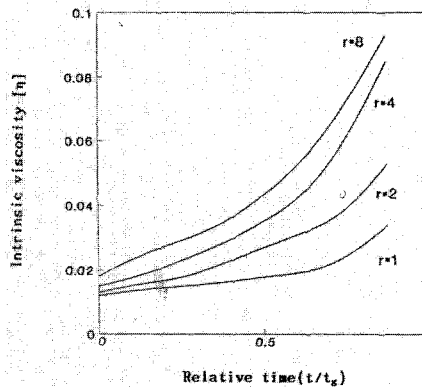


Fig. 5. Dependence of the intrinsic viscosity [ $\eta$ ] on the relative time ( $t/t_g$ ) for the benzene solutions of trimethylsilylated polymers from acid-catalyzed (the molar ratios HCl/alkoxide = 0.3 mol) alkoxide solution with different  $r$ 's

Table 2. The exponent  $\alpha$ 's for the polymer, properties of the mixed alkoxide solutions

Soluton	H <sub>2</sub> O(r)	$\alpha$	Type of polymer	Spinnability
1	1	0.56	Linear	Yes
2	2	0.81	Linear	Yes
3	4	0.41-0.51	Branched, Three-Dimensional particles	No
4	8	0.35	Three-Dimensional particles	No

No drastic change in  $\bar{M}_n$  with reaction time is observed for solution 1, while  $\bar{M}_n$  for solutions 3 and 4 increases more rapidly with the reaction time.  $\bar{M}_n$  vs.  $t/t_g$  plot for solution 2 has an induction period followed by a rapid increase up to about  $t/t_n = 0.64$ , which is then followed by the gradual increase.

Fig. 5 shows the variation of the intrinsic viscosity  $[\eta]$  of the benzene solutions of trimethylsilylated polymers from acid-catalyzed (the molar ratios HCl/alkoxide = 0.3 mol) solutions 1, 2, 3, and 4 with the reaction time  $t/t_g$ . The value of  $[\eta]$  has been estimated by extrapolating the  $(\eta_{sp}/C)$  vs.  $C$  plot to the  $C = 0$  axis[6]. Variation of the intrinsic viscosity  $[\eta]$  with the relative time  $t/t_g$  is shown for solutions 1, 2, 3, and 4. It can be seen that  $[\eta]$  of solutions 1 and 2 increases monotonously with increasing time, while  $[\eta]$  of solutions 3 and 4 gradually increases abruptly as the gelation point is approached.

### 3.3 The Relationship of the Intrinsic Viscosity and the Number Average Molecular Weight

The shape of particles formed in the solution can also be examined from the relation between the intrinsic viscosity,  $[\eta]$  and the number average molecular weight,  $\bar{M}_n$  in the course of gelation of the mixed alkoxide solutions with different water contents and a constant HCl content of HCl/alkoxide = 0.3. It is known that  $[\eta]$  of the polymer is related to  $\bar{M}_n$  by following equation:

$$[\eta] = K\bar{M}_n^\alpha$$

where  $K$  is a constant depending on the kinds of polymer, solvent, and temperature[14].

The exponent  $\alpha$ , the slope of the  $\log[\eta]$  vs.  $\log\bar{M}_n$  plot, takes a value between 0 and 2.0. The value depends on the shape of the polymer:  $\alpha = 0$  for the rigid spherical particles;  $\alpha = 0.5-1.0$  for the flexible, chain-like or linear polymer; and  $\alpha = 1.0-2.0$  for the non-flexible, or rigid, rod-like polymer[14].

Fig. 6 shows the  $\log\bar{M}_n$  vs.  $\log[\eta]$  plots. The slopes of the plots are larger than 0.5, that is, 0.56 and 0.81 for solutions 1 and 2, respectively, in which the water content is low. On the other hand,  $\alpha$  is smaller than 0.5, that is, 0.35 for solution 4 in which the water content is high. The slope for solution 3, which has an intermediate water content, is about 0.51 at the early stage of the hydrolysis polycondensation reaction and about 0.41 at the later stage, as have been reported for  $\text{Si}(\text{OC}_2\text{H}_5)_4$  solutions[14].

The above results are summarized in Table 2. Long-shaped particles are the main reaction products in solutions 1 and 2, which become spinnable. Three-dimensional polymers or particles are dominant in solutions 3 and 4, which do not show spinnability but from a large bulk gel.

### 4. Conclusion

The rheological properties were investigated for the sols and the metalloxane polymers derived from the mixed alkoxide solutions of  $\text{Si}(\text{OC}_2\text{H}_5)_4$  and  $\text{Zr}(\text{O}-\text{nC}_3\text{H}_7)_4$ .

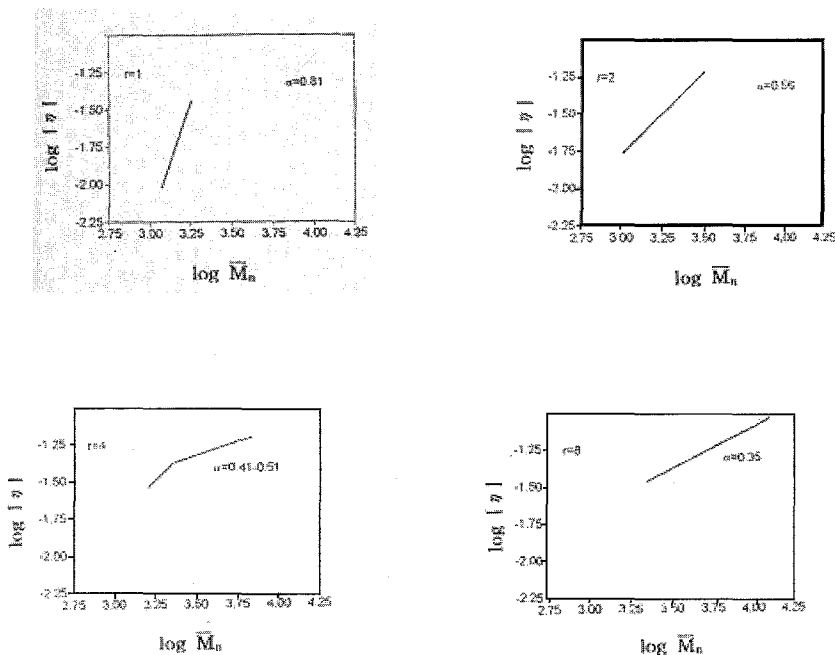


Fig. 6. The relationship the number the averagemolecular weight ( $\bar{M}_n$ ) and the intrinsic viscosity  $[\eta]$  of the trimethylsilylated polymers obtained from the alkoxide solutions of different  $r$ 's and a constant acid content of  $\text{HCl}/\text{alkoxide} = 0.3$

(1) The sols showed spinnability when the starting solutions were acid-catalyzed and contained small amounts of water, that is, where  $r(\text{H}_2\text{O}/\text{alkoxide}) \leq 2$ . When larger amounts of water or a basic catalyst were used, no spinnability was observed.

(2) Reduced viscosity and intrinsic viscosity were measured for the benzene solutions of trimethylsilylated polymers, and the molecular weight was measured for the trimethylsilylated polymers. Analysis on the relation between the reduced viscosity and the polymer concentration and the relation between the intrinsic viscosity and molecular weight showed that the spinnable sols consist of linear polymers, whereas non-spinnable sols contain three-dimensional particles.

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