

The effects of hydrolysis and condensation reactions of mixed $\text{Si}(\text{OC}_2\text{H}_5)_4$ and $\text{Zr}(\text{O}-n\text{C}_3\text{H}_7)_4$ solutions on the rheological behaviors and the structure of polymers in the silica-zirconia sol-gel process

Dae-Yong Shin*, Sang-Mok Han^a and Kyung-Nam Kim^b

Research Center for Advanced Mineral Aggregate Composite Products, Kangwon Nat'l Univ., Chuncheon 200-701, Korea

^aDept. of Advanced Materials Eng., Kangwon Nat'l Univ., Chuncheon 200-701, Korea

^bDept. of Advanced Materials Eng., Samcheok Nat'l Univ., Samcheok 245-711, Korea

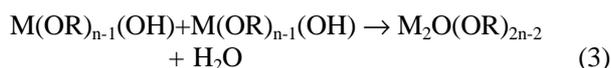
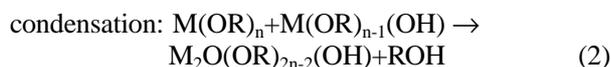
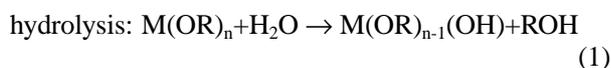
The hydrolysis and condensation reactions of mixed alkoxide solutions in the $\text{Si}(\text{OC}_2\text{H}_5)_4\text{-Zr}(\text{O}-n\text{C}_3\text{H}_7)_4\text{-H}_2\text{O}-\text{C}_2\text{H}_5\text{OH}-\text{HCl}$ system with $\text{H}_2\text{O}/\text{total alkoxide molar ratios}$ (r) from 1.0 to 8.0 were investigated by gas chromatography, the number average molecular weight (\overline{M}_n) and the intrinsic viscosity $[\eta]$ of the benzene solutions of the TMS polymers were measured. It is found that the amounts of evolved ethanol in the partial hydrolysis of $\text{Si}(\text{OC}_2\text{H}_5)_4$ reaches an equivalent values within 20 minutes, and do not depend on the temperature. In the mixed alkoxide solutions containing a large content of H_2O , the hydrolysis is fully completed, whereas the hydrolysis of solutions containing small contents of H_2O are not fully completed. Investigations on the relationship between (η_{sp}/C) and C or the relationship between $[\eta]$ and (\overline{M}_n) have made it clear that spinnable solutions have polymers with a linear structure and the non-spinnable solutions contain polymers with a 3-dimensional structure. It has been established that the spinnable solutions exhibit a Newtonian flow behavior up to high viscosities, where fibers can be drawn, while the non-spinnable solutions exhibit a structural viscosity.

Key words: Sol-gel process, Hydrolysis and condensation, Viscosity, Spinnability

Introduction

The basic principle of a sol-gel process is to form a solution of the desired compound in an organic solvent, polymerize the solution to form a gel, and dry and fire this gel to form a final product [1]. The typical precursors for preparing sol-gel solutions are metal alkoxides, of which the properties and reactions affect the process and determine the product features [2, 3].

Gelation, the transition from a solution into a solid, involves the hydrolysis and condensation of the metal alkoxides. These reactions are as follows:



where R is $\text{C}_n\text{H}_{2n+1}$. By the hydrolysis and condensation of the metal alkoxides the polymeric product formed is lead to the gelation of solution.

In the sol-gel process, the homogeneity of the gel is

very important in the further processing of the material. However, in the $\text{SiO}_2\text{-ZrO}_2$ system, the reactivity of zirconium alkoxides to hydrolysis is higher than that of silicon alkoxides because of the lower electronegativity of the zirconium atom and its tendency to exhibit multiple coordination states. Therefore, controlling the hydrolysis is required to obtain homogeneous gels, glasses and ceramics [2, 3]. This can be achieved by using chelating organic ligands, which control the hydrolysis rate of the more reactive alkoxide and the prehydrolysis of the slower-reacting component, such as silicon alkoxide.

In previous papers [4-10], the preparation conditions of several ceramics of the $\text{ZrO}_2\text{-SiO}_2$ system, and the effects of composition of the starting solution on the fiber drawing characteristics and on the structure of polymers were investigated. However, the effects of the hydrolysis and condensation reactions of the mixed $\text{Si}(\text{OC}_2\text{H}_5)_4\text{-Zr}(\text{O}-n\text{C}_3\text{H}_7)_4$ solutions on the rheological properties and the structure of polymers are not completely known as yet.

In this study, the hydrolysis and condensation reactions of mixed $\text{Si}(\text{OC}_2\text{H}_5)_4\text{-Zr}(\text{O}-n\text{C}_3\text{H}_7)_4$ solutions were studied using gas chromatography, and the effects of the hydrolysis and condensation of the mixed alkoxide solutions on the rheological properties and the structure of the polymers were investigated.

*Corresponding author:
Tel : +82-33-250-6261
Fax: +82-33-250-6260
E-mail: shinmater@hanmail.net

Experimental Procedure

Preparation of the mixed alkoxide solutions

Table 1 shows the compositions of the starting solutions for preparing the $30\text{ZrO}_2\cdot 70\text{SiO}_2$ gels. Several alkoxide- $\text{H}_2\text{O}-\text{C}_2\text{H}_5\text{OH}-\text{HCl}$ solutions with $\text{H}_2\text{O}/\text{total alkoxides}$ molar ratios (r) from 1.0 to 8.0 were prepared. The molar ratios of $\text{C}_2\text{H}_5\text{OH}$ and $\text{HCl}/\text{total alkoxides}$ were 1.0 and 0.3, respectively. $\text{Si}(\text{OC}_2\text{H}_5)_4$ was at first partially hydrolyzed by dropping it into the solution of HCl , $\text{C}_2\text{H}_5\text{OH}$ and $\text{H}_2\text{O}/\text{Si}(\text{OC}_2\text{H}_5)_4$ with molar ratios of 0.3, 1 and 1, respectively. After this the solution was stirred for 120 minutes, $\text{Zr}(\text{O}-n\text{C}_3\text{H}_7)_4$, the residual HCl , $\text{C}_2\text{H}_5\text{OH}$ and H_2O were added drop by drop, and then stirred for 120 minutes at 25°C . The solutions were kept standing at 25°C without cover.

Characterization

The partial hydrolysis of $\text{Si}(\text{OC}_2\text{H}_5)_4$ and the progression of hydrolysis and condensation of the mixed alkoxide solutions were examined as a function of the H_2O (r) content and the reaction time using gas chromatography. At approximately 20 minutes intervals the $5\ \mu\text{l}$ of sample solution was analyzed and methyl-ethylketone ($\text{CH}_2\text{COC}_2\text{H}_5$) was also tested as a standard solvent.

The metalloxane polymers in the solutions were stabilized by trimethylsilylation (TMS) in order to cap the reactive $-\text{OH}$ and $-\text{OR}$ groups, and dissolved into benzene to form a benzene solution. The number average molecular weight (\bar{M}_n) of the TMS polymers were estimated from the freezing point depression (ΔT_f) of the benzene solution calculated from the following equation, $\bar{M}_n = K_f \cdot 100 \cdot g / (G \cdot \Delta T_f)$: where g ; the weight of the TMS polymers, G ; the weight of benzene and K_f ; the freezing point depression constant for benzene, 5.12. The viscosities of the benzene solutions of the TMS polymers were measured by an Ostwald viscometer as a function of the concentration C in the range of 1-10 g/dl at 25°C . The relative viscosity (η_{rel}) could be converted to the specific viscosity ($\eta_{\text{sp}} = \eta_{\text{rel}} - 1$) and to the reduced viscosity (η_{sp}/C). Extrapolation of the plot of (η_{sp}/C) against C gives $[\eta]$. The rheological properties such as viscosity changes with shear rate and this effect on the structure of the polymers and the occurrence of spinnability of the solutions were measured by

a concentric cylinder viscometer.

Results and Discussion

The condensed polysilicates are formed by a complex sequence of reactions. First, $\text{Si}(\text{OR})_4$ is hydrolyzed as in eq. (1). The polysilicates are then formed through condensation according to eq. (2) and (3). The hydrolysis and condensation steps are repeated alternately until the ultimate molecular weight is reached and all the H_2O is consumed. In reality, the reactions of eq. (1), (2) and (3) occur simultaneously and are in general not completed [1, 9].

In general, the evolved ethanol can be taken as a measure of the progress of hydrolysis of $\text{Si}(\text{OC}_2\text{H}_5)_4$ [11, 12]. Figure 1 shows the volume percentage of evolved ethanol in the partial hydrolysis of $\text{Si}(\text{OC}_2\text{H}_5)_4$ as a function of reaction time and temperature. It is confirmed that by comparison to the standard solvent, the peaks observed in the gas chromatography results are only due to ethanol. In all cases, the volume percentage of evolved ethanol reaches an equivalent value within 20 minutes. Although the plateau of ethanol level is somewhat varied as temperatures are changed, there are no significant variations. The partial hydrolysis of $\text{Si}(\text{OC}_2\text{H}_5)_4$ does not depend on the temperature.

Figure 2 shows the amount of each compound in the partial hydrolysis of $\text{Si}(\text{OC}_2\text{H}_5)_4$ and the hydrolysis of mixed alkoxide solutions with different reaction time

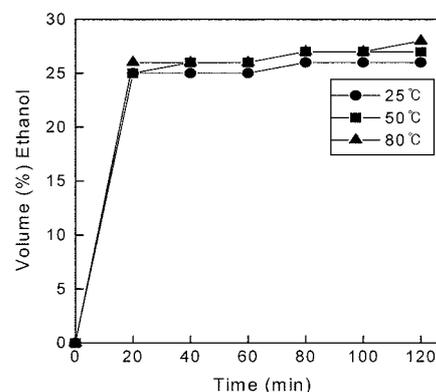


Fig. 1. Volume percentage of the evolved ethanol in the partial hydrolysis of $\text{Si}(\text{OC}_2\text{H}_5)_4$ with reaction time and temperature.

Table 1. Compositions and gelation time of the starting solutions

Solution	Composition of Solution					Gelation Time (h)
	$\text{Si}(\text{OC}_2\text{H}_5)_4$	$\text{Zr}(\text{O}-n\text{C}_3\text{H}_7)_4$	H_2O (r)	$\text{C}_2\text{H}_5\text{OH}$	HCl	
1			1			4.8
2			2			3.5
3	0.7	0.3	4	1	0.3	2.3
4			8			0.3

$\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH}:\text{HCl}$; the molar ratios of the total alkoxides

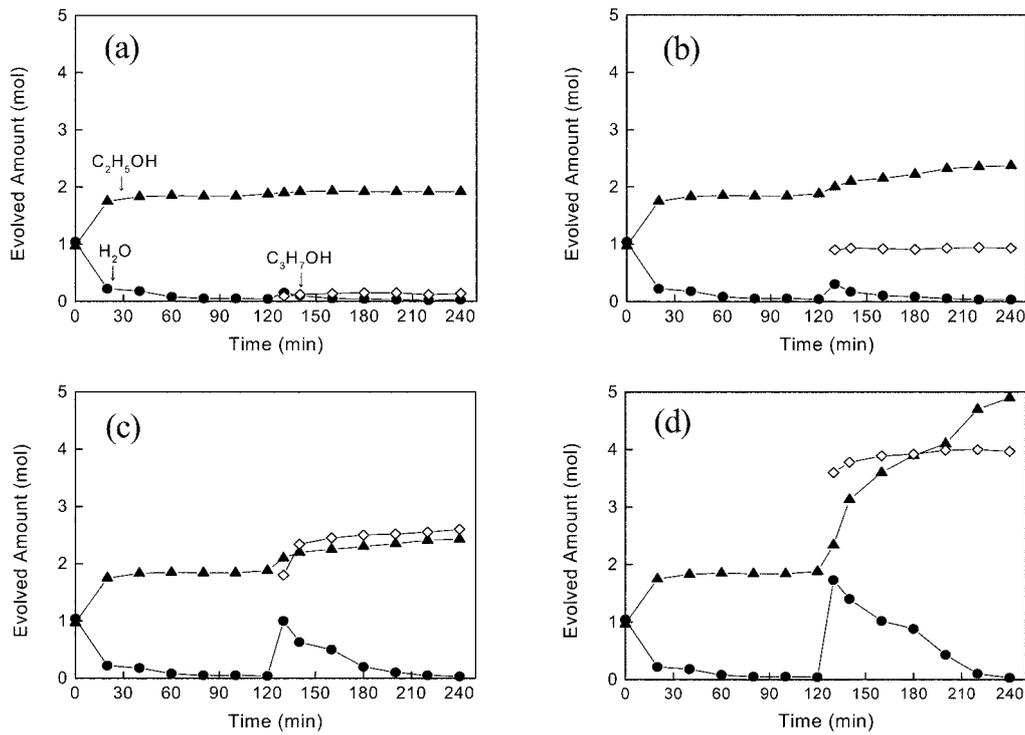
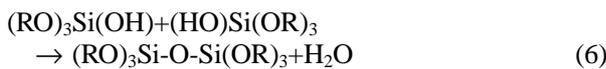
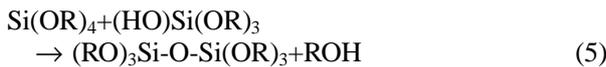


Fig. 2. The amounts of compounds in the partial hydrolysis of $\text{Si}(\text{OC}_2\text{H}_5)_4$ and the hydrolysis of the mixed alkoxide solutions with reaction time and content of H_2O (r). (a) $r=1$, (b) $r=2$, (c) $r=4$ and (d) $r=8$.

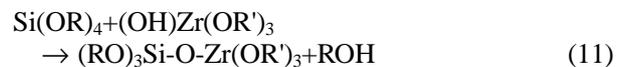
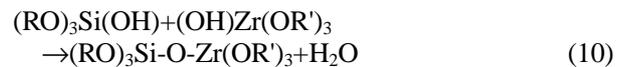
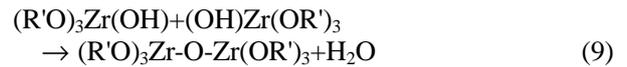
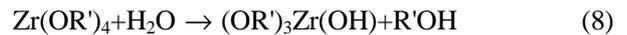
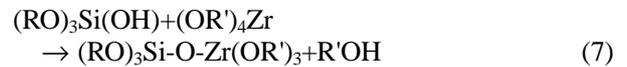
and the contents of H_2O (r) at 25°C . The amounts of H_2O and $\text{C}_2\text{H}_5\text{OH}$ changed as the reaction time elapsed.

The partial hydrolysis and condensation reactions of $\text{Si}(\text{OC}_2\text{H}_5)_4$ may be represented as follows [9];



The total amount of evolved ethanol in the partial hydrolysis of $\text{Si}(\text{OC}_2\text{H}_5)_4$ was both from the hydrolysis in eq. (4) and from that liberated by the condensation in eq. (5). Theoretically, the hydrolysis of $\text{Si}(\text{OR})_4$ in 4 mol of H_2O forms $\text{Si}(\text{OH})_4$ and 4 mol of ROH as the products. However, when the partial hydrolysis of $\text{Si}(\text{OC}_2\text{H}_5)_4$ was carried out in 1 mol of H_2O , partly hydrolyzed and condensed silicates $[(\text{RO})_3\text{Si}(\text{OH})]$ are produced as in eq. (4). The polysilicates $[(\text{RO})_3\text{Si}-\text{O}-\text{Si}(\text{OR})_3]$ were then formed through the condensation of either $(\text{RO})_3\text{Si}(\text{OH})$ or $(\text{RO})_3\text{Si}(\text{OH})$ and $\text{Si}(\text{OR})_4$. The polysilicates are formed by a complex sequence of reactions in eq. (5) and (6). However, the amount of H_2O decreased with an increase in the reaction time as shown in Fig. 2. Therefore, the Si-O-Si bonding is completed not by eq. (6) but by eq. (5). It can be suggested that about 3/4 of the unreacted $\text{Si}(\text{OR})_4$ still remains in the solution, and the hydrolysis of $\text{Si}(\text{OC}_2\text{H}_5)_4$ is not completed.

$\text{Zr}(\text{O}-n\text{C}_3\text{H}_7)_4$ reacts with the end or the side silanol ($\text{Si}-\text{OH}$) groups of the siloxane polymers to produce co-polymerized products as in the following reactions;



where R' is C_3H_7 . When $\text{Zr}(\text{O}-n\text{C}_3\text{H}_7)_4$ is added to the partial hydrolyzed $\text{Si}(\text{OC}_2\text{H}_5)_4$ solution, $\text{Zr}(\text{OR}')_4$ or $\text{Zr}(\text{OH})_{4-n}(\text{OR}')_n$ species react with $(\text{RO})_3\text{Si}(\text{OH})$ or $\text{Si}(\text{OR})_4$ and the polycondensation occurs simultaneously as in eq. (7)-(11). With solution 4 (Table 1, $r=8$), the hydrolysis is fully completed and the amounts of ROH (ethanol) and $\text{R}'\text{OH}$ (n -propanol) are increased. However, the hydrolysis of solutions 1, 2 and 3 (Table 1) are not fully completed because the contents of H_2O are small ($r=1, 2$ and 4). The amounts of evolved ethanol and n -propanol from the solutions 1, 2 and 3 are smaller than those from solution 4.

$\text{Zr}(\text{O}-n\text{C}_3\text{H}_7)_4$, which causes the self-polymerization according to eq. (9), results in the precipitation of zirconium hydroxide. However, in the present study,

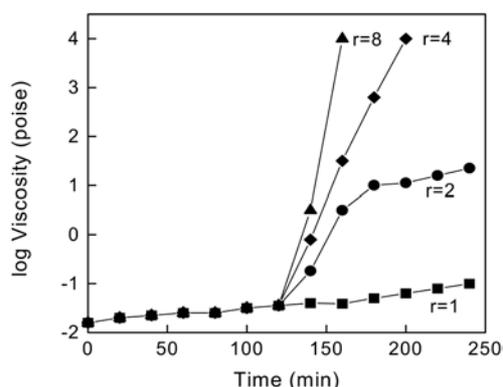


Fig. 3. Changes of the viscosities of the benzene solutions of TMS polymers with reaction time and content of H_2O (r).

the reaction of eq. (9) did not occur because zirconium hydroxide was not precipitated.

The polymeric solutions resulting from this method are clear, and the gelation occurs in a few hours continued polymerization. It was suggested that $\text{Zr}(\text{O}-n\text{C}_3\text{H}_7)_4$ should be reacted with the partially hydrolyzed $\text{Si}(\text{OC}_2\text{H}_5)_4$.

The mixed alkoxide solutions become viscous and sticky with increasing reaction time as a result of the polymerization of alkoxides. The gelation time of mixed alkoxide solutions depends on the contents of H_2O (r) as shown in Table 1. Large amounts of H_2O accelerate the gelation of the sol, when HCl was used as a catalyst [6]. Solutions 1 and 2 exhibit spinnability and solutions 3 and 4 show no spinnability before the gelation.

Figure 3 shows the changes of viscosities of the benzene solutions of the TMS polymers as a function of different contents of H_2O (r) and reaction time. The viscosity is not drastically changed in solution 1 as the reaction time is increased because the hydrolysis and condensation could be suppressed by the limited content of H_2O . In solution 2, the viscosity rises gradually and the increasing rate of viscosity decreases remarkably

after the viscosity reaches about 10 poise, which makes it possible to draw fibers. The decrease in the rate of increase of the viscosity can be attributed to the exhaustion of H_2O in the solution required for the hydrolysis reaction [6, 10]. The viscosity of solution 2, however, continues to increase at a low rate. This is thought to be caused by the absorption of moisture from the air [6, 10]. Solutions 3 and 4 are not spinnable and the viscosities increase sharply from the beginning of the reaction in comparison with solution 2. This viscosity increase is ascribed to the formation of polymeric oligomers by the hydrolysis and condensation of the mixed alkoxides, and should depend on the degree of polymerization.

The reduced viscosity (η_{sp}/C) of the polymeric solutions can be expressed by the following Huggins' equation [13], if the structure of polymers in the solution is the linear, $\eta_{sp}/C = [\eta] + K[\eta]^2C$: where K is the proportionality constant, and C is the concentration of polymer, defined usually as g/dl solution. This formula indicates that for the case of polymers with a linear structure, (η_{sp}/C) vs. C plot is a straight line with a slope of $K[\eta]$. On the other hand, (η_{sp}/C) of the solutions containing particles or polymers with a 3-dimensional structure is expressed by Einstein's equation [13], $\eta_{sp}/C = K/\rho$: where K is a constant and ρ is the density of particles or polymers. This formula indicates that (η_{sp}/C) is not dependent on C in the case of particles or 3-dimensional polymers and is expressed by a straight line parallel to the C axis.

Figure 4 shows (η_{sp}/C) vs. C plots of the benzene solutions of the TMS polymers obtained from solutions 2 and 4. It shows that the plots for polymers in solution 2 are straight lines with various values of the slope, indicating that the long shaped particles and linear structures included in the solution allow spinnability. For solution 4, there are no slopes in the plots indicating that the 3-dimensional structure of polymers in the solution do not permit spinnability.

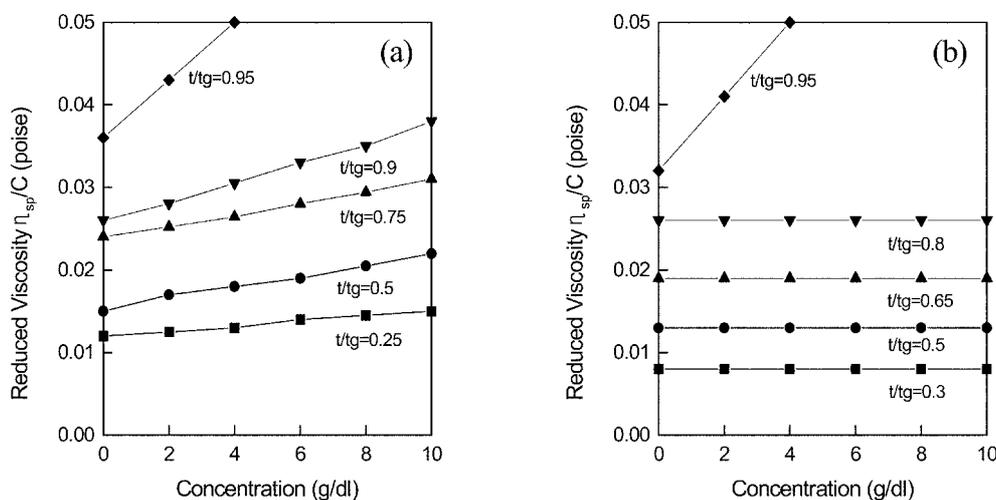


Fig. 4. Relationship between (η_{sp}/C) and (C) of the benzene solutions of TMS polymers in (a) solution 2 and (b) solution 4.

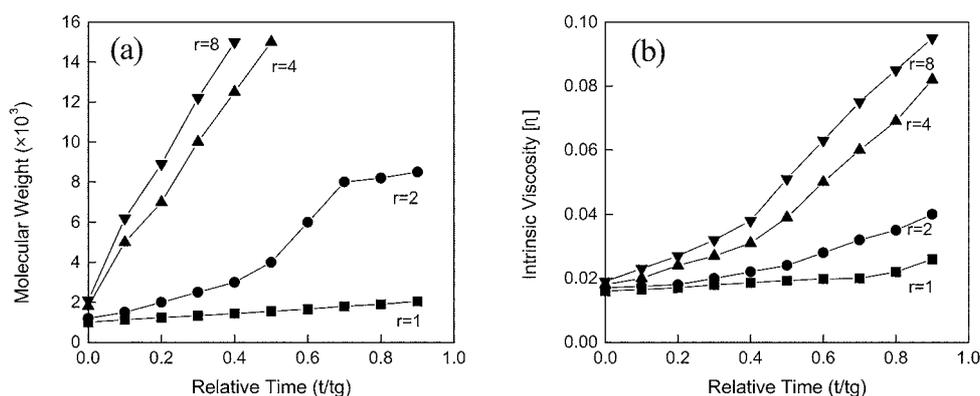


Fig. 5. Changes of (a) (\bar{M}_n) and (b) $[\eta]$ of the benzene solutions of TMS polymers with (t/tg) and content of H_2O (r).

Figure 5 shows the changes of (\bar{M}_n) (a) and $[\eta]$ (b) of the benzene solutions of the TMS polymers according to the relative time (t/tg) and the contents of H_2O (r). (\bar{M}_n) is not drastically changed with increasing reaction time in solution 1, while (\bar{M}_n) increase more rapidly with (t/tg) in solutions 3 and 4. (\bar{M}_n) in solution 2 has an induction period followed by a rapid increase up to about $t/tg=0.7$, and then by a gradual increase. The $[\eta]$ is estimated by extrapolating (η_{sp}/C) vs. C plot to the $C=0$ axis [13]. It can be seen that $[\eta]$ of solutions 1 and 2 increase monotonically with increasing time, while $[\eta]$ of solutions 3 and 4 gradually increase at small values of (t/tg) up to about 0.4 and then increase abruptly as the gelation point is approached.

The structure of polymers formed in solution can also be examined from the relationship between $[\eta]$ and (\bar{M}_n) during gelation of the mixed alkoxide solutions with different contents of H_2O (r). It is known that $[\eta]$ of the benzene solutions of the TMS polymers are related to (\bar{M}_n) by the following equation [13], $[\eta]=K\bar{M}_n^\alpha$: where K is a constant depending on the type of polymer, the solvent and temperature. The exponent α , the slope of $\log[\eta]$ vs. $\log(\bar{M}_n)$ plot, depends on the structure of the polymer; $\alpha=0$ for a rigid spherical particles or a 3-dimensional structure, $\alpha=0.5-1.0$ for a flexible, linear polymer and $\alpha=1.0-2.0$ for a non-

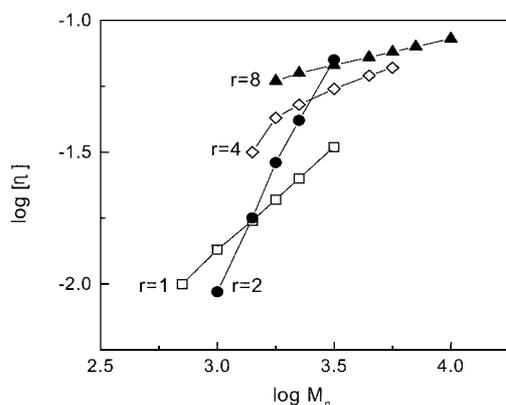


Fig. 6. Relationship between (\bar{M}_n) and $[\eta]$ of the benzene solutions of TMS polymers with content of H_2O (r).

Table 2. Exponent α 's for the structure of polymers with contents of H_2O (r)

Solution	H_2O (r)	α	Type of Polymers
1	1	0.56	Linear
2	2	0.81	Linear
3	4	0.41, 0.51	Branched, 3-dimensional particles
4	8	0.35	3-dimensional particles

flexible or rigid, rod-like polymer [13].

Figure 6 shows $\log[\eta]$ vs. $\log(\bar{M}_n)$ plots. The slopes of these plots are 0.56 and 0.81, respectively in solutions 1 and 2 ($r=1$ and 2), while it is 0.35 in solution 4 ($r=8$). The slope in solution 3 ($r=4$) is about 0.51 in the early stages and about 0.41 for the later stages of the reaction.

The above results are summarized in Table 2. The polymers with a linear structure are the main reaction products in solutions 1 and 2, which become spinnable. Polymers with a 3-dimensional structure are dominant in solutions 3 and 4, which do not show spinnability but form large bulk gels.

Figure 7 shows the viscosity as a function of the shear rates for the benzene solutions of the TMS polymers. Fibers, which are drawn from solution 2 ($r=2$) exhibiting spinnability, show a Newtonian behavior up to high viscosities, whereas solution 4 ($r=8$) shows non-spinnability and exhibits structural viscosity. The spinnable solution contains linear polymers and these polymers are not entangled because of the non-flexible nature of inorganic fibrous particles [14]. The non-spinnable solutions contain polymers with a 3-dimensional structure and these polymers show a non-elastic nature because of the formation of network structures.

Conclusions

The amounts of evolved alcohol can be taken as a measure of the progress of the hydrolysis and condensation reactions of the mixed alkoxide solutions. The volume percentage of evolved ethanol in the partial hydrolysis of $Si(OC_2H_5)_4$ reaches an equivalent value within 20 minutes and does not depend on the temper-

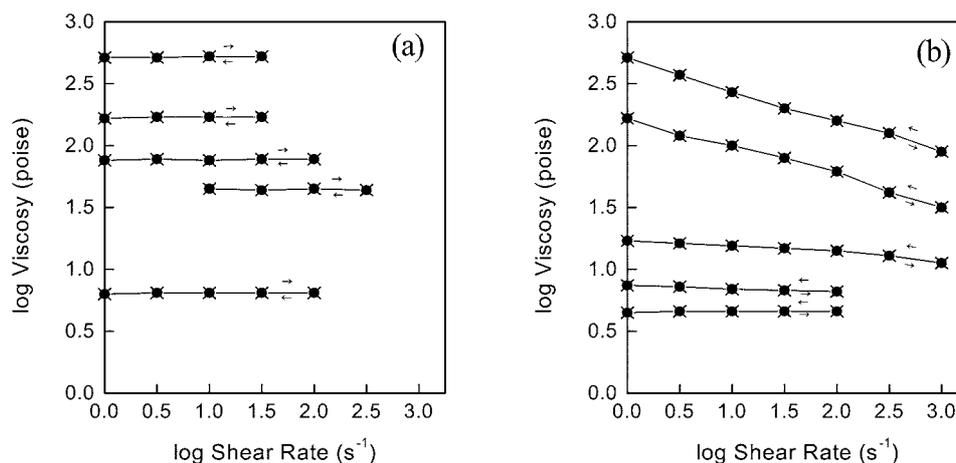


Fig. 7. Viscosity changes of the benzene solutions of TMS polymers with shear rates in (a) solution 2 ($r=2$) and (b) solution 4 ($r=8$). ● ; measurement on increasing shear rate, ×; measurement on decreasing shear rate.

ature. The partly hydrolyzed and condensed silicates $[(\text{RO})_3\text{Si}(\text{OH})]$ are produced during the hydrolysis of $\text{Si}(\text{OC}_2\text{H}_5)_4$ and the polysilicates $[(\text{RO})_3\text{Si}-\text{O}-\text{Si}(\text{OR})_3]$ are then formed through condensation. When $\text{Zr}(\text{O}-n\text{C}_3\text{H}_7)_4$ is added to the partial hydrolysed $\text{Si}(\text{OC}_2\text{H}_5)_4$ solution, $\text{Zr}(\text{OR}')_4$ or $\text{Zr}(\text{OH})_{4-n}(\text{OR}')_n$ species react with $(\text{RO})_3\text{Si}(\text{OH})$ or $\text{Si}(\text{OR})_4$ and the polycondensation occurs simultaneously. In the solution containing a large content of H_2O , the hydrolysis is fully completed, whereas the hydrolysis of a solution containing a small content of H_2O is not fully completed. The viscosity behaviors of the solutions are a measure of the rate of the hydrolysis and condensation reactions. Solutions containing small contents of H_2O exhibit spinnability at viscosities above 10 poise and become drawable into gel fibers, whereas no spinnability appears in the solution containing a large amount of H_2O . The investigations on the relationship between (η_{sp}/C) and C or the relationship between $[\eta]$ and (\bar{M}_n) have made it clear that spinnable solutions contain polymers with a linear structure and the non-spinnable solutions have polymers with a 3-dimensional structure. It has been established that the spinnable solutions exhibit a Newtonian flow behavior up to the high viscosities, where fibers can be drawn, while the non-spinnable solutions exhibit structural viscosity.

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