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〈연구논문〉

테트라에톡실란의 졸-겔 전이중 구조생성

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Structural Evolution during the Sol-Gel Transition of Tetraethoxysilane

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요 약

물량 및 촉매를 변화시키며 TEOS 용액에 대하여 점도를 측정하였다. 염기성 촉매를 사용한 TEOS 용액은 구형 입자를 갖는 것으로 나타났다. 적은 초기 물량과 산성 촉매를 사용한 TEOS 용액은 환원 점도의 실험결과로 미루어 선형의 고분자를 갖고 있는 것으로 보인다. 반면 많은 물량과 산성 촉매를 사용한 TEOS 용액은 많은 가지 사슬을 갖는 비선형 입자를 형성하는 것으로 사료된다. 적은 물량의 산성 촉매에서 생성하는 선형 고분자 구조는 삼중 규소 연쇄의 리본 형태로 생각된다.

Abstract — The viscosity was measured for a tetraethoxysilane (TEOS) solution with different water content and catalyst. A base catalyzed TEOS solution was shown to have spherical particles. An acid catalyzed TEOS solution with a low water content has been judged to form linear polymers from the analysis of reduced viscosity. However, the TEOS solution with a high water content is supposed to form highly branched polymers because the reduced viscosity is almost independent of the SiO_2 concentration. It is suggested that the formation of silicon oxides is based on a ribbon of three joined siloxane chains.

Keywords: TEOS/ Reduced viscosity/ Sol-gel/ Three chain ribbon

INTRODUCTION

Alkoxide method can produce various oxide-glasses which are not easily prepared by the conventional melting technique. Gel synthesis by hydrolysis and condensation of metal alkoxides allows the preparation of homogeneous and high purity inorganic polymers. Hence, the interest in the sol-gel process has grown in recent years. But a great deal of understanding of sol to gel transformation is still necessary for the application of various practical usages. A few works have been reported on the sol-gel transition of metal alkoxides [1-3]. Tetraethoxysilane (TEOS) is readily hydrolyzed by water and produces an amorphous silica gel. The structure of a gel is affected by preparation conditions, such as pH, concentration of starting material and rates of hydrolysis and condensation reaction, etc. Therefore, silica glass has been produced by the alkoxide method as fibers, thin films, coating films and monolithic bodies according to the preparation conditions [4, 5].

In this study, the transition behavior is investigated for different alkoxide compositions. Some of them are suitable for the preparation of fibers and others for monolithic bulk bodies.

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Table 1. Compositions of samples for the measurement of viscosity.

Sample	TEOS g	H_2O g	C_2H_5OH g	Mol. rat. H_2O/TEOS	SiO_2 g/100 cc	Cat*
V-1	93.3	16.1	20.6	2	18.9	HCl
V-2	65.3	113.0	14.4	20	9.4	HCl
V-3	130.6	22.8	28.9	2	18.9	NH_4OH

* Molar ratio of HCl or NH_4OH to TEOS is 0.03

Table 2. Compositions of samples for the capping of polymers.

Sample	TEOS g	H_2O + HCl g	C_2H_5OH* g	Mol. ratio. H_2O/TEOS	Temper. °C
C-1	144.2	25.0 (pH = 0.9)	108.1	2	30
C-2	144.2	25.0 (pH = 3.0)	108.1	2	30
C-3	186.6	64.6 (pH = 1.2)	107.1	4	30

* Ethanol was added to solution in order to maintain 15 SiO_2 wt%

EXPERIMENTAL

Measurements of Viscosity

Sample preparation

TEOS was supplied by Alfa Products. Ethanol was used as a solvent and HCl or NH_4OH as a catalyst. The compositions specific for the experiment are listed in Table 1. Water contents were adjusted to make the molar ratio of water to TEOS 2 and 20. The latter corresponds to the sufficient water content required for the complete hydrolysis of TEOS. Two solutions, TEOS solution with ethanol (1/2 molar ratio to TEOS) and the mixture of water, ethanol and HCl or NH_4OH, were mixed under stirring and made the total molar ratio of ethanol to TEOS unity. These operations were carried out at room temperature in a flask equipped with reflux condenser and magnetic stirrer. After 30 minutes stirring, the hydrolyzed solutions were maintained in an oven at 50-55°C until gelation.

Measurement of viscosity

The viscosity of an alkoxide solution was measured at 30°C. An Ostwald type viscometer was used to measure the viscosity below 10 poise and a Brookfield rotational viscometer (Medel RVT, Brookfield Engineering, U.S.A) above 10 poise.

Determination of an intrinsic viscosity

Huggins equation is used to calculate the intrinsic viscosity of a dilute solution[6]:

$$\eta_{sp}/C = [\eta] + k[\eta]^2C \quad (1)$$

where η_{sp}, $[\eta]$, k and C are the specific viscosity, the intrinsic viscosity, constant and the concentration of a solute, respectively. The unit of concentration is usually grams in 100 cm^3 solution. This equation is applied when the solute is assumed to be like a linear chain polymer. On the other hand, Einstein relation[7] is applied when the solute is like a spherical particle:

$$\eta_{sp}/C = K/\rho \quad (2)$$

where K is a constant, ρ is the particle density. Therefore it will be possible to predict the shape of a solute molecule in an alkoxide solution by plotting the variation of the reduced viscosity as a function of the concentration. Anhydrous ethanol (99.9%) was used for the dilution of a sampled solution.

Structures of Polymers

Sample preparation

The sample compositions are listed in Table 2. The materials and the procedure of sample preparation are the same as those in section 1.1 except that the solutions were maintained at 30°C.

Capping of silanol groups

A portion of solution was taken at an arbitrary time interval. Trimethylchlorosilane ($(CH_3)_3SiCl$) was used as a capping reagent. The capping proce-

dure followed the Bechtold experiment [8]. The mixture of equal weights of hydrolysate and $(CH_3)_3$ SiCl was stirred overnight at room temperature and the water insoluble was separated, washed with water and then dried. The capping reaction between hydrolysate and capping reagent is as follows:

$$Si(OC_2H_5)_a\ (OH)_bO_{(4-a-b)/2} + b\ (CH_3)_3\ SiCl \rightarrow$$

$$b\ HCl + Si\ (OC_2H_5)_a\ (OSi\ (CH_3)_3)_bO_{(4-a-b)/2} \quad (3)$$

The capping reaction is fast and complete even in the presence of large amounts of alcohol and water. A large amount of HCl do not change the structure or molecular weight of silicates [9].

Gas chromatography

GC-HP-5840A was used to measure the content of H_2O and C_2H_5OH in the solution and to monitor Si-OC_2H_5/Si and Si-OH/Si during gelation. All reactions of samples were performed in pyrex tubues with septum caps. While the reaction proceeds in the water bath, samples for gas chromatography (GC) were with-drawn through the septum cap. The column was 6 ft × 1/8 inch OD SS and the packing material was Porapak Q.A thermal conductivity detector was used for measuring the amounts of components in the helium carrier gas. The peak area were automatically calculated and converted to the weights of components using a calibration curve.

Number average molecular weight

Cryoscopy in benzene was used to determine the number average molecular weight, Mn, of the solute. Mn was calculated from the following equation: Mn = Cf*1000*g/(G*DT), where Cf is the freezing point depression constant, g is the weight of solute, G is the weight of solvent and DT is the freezing point depression. Cf is 5.12 for benzene.

RESULTS AND DISCUSSION

Appearance and Viscosity Change of Solution during the Sol-Gel Transition

The sample V-1 and V-2 solutions remained clear during the reaction. Solution V-3, however, became cloudy and had slightly cloudy precipitates during the reaction time. This may suggest that colloidal particles are involved in the base catalyzed solution. It has been known that spherical colloidal particles are fromed when the reaction of TEOS is carried out with the base catalyst. Nogami and Moriya [10] observed spherical SiO_2 particles in the gel produed from TEOS catalyzed by NH_4OH. Stober *et al* [11] prepared colloidal SiO_2 spheroids from TEOS by hydrolysis with NH_4OH.

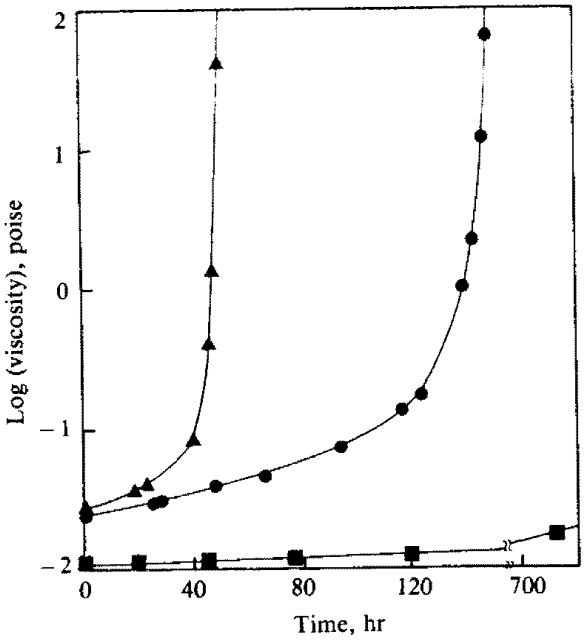

Fig. 1. Viscosity change of TEOS solutions with time. ●Sample V-1, ▲Sample V-2, ■ Sample V-3

Viscosity was measured on the sample withdrawn at an arbitrary time interval and plotted in Fig. 1. It is shown that the viscosity of V-1 and V-2 increases gradually in an initial stage and then abruptly near the gelling point. However, no gelation is observed for V-3 solution within a given time. Since the solution V-3 is kept in a closed reactor, it seems that V-3 contains the colloidal particles. In the colloidal systems, gelation is a resultant of the evaporation of solvent and the interparticle distance narrowness. The solution V-2 shows the gelation in a shorter time than other solutions despite of low SiO_2 concentraction. This means that the gelation of solution is affected largely by the water content as well as the type of catalysts.

Reduced Viscosities

The reduced viscosity (η_{sp}/C) of sample V-1 shows slightly dependence on SiO_2 concentration in the early stage of the reaction, but much depen-

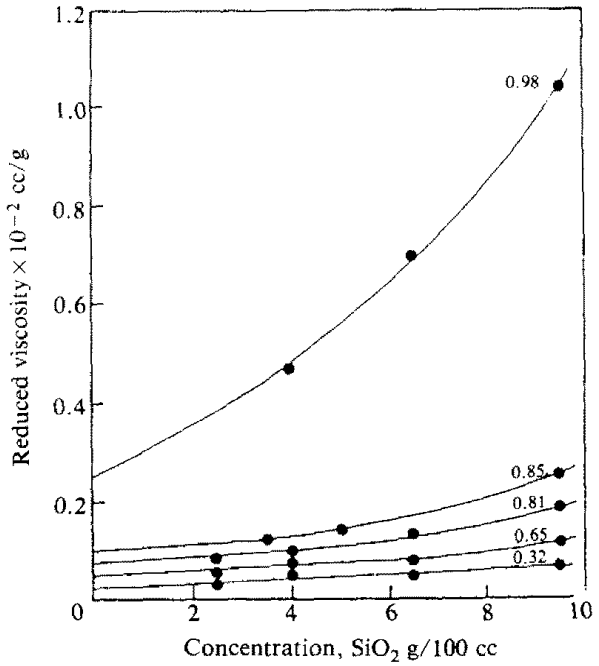

Fig. 2. Reduced viscosities plotted against oxide concentration for sample V-1 (R = 2). The attached numbers denote the relative reaction time to the gelling time, t/t_g.

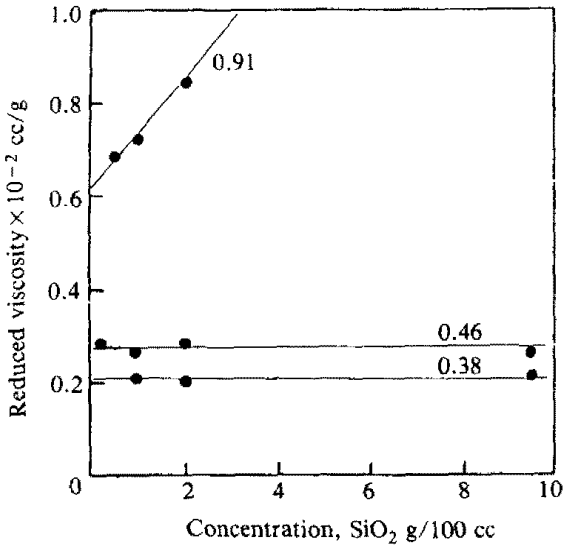

Fig. 3. Reduced viscosities plotted against oxide concentration for sample V-2 (R = 20). The attached numbers denote the relative reaction time to the gelling time, t/t_g.

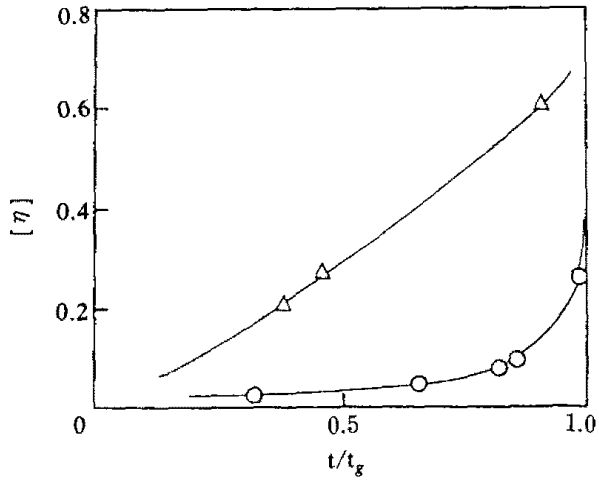

Fig. 4. Intrinsic viscosity, $[\eta]$ of TEOS solutions with the relative reaction time to the gelling time, t/t_g.
○ Sample V-1, △ Sample V-2

dence in the later stage as shown in Fig. 2. According to Huggins equation as described before, it may suggest that the product in the solution is not a spherical particle but a linear chain molecule. However, for the sample V-2, as shown in Fig. 3, the reduced viscosity does not change with the concentration although the intrinsic viscosity is relatively large, whereas it increases with the concentration near the gelling point showing the aggregation of discrete particles. This may suggest that the TEOS solution with a high water content contains highly condensed clusters rather than chain-like structures and has a high intrinsic viscosity. Fig. 4 shows the variation of the intrinsic viscosity with the relative reaction time to the gelling time for the TEOS solutions with different water contents. The increase of the intrinsic viscosity with time implies that the size of particles or the degree of polymerization increases with time. Therefore it is supposed that an acidified solution with a high water content has larger or more highly branched structure molecules than that with a low water content. It is, however, difficult to give an exact explanation to the type of structure produced in solution V-2.

Structure Model of Polymeric Particles

Generally, it has been shown that the alkoxide solution becomes spinnable when the content of water used for hydrolysis is low and the catalyst is acid[4]. It has also been found that only the solutions containing linear polymers were spinnable. Hirai [12] examined the occurrence of spinnability in many kinds of polymer solutions and came to the conclusion that only the solutions containing linear polymers were spinnable. It is very important which type of structure is formed during the reaction of metal alkoxide solution. It could be noted that the usage and properties of products obtained from metal

Table 3. Properties of capped polymers.

Sample	Time, hr	Mn	DP_n	$SiOC_2H_5/Si$	SiOH/Si	State*
C-1	1.5	900	6.1	1.11	0.5	L
	23.0	1120	9.5	0.9	0.31	L
	44.3	1170	10.5	0.85	0.25	L
	94.4	1330	12.4	0.82	0.19	L
	146.5	1420	13.4	0.82	0.21	L
	358.2	1500	14.4	0.74	0.21	S
C-2	1.2	1343	6.6	0.81	1.4	S
	42.3	2200	18.1	0.54	0.51	S
	141.4	3110	26.4	0.52	0.46	S
	186.6	3580	27.9	0.5	0.48	S
	214.7	4570	47.5	0.48	0.42	S
C-3	1.1	520	3.0	2.56	0.15	L
	144.3	1390	14.1	0.85	0.1	L
	360.6	2200	21.9	0.81	0.11	S

* S: Solid, L: Liquid

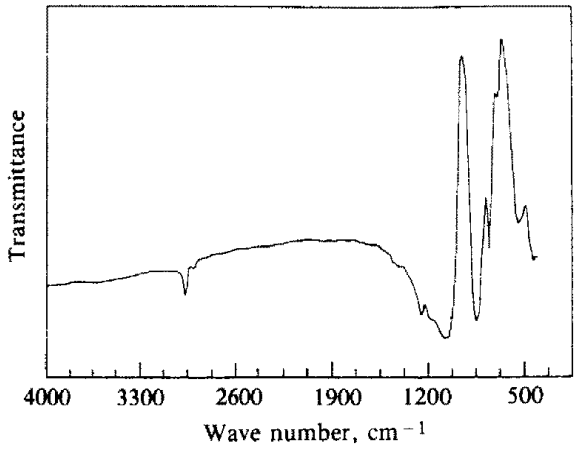

Fig. 5. IR spectrum of the capped polymer.

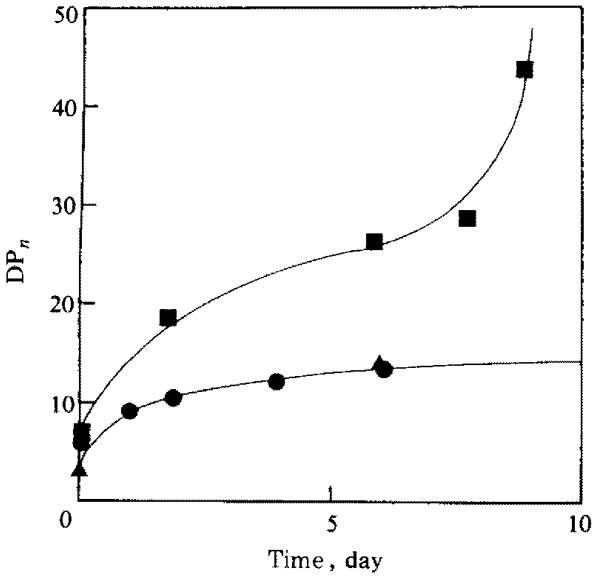

Fig. 6. Degree of polymerization, DP_n, vs. time for the TEOS solutions.
● Sample C-1, ▲ Sample C-2, ■ Sample C-3

alkoxide solution depend on the process of structure growth during sol-gel transition. Unfortunately, the nature of the polymeric particles is not exactly known yet; it is not known yet whether they have linear chains, branched chains, or linear aggregates of fine and round beads.

The infrared spectrum of the capped mixture is shown in Fig. 5. Major peak bands are assigned to CH (2900-3000 cm^{-1}), Si-CH_3 (1255, 758, 850 cm^{-1}), Si-O (1085 cm^{-1}) and Si-O-Si (465 cm^{-1}). The curve shows no absorption for hydroxyl group. The values of Si-OH/Si and Si-OC_2H_5/Si obtained from GC analysis and number average molecular weights obtained from cryoscopic method for the capped polymers are shown in Table 3. DP_n denotes number average degree of polymerization calculated from the following stoichiometry equation:

$$n\ Si(OR)_4 + n\ (4-a+b)/2\ H_2O \longrightarrow n(4-a)\ ROH + n\ Si(OR)_a\ (OH)_b\ (O)_{(4-a-b)/2} \quad (4)$$

where R is C_2H_5 and a and b are the numbers of Si-OR and Si-OH per unit Si, respectively. Provided that the amounts of water and ROH were known, the values of a and b can be calculated by setting the molar consumption and production of water and ROH

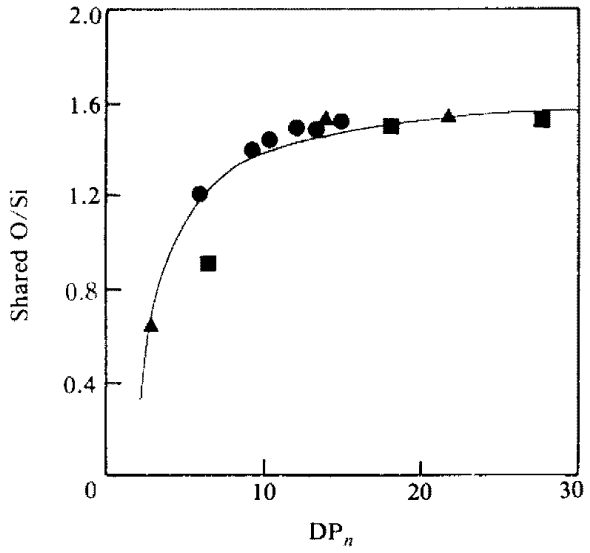

Fig. 7. Increase of shared oxygen with degree of polymerization, DP_n, in TEOS solutions. Continuous line denotes the theoretical values assuming the three-chain ribbon.
● Sample C-1, ▲ Sample C-2, ■ Sample C-3

per TEOS equal to (4-a + b)/2 and (4-a), respectively. Therefore, DP_n may be obtained by dividing the number average molecular weight of capped polymer by the weight of monomer. The monomer formula may be described as follow from eq. (3)

$$Si\ (OC_2H_5)_a\ (OSi\ (CH_3)_3)_bO_{(4-a-b)/2} \quad (5)$$

Fig. 6 shows the plot of DP_n vs. time. For the case of samples C-1 and C-2, the initial part of the curve is concave downward, indicating the insufficient number of functional groups for the gelation. The early steep slope confirms a rapid precondensation and the polymerization proceeds until the gelation as hydrolysis is going on slowly. For the case of sample C-3, since the gelation occurs at around 200 hrs and the curve becomes concave upward, the functionality of the monomer must be more than two. Polymerization proceeds continuously because the slope of the line increases continuously. A plot of shared O/Si vs. DP_n is shown in Fig. 7. It is seen that the data fit mostly the theoretical values derived from three Si unit chains which is shown as a continuous line. This tendency is in agreement with the result reported by Bechtold *et al*[8]. The theoretical values are calculated from the following equation.

$$DP_n = 3/(1.667\text{-}O/Si) \quad (6)$$

However, there is another possibility of four-chain ribbon, because it also fits relatively well. Further data will be required to determine the structure in TEOS solutions more precisely.

CONCLUSION

The structures and properties of the solute molecule in TEOS solution are affected by the water content and the acidity or the basicity. They are examined by measuring the viscosities of solutions. The TEOS solution catalyzed by a base, NH_4OH, has shown the presence of spherical particles. A solution containing a small amount of water and HCl catalyst has shown the dependence of the reduced viscosity on the SiO_2 concentration and the spinnability, from which the formation of linear polymers is recognized. But the acidic solution with a large amount of water has exhibited little concentration dependence except near a gelling point. This has suggested the formation of highly branched polymers. Degree of polymerization was determined from the GC analysis and the numbers of ethoxy, hydroxy and silicon shared oxygen per silicon atom. Data for the degree of polymerization fit the theory derived from a ribbon of three joined siloxane chains.

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