

Monte Carlo simulation of the sol–gel process for the hydrolysis and polycondensation of tin tetra-*n*-butoxide

Yasushi Murakami *, Taki Matsumoto, Kiyochika Yahikozawa, Yoshio Takasu

Department of Fine Materials Engineering, Faculty of Textile Science and Technology, Shinshu University, 3-15-1 Tokida, Ueda 386, Japan

Abstract

The sol–gel process for the hydrolysis and polycondensation of tin tetra-*n*-butoxide in butanol was followed by viscosity measurements. The precipitation of tin-containing ultrafine particles was observed without any variation in the solution viscosity in the absence of diethylene glycols, while the viscosity increase was made without any precipitation by the addition of diethylene glycol. The induction period and the rate of the viscosity increase after the induction period was independent of the diethylene glycol content but depended upon the water content. The Monte Carlo simulation data were consistent with data for the viscosity experiment. The simulation was based on a kinetic model of the slow hydrolysis of tin tetra-*n*-butoxide, the reverse reaction of hydrolysis, and the polycondensation of the hydroxy derivatives.

1. Introduction

Sol–gel methods, especially using metal alkoxides, have been developed for the preparation of thin films, fine particles and fibers of high-quality ceramics and glasses [1]. Since all the starting chemical reactants for sol–gel processing are purified conveniently and mixed at the molecular level in the solution, a high purity, homogenous film can be expected. Sol–gel processing facilitates the fabrication of films or coating of complex oxides and the control of composition and microstructure of the deposited films or coatings in preference to conventional thin-film forming processes such as evaporation, sputtering, and chemical vapor deposition.

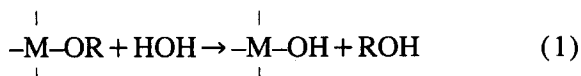
In the sol–gel solution, the hydrolysis and polycondensation of the precursors which are dissolved in a suitable organic solvent leads to

gelation. The obtained gel is dried and calcined to displace the organic components with an oxide ion. Since the solution properties affect the sol–gel process and determine the product features, the precursor and solvent must be carefully selected. Metal alkoxides are typical precursors for making sol–gel solutions in inorganic and organic salts. The alkoxides generally react with water, producing metal hydroxides or hydrated oxides. Since alkoxides with different alkyl groups show different reactivities of hydrolysis, it is possible to adjust the gelation rate for a given alkoxide by using a different solvent. Chelated solutions are also effective for controlling the sol–gel process. Chelating organic ligands such as organic acids, glycols, and β -diketones are added to the solution to control the hydrolysis rates of the highly reactive alkoxide. For example, glycols are dihydroxy alcohols and have been found to be sufficiently reactive with alkoxides to form the corresponding glycolate derivatives. In some

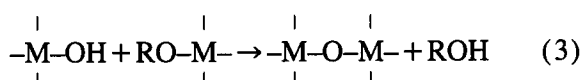
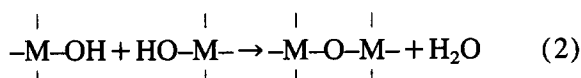
* Corresponding author.

cases, the glycolate derivatives of alkoxides are more resistant to hydrolysis than their counterpart metal alkoxides and thereby have the tendency to form more highly polymeric derivatives compared to the analogous alkoxide derivatives.

Gelation of the solution involves the hydrolysis and polycondensation of alkoxides to form a polymeric product [2–9]. Hydrolysis initiates the gelation to transform alkoxide precursors into the hydroxy intermediates for polycondensation, as described in the following reaction.



where M and R are a metal ion and an alkyl species, respectively. To some extent it may be possible to control the initiation of gelation by using the proper amount of water. The nucleophilic solvents and chelating additives also depress the degree of hydrolysis (1). The reaction of a hydroxy intermediate has been proposed with another hydroxy intermediate to form the polymeric derivative and water or with the other alkoxide precursor to form the polymeric derivative and alcohol:



Reactions (1)–(3) may simultaneously occur so that it is impossible to resolve the hydrolysis and polycondensation reactions. It is not clear which reaction would be affected by water content, solvent, complex ligands, temperature and pH value. Reaction mechanisms and kinetics are therefore essential for the control of the sol–gel process and the nature of the final oxide systems.

Although it is difficult to follow the degree of hydrolysis, the polycondensation degree corresponding to the molecular weight can be reflected by the intrinsic viscosity as

$$[\eta] = K M^\alpha \quad (4)$$

where K is a constant and α is the topological factor of the polymer (normally 0.5–1.0). When polymers dissolved in the solution are chain-like or linear, the relationship between the reduced viscosity η_{sp}/C and the concentration C , where η_{sp} is the specific viscosity, is described as in the following equation, [10]

$$\eta_{sp}/C = [\eta] + k[\eta]^2 C \quad (5)$$

where $[\eta]$ is the intrinsic viscosity and k is a viscosity constant. Assuming that the solution contains chain-like or linear polymers, the kinetics for the hydrolysis and polymerization will be revealed by tracing the viscosity change with $\alpha \sim 1.0$. Unfortunately, there is a lack of data on the viscosity change with hydrolysis and polycondensation.

In this study, the sol–gel process for hydrolysis and polycondensation of tin tetra-*n*-butoxide (TTBO) in butanol was followed by viscosity measurements. Monte Carlo simulation was performed by assuming the kinetic model of hydrolysis and polycondensation.

2. Experimental

2.1. Preparation of tin tetra-*n*-butoxide solutions

Tin tetra-*n*-butoxide (TTBO) with a purity greater than 99.9% was obtained from Tri Chemical while diethylene glycol (DEG) and 1-butanol were purchased from Wako Pure Chemicals. After TTBO was dissolved in butanol, appropriate amounts of DEG in the range between 2.5 and 12.5 mmol were added to the solutions. The hydrolysis and polycondensation in TTBO solution were initiated by the additional butanol containing either 5.0, 7.5, 10.0 or 12.5 mmol aliquot of water. The amounts of TTBO and butanol were adjusted for the preparation of 25 ml of the 0.05 M TTBO solution. All operations before the water addition were performed in an atmosphere of dry nitrogen.

2.2. Viscosity measurements

The viscosity of the solution was measured with a vibrating probe of VISCOMATE VM-1A-L (Yamaichi Denki). During the viscosity measurement, the solution was maintained at 25°C in a circulating thermostatted water bath. The viscosity was determined from the vibrating resistance using a digital voltmeter connected with the time-course recorder.

The specific viscosity η_{sp} in Eq. (5) was defined by

$$\eta_{sp} = (\eta/\eta_0) - 1 \quad (6)$$

where η and η_0 are the viscosity of the solution and the solvent, respectively.

The intrinsic viscosity $[\eta]$ is defined as the reduced viscosity of the polymer solution at its infinite dilution (Eq. (5)) and can be determined by extrapolation of the η_{sp}/C versus C relation to zero concentration of the polymer solution. The viscosity constant k was determined by the dilution of a TTBO-polycondensed butanol solution. The solution was collected for the determination after the increase of the viscosity of the TTBO solution containing 0.1 M of DEG and 0.5 M of H₂O became slow. Under all TTBO concentration studied, the experimental data gave liner plots, as shown in Fig. 1. The viscosity constant k was

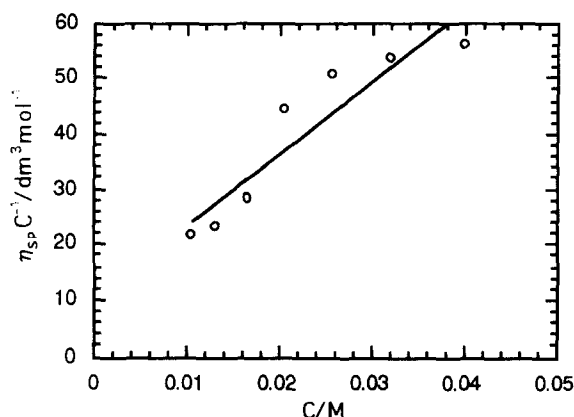


Fig. 1. The reduced viscosity vs. the concentration for the dilution of the TTBO-polycondensed butanol solution prepared from a solution of [TTBO] = 0.05 M, [DEG] = 0.1 M and [H₂O] = 0.5 M.

estimated from the approximately linear relationship to be 12.

3. Results and discussion

3.1. DEG content effects

When water was added to the TTBO solution in the absence of DEG, the precipitation of tin-containing ultrafine particles was observed without any increase of the solution viscosity. By the addition of DEG, the viscosity increased without any precipitation. The intrinsic viscosity of the TTBO solution was measured for the variation of the DEG content as shown in Fig. 2. Although no increase of the viscosity was observed at the initial stage, the viscosity of the TTBO solution rose after some time which was followed by a slower increase of the viscosity. The variation of the TTBO solution viscosity was independent of the DEG contents. The independence of the DEG contents suggests that the hydrolysis was sufficiently depressed by the contents of DEG in our experiments.

The hydrolysis of TTBO proceeded in the presence of water as in reaction (1). Since the hydrolysis proceeded rather fast in the absence of DEG, the di-, tri- and tetra-hydroxy derivatives of tin alkoxides could be obtained by successive hydrol-

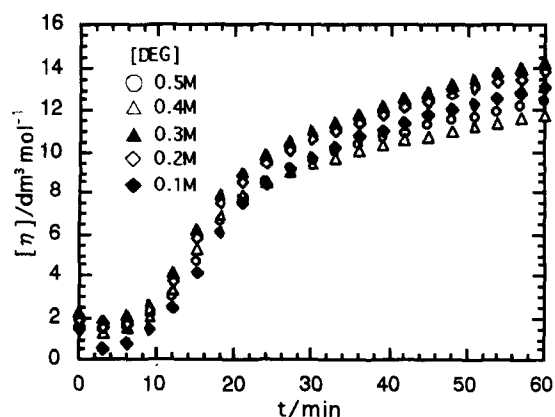
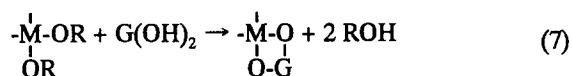


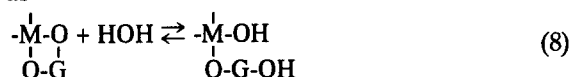
Fig. 2. The time-course of the intrinsic viscosity and its dependence on the DEG content. [TTBO] = 0.05 M and [H₂O] = 0.5 M in the solution.

ysis. The tri- and tetra-hydroxy derivatives would form spherical particles by three-dimensional polycondensation. The condensed particle was precipitated while chain-like or linear polymers were dissolved in the solution.

In the presence of DEG, diethylene glycolate derivatives was mainly formed in the solution since the glycols were sufficiently reactive with alkoxides to form the corresponding glycolate derivatives as



where G(OH)_2 is diethylene glycol. The hydrolysis of diethylene glycolate derivatives proceeds as



Since the above reaction was sufficiently depressed by even a small content of DEG, the reverse reaction was faster than the hydrolysis.

At an initial stage in Fig. 2, no increase of the viscosity was observed in any solution. The absence of an increase in the viscosity suggests that polycondensation was depressed. In the presence of DEG, small amounts of monohydroxy derivatives were formed at the initial stage because hydrolysis was depressed by DEG. If the monohydroxy derivative reacts with the nonhydroxy derivative which is a large portion of the

TTBO derivatives as in reaction (3), polycondensation must proceed even at the initial stage. In practice, however, polycondensation was then depressed. The presence of the induction period rules out the possibility of reaction (3). Assuming that the polycondensation is responsible only for reaction (2), the reaction between the two monohydroxy derivatives would proceed at the initial stage. Moreover, polycondensation must decrease monohydroxy derivatives because of the disappearance of two hydroxy groups by dehydration as in reaction (2). This assumption is consistent with the presence of the induction period.

3.2. H_2O content effects

The intrinsic viscosity of the TTBO solution was measured for the variation of the water content as shown in Fig. 3. The induction period was shortened with an increase in the water content. Since the induction period reflects the time requirement for sufficient formation of derivatives by hydrolysis, the variation of the induction period suggests that the hydrolysis rate increases with an increase of the water content.

The rapid rise in the viscosity after the induction period was remarkably enhanced with an increase in the water content. This enhancement suggests that hydroxy derivatives which are reactants for polycondensation were formed by the addition of water since the intrinsic viscosity reflects the average molecular weight (M_a).

3.3. Monte Carlo simulation for hydrolysis and polycondensation

Monte Carlo simulation was made on the basis of a simple kinetic model which consisted of hydrolysis (1) and polycondensation (2) as shown in Fig. 4. Ten thousand molecules of TTBO ($N(t=0)$) and an appropriate number of H_2O molecules ($H(t=0)$) were introduced to the reactor in the simulation system. The reactions were operated in multiple steps which consisted of alternating hydrolysis and polycondensation. The number of each TTBO derivative which contained

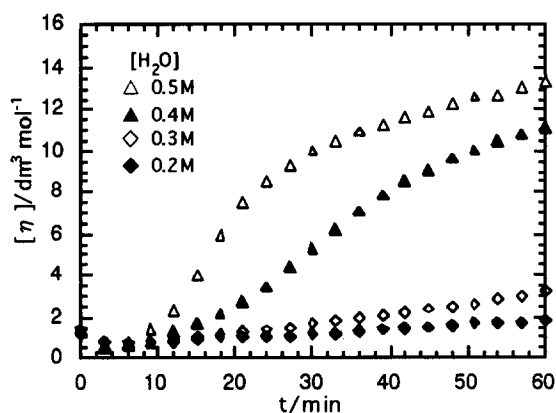


Fig. 3. The time-course of the intrinsic viscosity and its dependence on the H_2O content. $[\text{TTBO}] = 0.05 \text{ M}$ and $[\text{DEG}] = 0.1 \text{ M}$ in the solution.

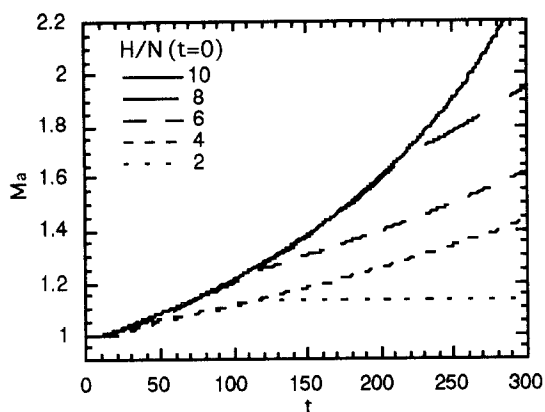
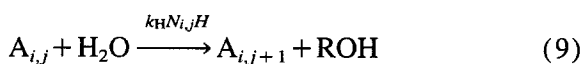


Fig. 4. Monte Carlo simulation on the simple model. $N(t=0) = 10000$, $k_H = 3.0 \times 10^{-9}$ and $k_P = 3.0 \times 10^{-8}$.

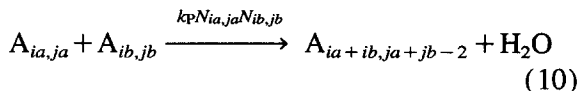
the specified numbers of tin ions (i) and hydroxy groups (j) was calculated after each step of the reactions. After a series of reactions, the average molecular weight was determined from the distribution of the TTBO derivatives with different molecular weights, and plotted against the times of the reaction series.

In hydrolysis, a TTBO derivative reacted with a H_2O molecule at a certain frequency. In the case of a TTBO derivative ($A_{i,j}$), the reaction was described as



where $N_{i,j}$ is the number of the derivative $A_{i,j}$ and k_H is the rate constant for hydrolysis. The number of reacted molecules in a reaction series is written over the arrow. The TTBO derivatives obtain a hydroxy group while the H_2O disappears. If the rate of hydrolysis is sufficiently slow, the presence of derivatives containing more than two hydroxy group is negligible at the initial stage. TTBO derivatives which contain more than two hydroxy groups were omitted from the simulation system since the polycondensation process was simplified to exclude branching. In the simple kinetic model, however, hydrolysis proceeded to a considerable extent after sufficient progress of the reaction so that the presence of derivatives containing more than two hydroxy groups was not negligible. Therefore, a corrected model for the hydrolysis will be required.

In polycondensation, a TTBO derivative reacted with another TTBO derivative at a certain frequency. In the case of a TTBO derivatives ($A_{ia,ja}$) and another ($A_{ib,jb}$), the reaction was described as



where k_P was the rate constant for polycondensation. The number of reacted molecules in a reaction series was also written over the arrow. Each hydroxy group disappeared in a mutual reactant derivative when a polycondensed derivative was formed. At the initial stage, two monohydroxy derivatives reacted together to lose mutual single hydroxy groups and thereby form a nonhydroxy derivative by polycondensation. Needless to say, the resulting nonhydroxy derivative is not concerned with polycondensation. Further polycondensation of the resulting derivative from the polycondensation of the two monohydroxy derivatives needs another hydrolysis. Polycondensation was therefore depressed at the initial stage as an induction period.

Fig. 5 shows a Monte Carlo simulation of the average molecular weight with the correction for the hydrolysis depression. The step of hydrolysis depression was added between the steps of hydrolysis and polycondensation. In the case of a TTBO derivative ($A_{i,j}$), the reaction was described as

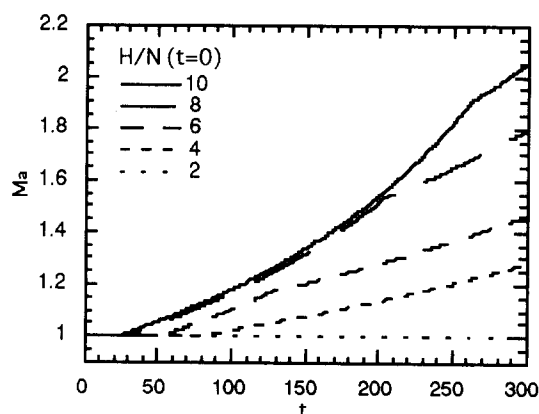
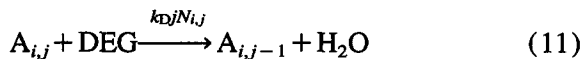


Fig. 5. Monte Carlo simulation on the corrected model for the hydrolysis depression. $N(t=0) = 10000$, $k_H = 3.0 \times 10^{-9}$, $k_D = 8.0 \times 10^{-3}$ and $k_P = 3.0 \times 10^{-8}$.



where k_D was the rate constant for the hydrolysis depression. The number of reacted molecules in a reaction series was also written over the arrow. Since the DEG content the reaction rate, the rate was proportional to the number of hydroxy groups of the derivative ($N_{i,j}$).

The difference between the first and the second set of simulation data is remarkable for the induction period. This induction period was independent of the water content in the first simulation (Fig. 4), while a long induction period was obtained in the case of a small content of water in the second simulation (Fig. 5). Since the induction period is shortened with an increase in the water content, as shown in Fig. 3, the second model is an improvement. At the later stages, however, the average molecular weight still remarkably increases, which is different from the viscosity experimental data.

Fig. 6 shows a further correction of the Monte Carlo simulation to account for the molecular size effect of polycondensation. As the molecular size increased, the ratio of the reactive site to all sites in the derivative was reduced. If the molecular size effect is considered for polycondensation, the reaction can be described as

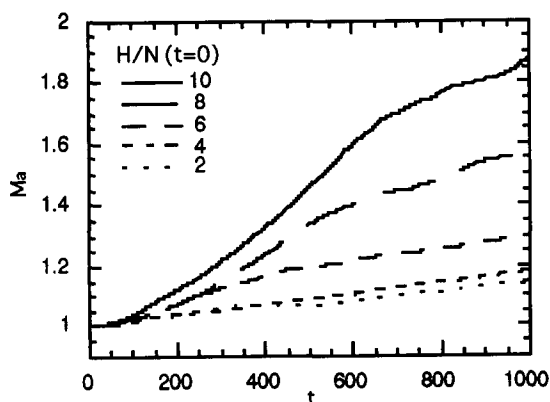
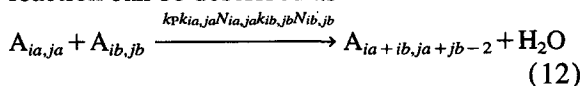


Fig. 6. Monte Carlo simulation on the corrected model involving the molecular size effect on polycondensation. $N(t=0) = 10000$, $k_H = 3.0 \times 10^{-9}$, $k_D = 3.0 \times 10^{-4}$ and $k_p = 3.0 \times 10^{-7}$.

where k_p is the probability for polycondensation and $k_{i,j}$ is the factor of the reactive site to all sites in the derivative as

$$k_{i,j} = j / (2i + 2) \quad (13)$$

At a later stage, the increase in the average molecular weight was accelerated in the second simulation (Fig. 5), while it was suppressed in the third simulation (Fig. 6). Since the increase in the intrinsic viscosity was suppressed with an elapse of time as shown in Figs. 3 and 4, the third model was adopted to explain the progress of gelation.

4. Conclusion

(1) The precipitation of tin-containing ultrafine particles was observed without any variation of the solution viscosity in the absence of diethylene glycol while a viscosity increase was made without any precipitation by the addition of diethylene glycol.

(2) The sol-gel process for the hydrolysis and polycondensation of tin tetra-*n*-butoxide (TTBO) in butanol was followed by viscosity measurements. The variation of the TTBO solution viscosity was independent of the DEG content, suggesting that hydrolysis is sufficiently depressed with DEG.

(3) No increase of the intrinsic viscosity was observed at the initial stage of hydrolysis and polycondensation. The induction period was independent of the DEG content and was shortened with an increase of the water content, since hydrolysis of TTBO proceeded in the presence of water.

(4) The intrinsic viscosity of the TTBO solution rapidly rose after the induction period. The rapid rise in the viscosity was enhanced with an increase of the water content since hydroxy derivatives which were reactants for polycondensation were formed in the presence of water.

(5) The increase rate of the intrinsic viscosity at the larger molecular size of TTBO derivatives was slower than the rapid rise after the induction period. As the molecular size increases, the ratio of the reactive site to all sites in the derivative is

reduced. Therefore, the polycondensation of the large TTBO derivatives is depressed.

(6) The Monte Carlo simulation data were consistent with the viscosity experimental data, by assuming the kinetic model which consisted of the slow hydrolysis of tin tetra-*n*-butoxide, the reverse reaction of hydrolysis and the polycondensation between the hydroxy derivatives taking into consideration the molecular size effect.

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