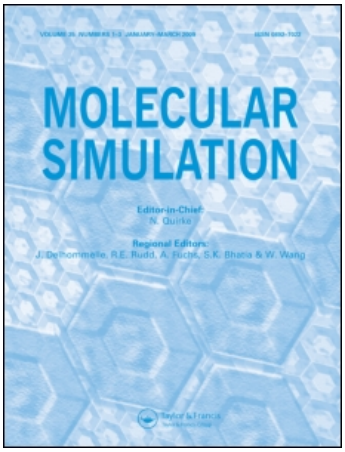

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The Effects of the Water Content, Acidity, Temperature and Alcohol Content on the Acidic Sol-Gel Polymerization of Tetraethoxysilane (TEOS) with Monte Carlo Simulation

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THE EFFECTS OF THE WATER CONTENT, ACIDITY, TEMPERATURE AND ALCOHOL CONTENT ON THE ACIDIC SOL-GEL POLYMERIZATION OF TETRAETHOXYSILANE (TEOS) WITH MONTE CARLO SIMULATION

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The effects of the water/TEOS ratio, pH, temperature and alcohol/TEOS ratio on the degree of polymerization and gelation time in the acid-catalyzed sol-gel polymerization of TEOS have been studied systematically with Monte Carlo simulation. Although linear polymerization by bimolecular reaction was assumed, the reversibility of hydrolysis and condensation, the substitution effect and the effect of molecular separation were considered. The enhanced gelation with water/TEOS ratio resulted from increased water-producing condensation between fully hydrolyzed chain polymers. When pH varies, the fastest gelation occurs when the ratio of condensation to hydrolysis rate moves toward 1 as successive condensation after hydrolysis becomes possible. The accelerating effect of temperature enhances diffusion and increases the rate ratio of condensation to hydrolysis. Alcohol retards gelation due to its dilution effect. The qualitative results obtained in this model explain the experimental behaviors of sol-gel polymerization of TEOS, especially the change in the degree of polymerization, and gelation time with the experimental variables.

Keywords: Simulation; Monte Carlo; Sol-Gel; Polymerization; TEOS

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1. INTRODUCTION

The dependence of acid-catalyzed sol-gel polymerization of TEOS on the water content [1–7], pH[1], temperature [3, 5, 8–10], and alcohol content [1, 11, 12] has been tested extensively. Kinetic approaches [6, 7, 12–20] and computer simulations [21–24] also have also been reported. By using kinetic parameters such as the hydrolysis and condensation rate and monitoring the trends [1, 7–9, 14, 16–18], we intend to trace the processes involved in gelation when the experimental conditions vary and clarify the effects of each experimental variable on gelation behaviors. We have assumed linear polymerization and neglected branching and the cyclization of chain polymers. The experimental gelation behavior and the degree of polymerization and gelation time could be explained well. Although the reversibility of hydrolysis and condensation [6, 7, 12], substitution effect [6, 7, 14–20, 24, 25], the effect of molecular separation [6, 7, 26], and the possibility of reactions with all intermediates [6, 7] had been only partially considered in previous studies, we thought over in this model.

2. METHODOLOGY

The following are major assumptions made in this model. (1) The "ideal" system assumed that all functional groups of the same type are equally reactive and all groups react independently of one another [24]. (2) Hydrolysis and condensation occur at the end groups of the chain polymer exclusively by bimolecular reaction, thus excluding the branching and cyclization [1]. (3) The hydrolysis and condensation rate constants are not changed by initial water/TEOS and alcohol/TEOS ratios. This model consists of the following four steps and the algorithm shown in Figure 1.

2.1. Input of Rate Constants and Initial Number of Monomers

By storing the information of the number and type of the functional groups of the end group of chain molecule and number of connected metal atom(Si) within a molecule, the various intermediates can be discriminated individually when they take part in hydrolysis and condensation. In this model, $Si(OEt)_{4-n}(OH)_n$ is represented by M^n according to the extent of hydrolysis. The chain polymer (C) such as $(OR)_2(OH)SiOSiOSiOSi(OH)_2(OR)_1$

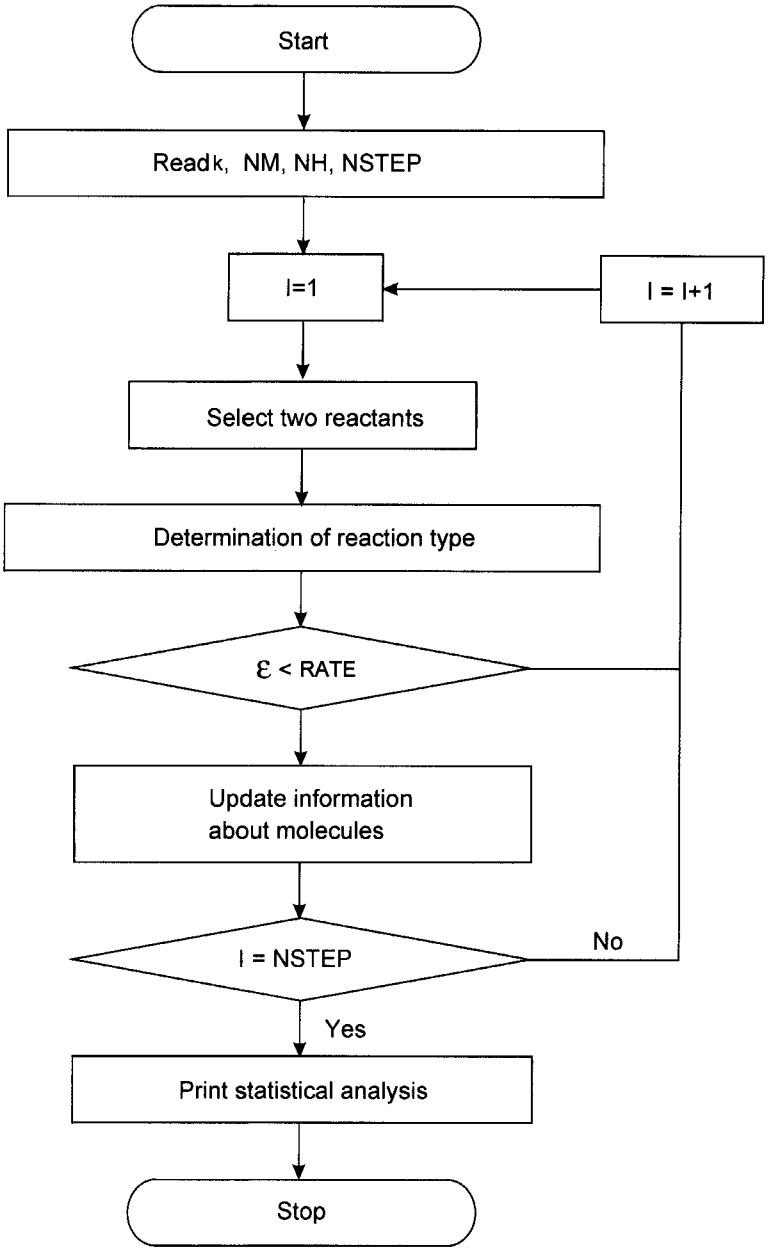

FIGURE 1 Algorithm of our model. NM, NH, NSTEP, k and ε denotes the number of monomer, water, the last step number, hydrolysis and condensation rate constant, and random number, respectively.

is denoted by $C_4^{1,2}$. The subscript of C denotes the number of linked silicon atoms. The first and second postscript of C is the amount of OH on the left and right end of the chain, respectively. H represents H_2O and R represents ROH.

The hydrolysis and condensation rate constants reported by Ro and Jung [14] were used over all the intermediates irrespective of their size and functionality as the initial rate constants at the starting point. Then each rate constant (k_i) of the molecule was converted to the relative rate (R_i) by dividing with the maximum rate constant (k_{max}) among all rate constants for faster computing.

$$R_i = k_i/k_{max} \tag{1}$$

Initial number of M^0 was 10^4. Molar concentration of a species has been converted to the number of molecules. Input data included the number of monomers (NM), the amount of water (NH), and the total step number (NSTEP) where we want to finish the program.

2.2. Selection of Two Reactants

The two reactants have been selected by using the Monte Carlo method. Table I shows the sample space Ω, which is comprised of the seven

TABLE I Sample space, Ω which is comprised of the seven combinations of two reactants and the respective probability of event $C(i)$, P_i

Ω	*Reactant pair*	P_i	*Possible reaction types*
$C(1)$	M+H	$P_1 = (2 \cdot NR_1(1) \cdot NR_2(1)/NR_T) \times 4$	1
$C(2)$	M+R	$P_2 = (2 \cdot NR_1(2) \cdot NR_2(2)/NR_T) \times 4$	2
$C(3)$	M+M	$P_3 = (NR_1(3) \cdot NR_2(3)/NR_T) \times 4 \times 4$	3,4
$C(4)$	C+H	$P_4 = (2 \cdot NR_1(4) \cdot NR_2(4)/NR_T) \times 6$	5
$C(5)$	C+R	$P_5 = (2 \cdot NR_1(5) \cdot NR_2(5)/NR_T) \times 6$	6
$C(6)$	C+M	$P_6 = (2 \cdot NR_1(6) \cdot NR_2(6)/NR_T) \times 4 \times 6$	7,8
$C(7)$	C+C	$P_7 = (NR_1(7) \cdot NR_2(7)/NR_T) \times 6 \times 6$	9,10

Where M, C, H, R, NR_1, and NR_2 denote monomer, chain, water, alcohol, and the number of first and second reactant, respectively.

$$NR_T = 2 \cdot \left\{ 4 \cdot \sum_{i=1}^{2} NR_1(i) \cdot NR_2(i) + 6 \cdot \sum_{i=5}^{6} NR_1(i) \cdot NR_2(i) + 24 \cdot \sum_{i=7}^{8} NR_1(i) \cdot NR_2(i) \right\} + 16 \cdot \sum_{i=3}^{4} NR_1(i) \cdot NR_2(i) + 36 \cdot \sum_{i=9}^{10} NR_1(i) \cdot NR_2(i)$$

combinations of reactants.

$$\Omega = \{c(1), c(2), \ldots, c(7)\} \tag{2}$$

The first reactant is set to be a larger molecule than the second reactant in order to define the reactant combination clearly. The respective probability of selecting the i th combination, $c(i)$, should be proportional to the amount of each molecule in $c(i)$, so P_i is introduced which is proportional to the population of each reactant and ranges from 0 to 1. The method used in the molecular selection is Piecewise Fitting (PF) which was used by Mikes and Dusek [22]. The i th combination is selected when the following inequalities are satisfied stepwise.

$$\sum_{k=1}^{i-1} P_k < \varepsilon \cdot \mathrm{NR}_T \leq \sum_{k=1}^{i} P_k \tag{3}$$

where ε is a random number called from a uniform distribution in the interval (0, 1) and NR_T is defined at the Table I.

The following functional group kinetics have been adapted from Ro and Jung [14].

$$\mathrm{Si{-}OR} + \mathrm{H_2O} \underset{k_E}{\overset{k_H}{\longleftrightarrow}} \mathrm{Si{-}OH} + \mathrm{ROH} \tag{4}$$

$$\mathrm{Si{-}OR} + \mathrm{HO{-}Si} \xrightarrow{k_A} \mathrm{Si{-}O{-}Si} + \mathrm{ROH} \tag{5}$$

$$\mathrm{Si{-}OH} + \mathrm{HO{-}Si} \xrightarrow{k_W} \mathrm{Si{-}O{-}Si} + \mathrm{H_2O} \tag{6}$$

Where k_H is the hydrolysis rate constant, k_E the esterification rate constant, k_A the alcohol-producing condensation rate constants, and k_W the water-producing condensation rate constant. In a viewpoint of sites, four Si—OH and/or Si—OR in a monomer take part in the hydrolysis and esterification, whereas only one monomer does in this system. To compensate for the collision probability between monomer-water/alcohol with respect to functional group-water/alcohol, the probability of selecting reactant combination, P_i was adjusted by introducing the compensating factor (w), which is defined as total site number per molecule. So the respective probability of selecting M—H or M—R combination becomes proportional to $4 \cdot \mathrm{NM} \cdot \mathrm{NH}$ or $4 \cdot \mathrm{NM} \cdot \mathrm{NR}$ where 4 denotes the compensating factor, respectively.

The average intermolecular distance of water, alcohol, and monomer (TEOS) was reported as 3.2 Å 4.6 Å (calculated), and 7.2 Å, respectively [25]. Because the M—H interaction distance is known as ≈ 2.1 Å [25], the volume (ΔV) in which the reaction between monomer and water can occur becomes 431.1 $Å^3$ by calculation [25], so the maximum number of water molecule can exist in ΔV becomes 13. Likewise, M—R interaction distance is assumed as 2.1 Å, the maximum number of alcohol molecules which can exist in ΔV becomes 4. If the H/M ratio in the system is smaller than 13, all water can have chance to collide with monomers. Likewise if the R/M ratio is greater than 4, only four alcohols within ΔV can react with one monomer, so the excess alcohol beyond $4 \cdot NM$ should be excluded from the reactant population. For the above reasons, under $NR/NM < 4$ conditions, the probability of selecting a monomer-alcohol pair is proportional to $NM \cdot NR$ but under $NR/NM > 4$ conditions, the probability of selecting a M—R combination is proportional to $NM \cdot (4 \cdot NM)$. Similarly, all functional groups in a chain molecule can contribute to the hydrolysis and esterification in the site-based model, whereas only one chain polymer can do so in this model. The compensating factor, w, and the probability of selecting C—H or C—R is defined as 6. This is the number of Si—OH group at the end of one chain polymer.

The intermolecular distance between C—H or C—R increases with the chain size due to the increased excluded volume of the chain, so diffusion is the main controlling factor in the chain growth when the polymer grows to a sufficient large size [6, 7, 25]. Because we have considered only the reaction at the end group of the chain, the reacting volume ΔV around the right or left end of the chain has been assumed as 3/4 of that of the monomer. Thus the maximum number of water and alcohol within ΔV around the end of one chain become 18 and 6, respectively. After the selection of reactant pairs, the reacting functional group has been determined. If the monomer is one of the reactants, the number of the OH group of monomer is determined as i if the following inequalities are satisfied.

$$\sum_{k=1}^{i-1} \mathrm{NR}^k_{1 \text{ or } 2} \langle \mathrm{int}(\varepsilon \cdot \mathrm{NR}_{1 \text{ or } 2}) + 1 \leq \sum_{k=1}^{i} \mathrm{NR}^k_{1 \text{ or } 2} \tag{7}$$

where int(x) is the lowest integer to x and $NR_{1 \text{ or } 2}$ denotes the number of first and second reactants determined by the subscript. Likewise as a monomer, the number of metal atoms, OH groups at the left and right end of the selected chain becomes k, i', and j', respectively, if the following

inequalities are satisfied.

$$\sum_{k=2,i=0,j=0}^{k'-1,i'-1,j'-1} \mathrm{NR}_{1\text{ or }2}^{k,i,j} \langle \mathrm{int}(\varepsilon \cdot \mathrm{NR}_{1\text{ or }2}) + 1 \leq \sum_{k=2,i=0,j=0}^{k'-1,i'-1,j'-1} \mathrm{NR}_{1\text{ or }2}^{k,i,j} \tag{8}$$

2.3. Determination of Reaction Type

Table II shows the set of reactions. According to the products, all reactions have been classified as 10 types. First, we carried out a calculation by 14 reactions including all possible dissolution which is the reverse reaction of condensation. They could be ignored due to rare occurrence. After the selection of the reaction type it can be determined whether the reaction will occur or not. If the reaction is accepted, the changed information including the population of consumed, produced and remained molecules is stored. We assumed that both the hydrolysis and condensation rate constants increase with OH numbers in a molecule and decrease with the size of molecule which correspond to the positive and negative substitution effect, respectively [6, 7, 16–21]. To consider these substitution effects, factor 1 and 2 have been introduced which denote the effects of OH number and the connected metal number of chain polymer on the hydrolysis and condensation rate constants, respectively. The probability of j type reaction, p_j is defined by multiplying the substitution effect terms with the relative rate constant, R_j.

$$p_j = R_j \cdot \text{factor 1} \cdot \text{factor 2} \qquad j = 1, 2, \ldots, 10 \tag{9}$$

$$\text{Factor 1} = \left\{ \frac{1}{(4 - \mathrm{NOH}_1)} \times \frac{1}{(4 - \mathrm{NOH}_2)} \right\}^a$$

for hydrolysis and esterification (10)

$$= \left\{ \frac{1}{(4 - \mathrm{NOH}_1)} \times \frac{1}{(4 - \mathrm{NOH}_2)} \right\}^b$$

for condensation and dissolution (11)

where NOH_1 and NOH_2 denote OH number of the end group of reactant 1 and 2, respectively.

$$\text{Factor 2} = \left\{ \frac{1}{\mathrm{NMETL}_1} \times \frac{1}{\mathrm{NMETL}_2} \right\}^{(1/4)} \tag{12}$$

TABLE II 10 reaction types. The 'i' and 'j' denotes the number of hydroxyl group of monomer or that of left-end and right-end of chain, respectively. The subscript 'k' of chain denotes connected metal number and 'N' corresponds to 10^4 which is maximum connectivity

Type	*Reaction*	*Simplified notation*
1	Hydrolysis of monomer	$M^i + H \underset{p_2^i}{\overset{p_1^i}{\rightleftarrows}} M^{i+1} + R \quad i \in [0,3]$
2	Esterification of monomer	
3	Water-producing condensation between monomers	$M^i + M^j \xrightarrow{p_3^{i,j}} C_2^{i-1,j-1} + H \quad i,j \in [1,4]$
4	Alcohol-producing condensation between monomers	$M^i + M^j \xrightarrow{p_4^{i,j}} C_2^{(i-1,j)/(i,j-1)} + R \quad i \in [0,4]; \quad j \in [1,3]$
5	Hydrolysis of chain	
6	Esterification of chain	$C_k^{i,j} + H \underset{p_6^{k,i,j}}{\overset{p_5^{k,i,j}}{\rightleftarrows}} C_{k+1}^{(i-1,j)/(i,j-1)} + R \quad i \in [0,2]; \quad j \in [0,3]; \quad k \in [2,N]$
7	Water-producing condensation between chain and monomer	$C_k^{i,j} + M^{i'} \xrightarrow{p_7^{k,i,j,i'}} C_{k+1}^{(i-1,j)} + H \quad i \in [1,3]; \quad i' \in [1,4]; \quad j \in [0,3]; \quad k \in [2,N]$
8	Alcohol-producing condensation between chain and monomer	$C_k^{i,j} + M^{i'} \xrightarrow{p_8^{k,i,j,i'}} C_{k+1}^{(i,j)/(i-1,j)} + R \quad i \in [1,3]; \quad i' \in [0,3]; \quad j \in [0,3]; \quad k \in [2,N]$
9	Water-producing condensation between chains	$C_k^{i,j} + C_{k'}^{i',j'} \xrightarrow{p_9^{k,k',i,j,i',j'}} C_{k+k'}^{j,j'} + H \quad i,i' \in [1,3]; \quad j,j' \in [0,3]; \quad k,k' \in [2,N]$
10	Alcohol-producing condensation between chains	$C_k^{i,j} + C_{k'}^{i',j'} \xrightarrow{p_{10}^{k,k',i,j,i',j'}} C_{k+k'}^{j,j'} + R \quad i \in [1,3]; \quad i' \in [0,2]; \quad j,j' \in [0,3]; \quad k,k' \in [2,N]$

where $NMETL_1$ and $NMETL_2$ denote metal number of reactant 1 and 2, respectively. The exponents of the factor 1 and 2 was assigned properly with a consideration of published data [6, 7, 12, 14, 16–21].

Table III summarized the 10 reaction probability($p_1 \sim p_{10}$), factor 1, and factor 2 which are based on the reported rate constants. The reaction type is determined as $j+1$ after the selection of the combination i if the following inequalities are satisfied stepwise.

$$\sum_{k=j}^{j} p_k \langle \varepsilon \cdot p_{i,T} \leq \sum_{k=j}^{j+1} p_k \tag{13}$$

$$\text{where } p_{i,T} = p_3 + p_4 ; (j = 3) \quad \text{when } i = 3$$

$$\text{or} \quad p_7 + p_8 ; (j = 7) \quad \text{when } i = 6$$

$$\text{or} \quad p_9 + p_{10} ; (j = 9) \quad \text{when } i = 7$$

Additional random number, ε is called and if it is lower than p_j, then the choice of j type reaction is accepted.

2.4. Statistical Analysis of the Results

The intermediate and final results of the program such as the distribution of the molecular size and the degree of polymerization of the system have been analyzed statistically. All calculations have been performed using an IBM PC using programs written in Fortran77.

TABLE III The 10 reaction rate, $p_n(n = 1 \sim 10)$ is determined by $R_n(\simeq k_n/k_{max}) \times$ factor 1 $\times$ factor 2. Notation is same as Tables I and II. In factor 2, k and k' denotes metal connectivity of reacting chain polymer, respectively

Reaction type(n)	k_n [14] (pH 1)	k_n [14] (pH 2)	*Factor* 1 $a = 1/2$, $b = 3/2$	*Factor* 2
1	$9.6(=k_{max})$	$1.23(=k_{max})$	$1/(4-i)^a$	1
2	1.6	0.35	$1/(5-i)^a$	1
3	0.48	0.69	$1/[(5-i)\cdot(5-j)]^b$	1
4	0.09	0.16	$1/[(5-i)\cdot(5-j)]^b$	1
5	9.6	1.23	$1/(3-(i/j))^a$	$k^{1/4}$
6	1.6	0.35	$1/(4-(i/j))^a$	$k^{1/4}$
7	0.48	0.69	$1/[(4-i)\cdot(5-j)]^b$	$k^{1/4}$
8	0.09	0.16	$1/[(4-i)\cdot(5-j)]^b$	$k^{1/4}$
9	0.48	0.69	$1/[(4-i)\cdot(4-j)]^b$	$k\cdot k'^{1/4}$
10	0.09	0.16	$1/[(4-i)\cdot(4-j)]^b$	$k\cdot k'^{1/4}$

3. RESULTS AND DISCUSSION

3.1. The Effect of pH and Water Content

Figure 2 shows the effects of the pH and water content on the change of the gelation steps(S_g) and average degree of polymerization (DP) of the system.

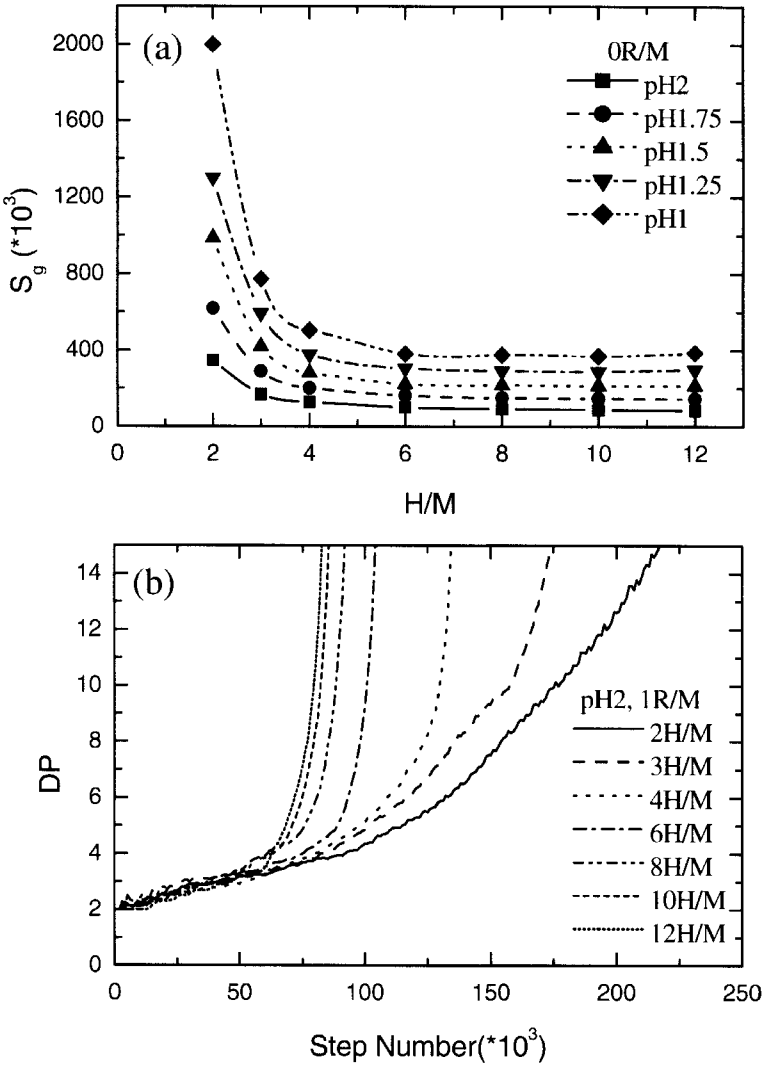

FIGURE 2 (a) The effects of pH and water content on the gelation step(S_g). (b) The increase of degree of polymerization(DP) with water content.

DP is defined by $\sum_{k=2}^{10000} k \cdot \mathrm{NC}(k) / \sum_{k=2}^{10000} \mathrm{NC}(k)$ $\mathrm{NC}(k)$ denotes the number of chains which have k connectivity. S_g is determined by the step where DP grows abruptly and the slope of DP curve goes to ∞[1 – 5]. As shown in Figure 2(a), S_g has a minimum at 10 H/M below pH1.5 but S_g decreases with the H/M ratio above pH1.5. Under the same H/M conditions, S_g increases with pH. The relative ratio of k_H and k_W at pH1 and pH2 is about 10 and 1, respectively[14]. Although k_H and k_W values are different between literatures, the relative ratio of k_H and k_W at certain pHs has the same order [1, 7, 12, 14, 18, 20]. As Colby *et al.*, pointed out[8], above a stoichiometric ratio of hydrolysis(4 H/M), the effect of excess water on the gelation time can be neglected as shown in Figure 2(a). Below pH1.5, S_g can have a minimum value of 10 H/M and above pH1.5, S_g decreases with the H/M ratio. Our other calculation shows that if the k_H/k_W ratio increases above that of pH1, the S_g tends to minimize near 4 H/M and S_g curve resembles the Klein's result, which did not show kinetic parameters[11]. Figure 2(b) shows that DP increases more rapidily and abruptly as water increases[2].

Figure 3(a) shows the each reaction frequency during gelation and it is representative plot of various conditions. In comparison with Figure 2(b), abrupt increases of DP is largely due to water-producing condensation between chain polymers(reaction 9) as monomer contribution is excluded in DP calculations so the effect of reaction 7 could be small. Figure 3(a) shows that contribution of alcohol-producing condensation on DP is very low compared to water-producing condensation. In engineering aspects, it can be possible to ignore the alcohol-producing condensation [7, 8, 12, 17].

Figure 3(b) shows the variation of chain polymer distribution during an increase in DP. The increasing curvature of total chain polymer distribution supports or is comparable to other data [7, 12]. Chain polymers whose number is small are not shown in Figure 3(b). The chain polymers that have fully hydrolyzed ends on either side($C^{3,3}$), constitute a major portion of the total chain polymers. Abrupt DP increases in Figure 2(b) correspond to the decreasing range of chain polymers with fully hydrolyzed ends($C^{3,3}$). Due to fast hydrolysis, the OR group of partially hydrolyzed chain polymers is converted to a OH group rapidly so that $C^{3,3}$ constitutes most chain polymers during condensation. Figure 3(a) and (b) show an abrupt DP increase due to water-producing condensation between chain polymers that have fully hydrolyzed ends. As the H/M ratio goes higher, and steeper the decreasing curve of the polymer number enters into our calculation.

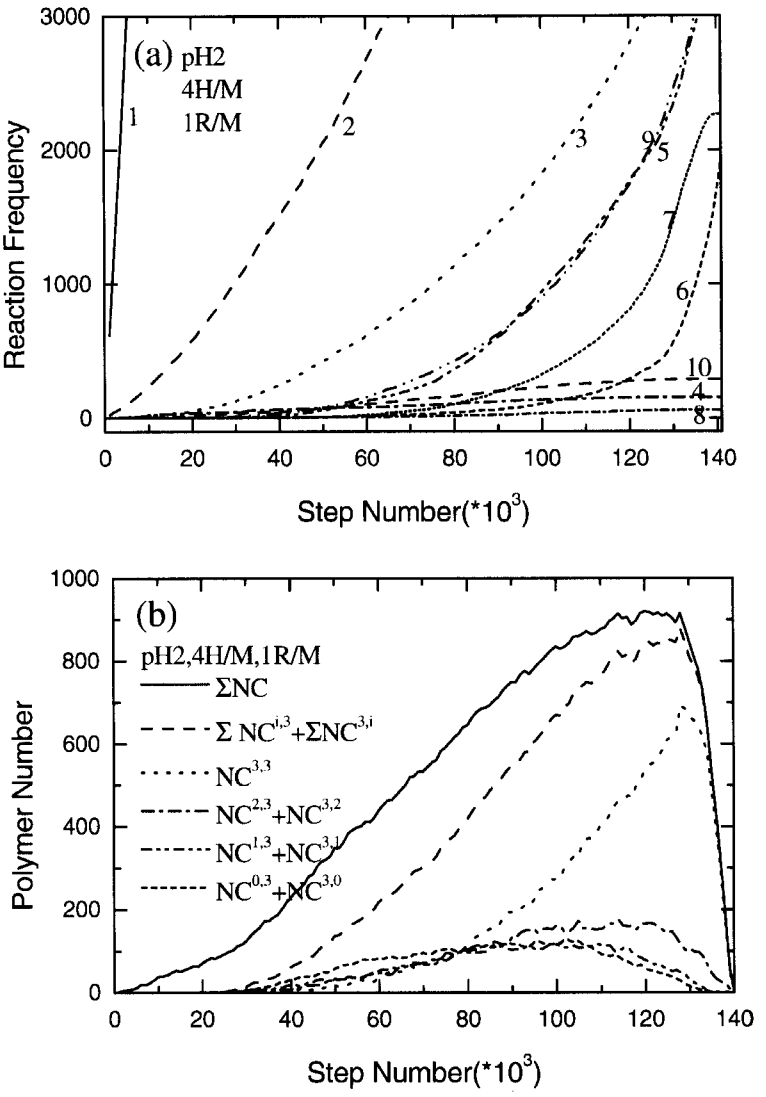

FIGURE 3 (a) The change of each reaction frequency during the gelation. (b) The change of polymer number during the gelation.

3.2. The Effect of Temperature

Figure 4(a) shows the effects of temperature on S_g and DP on the system. The hydrolysis and condensation rates are known to follow the Arrhenius equation [8–10]. The activation energy of the hydrolysis-esterification and

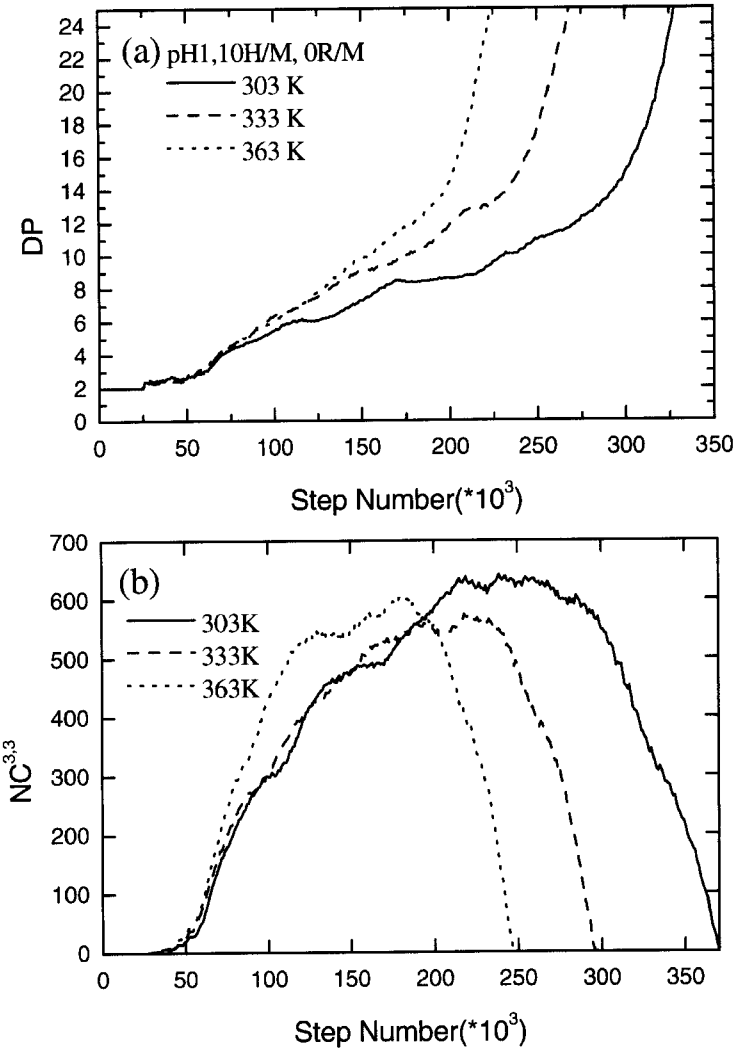

FIGURE 4 (a) The temperature effect on the gelation. (b) The change of $C^{3,3}$ distribution with temperature.

condensation-dissolution was assumed as 6000 Kcal/mole and 8000 Kcal/mole, which is adapted from the reported minimum activation energy, respectively[8–10]. Table IV shows the rate constants calculated by the Arrhenius equation at 303, 333, 363 K. S_g decreases with temperature at pH1 and pH2. As temperature increases, the steeper the DP curve becomes. Figure 4(b) shows the distribution of $C^{3,3}$ with temperature. The distribution

TABLE IV The rate constants calculated by Arrhenius equation at 303, 333, 363 K. The activation energy of hydrolysis-esterification and condensation-dissolution is assumed as 6000 Kcal and 8000 Kcal, respectively

	Rate constant	303 *K*[14]	333 *K*	363 *K*
	k_H	9.60	23.70	50.30
	k_E	1.60	3.90	8.40
pH1	k_W	0.48	1.60	4.36
	k_A	0.09	0.30	0.82
	k_H	1.23	3.03	6.44
pH2	k_E	0.35	0.86	1.83
	k_W	0.69	2.30	6.27
	k_A	0.16	0.53	1.45

of $C^{3,3}$ is largely determined by the k_H/k_W ratio and the order of S_g is determined by water-forming condensation between $C^{3,3}$. Table IV shows that the k_H/k_W ratio approaches 1 as the temperature rises, so the enhanced gelation can be explained analogous to pH condition.

But the S_g gap between low and high temperature is small compared to other results [3, 4, 8, 9, 11], so diffusion effect must be considered. As temperature rises, chain polymers can diffuse more rapidly so the probability of a collision between chain polymers may increase. By decreasing factor 2 with temperature, the S_g gap between low and high temperature can be larger than Figure 4(a) that is confirmed by our other calculation.

3.3. The Effect of Alcohol Content

Figure 5 shows that the gelation is retarded with R/M ratio from 0 to 3 at pH2. As alcohol increases, esterification of monomer(reaction 2) increases by le Chatelier's principle [11, 12, 28] so dimer formation is retarded(reaction 3). Because formation of a dimer which is seed of condensation occurs slow, water-producing condensation between fully hydrolyzed chains(reaction 9) are also delayed in a alcohol-rich systems. But the S_g gap between low and high alcohol systems is less than Klein's result[11], so the dilution effect and intermolecular interaction distance[7] are thought to be underestimated. Changing the intermolecular interaction distance of alcohol has little effect on expanding the S_g gap between low and high alcohol systems. By increasing factor 2 with alcohol content, it is possible to broaden the S_g gap between low and high alcohol systems. Our calculations show that retarded gelation with alcohol is largely due to the dilution effect.

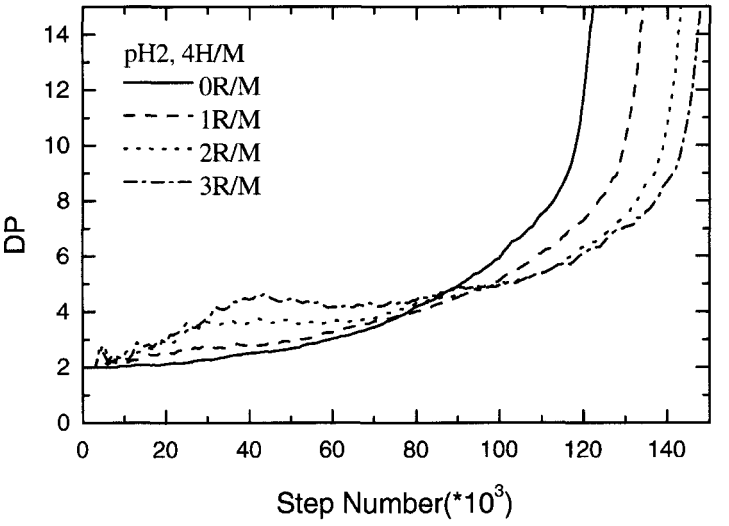

FIGURE 5 The alcohol effect on the gelation.

4. CONCLUSIONS

Water-producing condensation between fully hydrolyzed chain polymers increases with water content and thus causes a faster increase of DP and shorter S_g in a high water content system. The effect of pH and temperature on DP and S_g mainly results from the rate ratio of hydrolysis to condensation. Enhanced gelation at a high pH and temperature is possible because the rate ratio of hydrolysis to condensation approaches 1 and successive condensation can occur immediately after hydrolysis. Alcohol decelerates the gelation and this may be caused by the dilution effect.

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