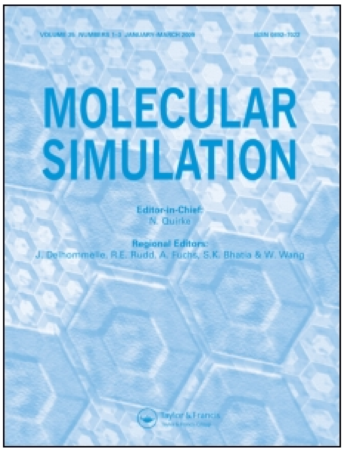

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The Role of Excess Water in Acidic Sol–Gel Polymerization of Tetraethoxysilane(TEOS) Using Molecular Dynamics Simulation

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To study the role of excess water in acidic sol–gel polymerization of TEOS, structural changes in $Si(OH)_4$ and $Si(OH)_4$ with H_2O were compared in the temperature range from 298 to 373 K and pressure range from 1 bar to 10 kbar using molecular dynamics (MD) simulation. The intermolecular interaction distance determined from a radial distribution function results is used as a criterion of bond formation between two $Si(OH)_4$ molecules. In the $Si(OH)_4$ system, the number and relative occupancy of large ring-like structures increases with pressure under all temperature conditions. In $Si(OH)_4$ with H_2O, the formation of ring-like structure hardly occurs under all temperature and pressure conditions. Water hinders the formation of the ring-like structures due to excluded volume effects caused by its hydrogen bond to the silanol group. It can be deduced that the remaining water after full hydrolysis of TEOS retards gelation of TEOS solutions.

Keywords: Simulation; Molecular dynamics; $Si(OH)_4$; Sol–gel; TEOS

INTRODUCTION

The dependence of acid-catalyzed sol–gel polymerization of TEOS on the water content has been extensively studied [1–9]. Under acidic conditions, there are three experimental results concerning the role of excess water above a stoichiometric ratio of hydrolysis (water/TEOS = 4) on gelation time depending on the experimental conditions, especially pH and alcohol content. The first is that gelation time gets shorter as the ratio of water to TEOS increases [3,6]. The second is that the effect of excess water on the gelation time can be neglected above a stoichiometric ratio of hydrolysis [8]. The third is that a minimum gelation time exist near the stoichiometric ratio of hydrolysis [9]. Our previous calculations showed [10] that the role of excess water on gelation time can change depending on the rate ratio of hydrolysis to condensation. Under acidic or neutral condition, ring (or cyclic polymer) structure is important to explain the anomalous high gel conversion of TEOS [11]. It is simply assumed that the number of ring-like structures represents the extent of polymerization. Fully hydrolyzed TEOS monomer ($Si(OH)_4$) has been used as the starting material because hydrolysis occurs quickly and water-producing condensation is the predominant process under acidic condition. In this paper, we intend to investigate the role of excess water in the sol–gel polymerization of TEOS using molecular dynamics (MD) under various temperature and pressure conditions.

MOLECULAR DYNAMICS SIMULATION METHOD

An energy minimized starting structure of $Si(OH)_4$ was generated with Molecular Orbital Calculation Package (MOPAC) [12]. Figure 1 shows the initial $Si(OH)_4$ molecule. The partial charge of Si, O and H atom used in this study is 1.2072, −0.7673, 0.4655 eV,

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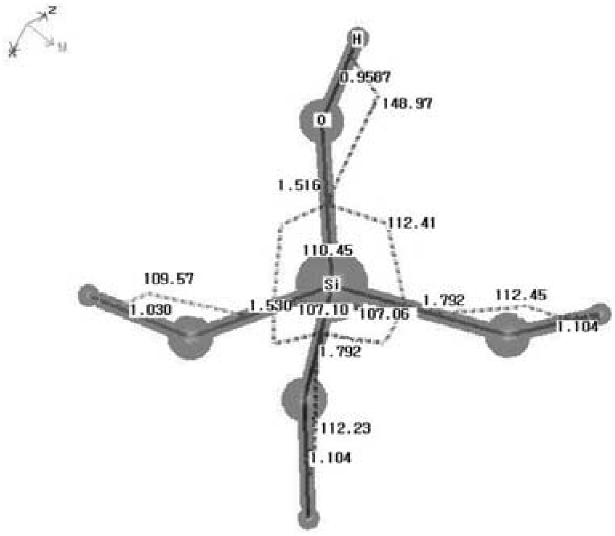

FIGURE 1 Starting structure of $Si(OH)_4$.

respectively, values reported by Pereira *et al.* [13]. A TIPS3P model was used for describing water [14]. Water bonds and angles were constrained by SHAKE [15]. All simulations are done using the CHARMM program (version 24.1) modified for use on the SGI INDIGO workstation [15]. In system S, 64 $Si(OH)_4$ were placed in a cubic MD cell with a side of 21.6974 Å. The system (SW) which is made up of 64 $Si(OH)_4$ and 64 H_2O which are distributed randomly in the orthorhombic MD cell with a dimension of $X = 20.72478$, $Y = 25.07920$, $Z = 16.53661$ Å was prepared by MD simulation at 698 K. The density of $Si(OH)_4$ in each box was 1.0 g/cm^3.

The conditions of MD simulations were as the follows: the time step employed was 1 fs(10^{-15} s). The nonbonded interactions were spherically truncated at 9 Å (CTOFNB). The electrostatic interactions were shifted to zero at 8 Å (CTONNB) and van der Waals interactions were switched off from 7 to 8 Å.

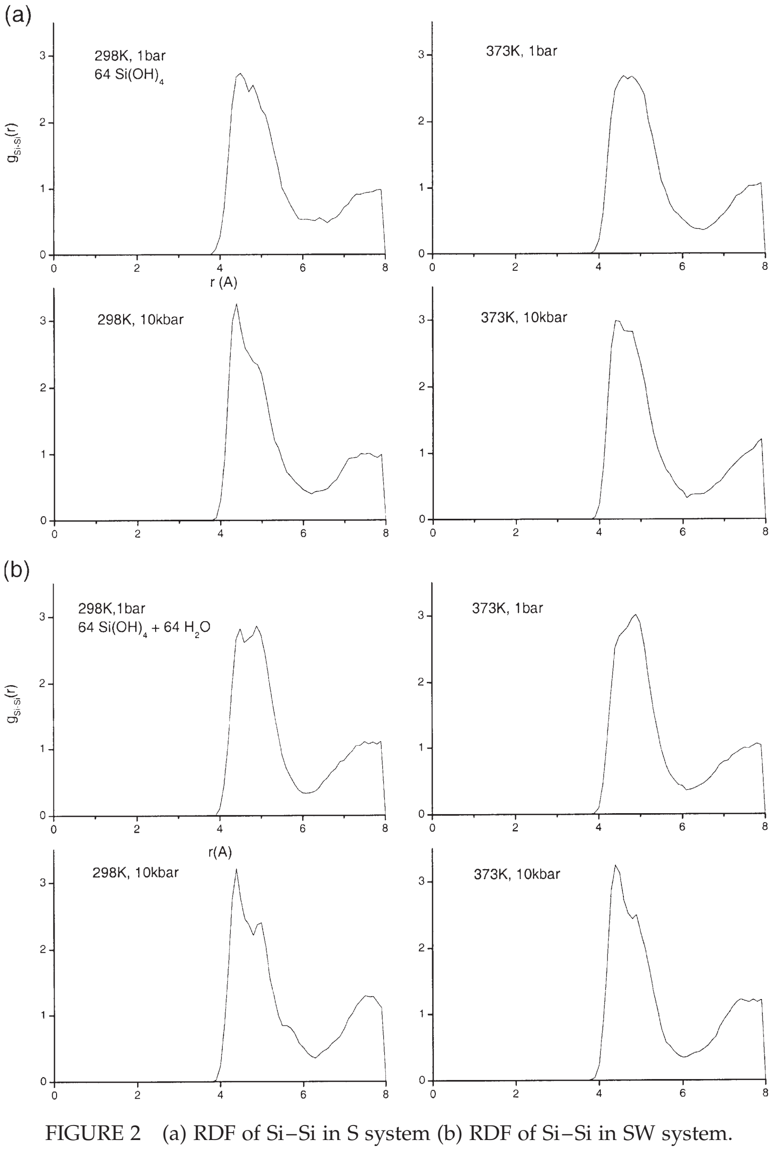

FIGURE 2 (a) RDF of Si–Si in S system (b) RDF of Si–Si in SW system.

The nonbonded list was generated with a 9 Å cutoff (CUTNB). For the nonbonded list update, the heuristic test was performed every time energy was called for and a list update was done if necessary. The conventional periodic boundary conditions were applied during the simulations.

An Ewald sum with $\alpha = 0.33$ and $K_{\max} = 5$ was used to calculate the long-range Coulombic interactions for all conditions. The system was warmed up to 298 K for 5 ps then equilibriated for 30 ps (298 K) by periodic velocity scaling. After performing 298 K dynamic run, each higher temperature (323,348 and 373 K) configuration was obtained by heating by 25 K for 0.5 ps and equilibriated for 20 ps, respectively. The production runs for analysis were continued for 10 ps at each temperature. The temperature range was determined from the experimental condition. The equations of motion were integrated using the leapfrog algorithm which is considered to be the most stable in MD, especially in NPT simulation [16]. The temperature and pressure of the systems were controlled by the Langevin piston method [17]. For the pressure and temperature mass, we used 500 atomic mass unit (amu) and 1000 Kcal ps^2, respectively. The used collision frequency (γ) was 20 ps^{-1}.

The ring-like structure of $Si(OH)_4$ is defined by the following geometrical criteria for computational convenience. If the Si–Si distance between two $Si(OH)_4$ molecules lies within the first peak of radial distribution function (RDF) of Si's two $Si(OH)_4$ were treated as bonded ones.

RESULTS AND DISCUSSION

Figure 2 shows the radial distribution function (RDF, $g(r)$) of silicon atoms in S and SW system under

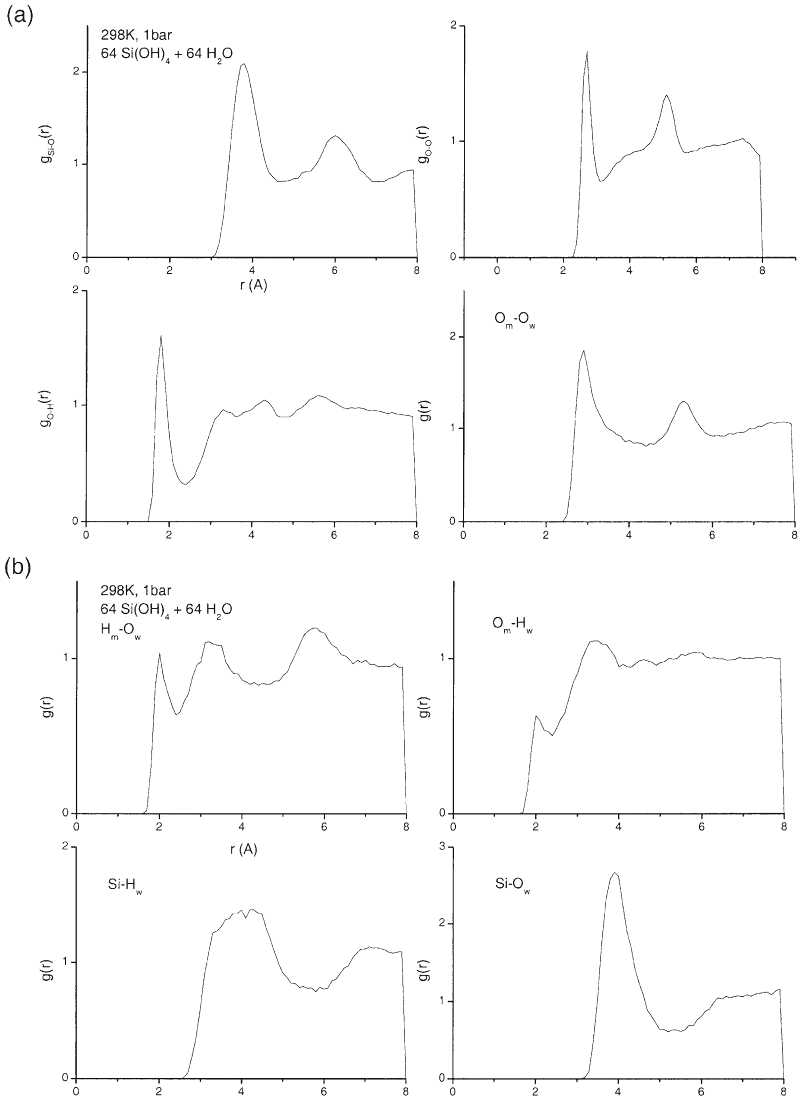

FIGURE 3 (a) RDF of Si—O, O—O, O—H and O_m—O_w (b) H_m—O_w, O_m—H_w, Si—H_w, Si—O_w in SW system. Subscript "m" and "w" denotes $Si(OH)_4$ monomer and water, respectively.

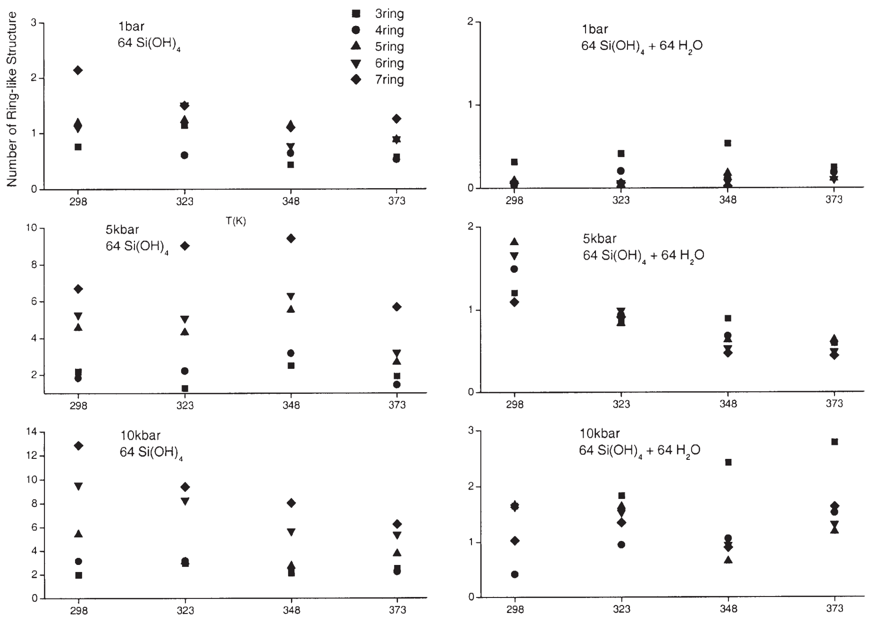

FIGURE 4 The distribution of ring-like structure with temperature and pressure.

various temperature and pressure conditions. Figure 2 shows that first peak of RDF becomes sharper and higher with pressure. At 1 bar, first peak occurs at longer distance in SW system, but at 10 kbar RDFs in two systems becomes similar at each temperature. The RDF's of other interatomic pairs are somewhat insensitive to pressure and temperature [13], representative ones are shown in Fig. 3. First peak position corresponds to the critical distance in which two atoms can interact with each other. Feuston *et al.* [18,19] found the minimum energy structure of Si(OH)$_4$ monomer and the H$_2$O molecule and reported the interaction distance between atoms by MD simulation. These data agree with our RDF peak positions for each RDF. Figure 4 shows the distribution of the Si(OH)$_4$ ring-like structure under various temperature and pressure conditions. At the same temperature and pressure condition, the number of ring-like structures in the SW system is smaller than in the S system and this trend becomes clear with increasing pressure. In the S system, large rings such as 7, 6 and 5 ring-like structures are dominant but in SW system, the formation of ring-like structures much less frequent under all temperature and pressure conditions.

Figure 5(a) shows formation of intermolecular hydrogen bond in 3 ring-like structure which is analogous to the intramolecular hydrogen bonds of silica 3 ring reported by Pereira *et al.* [20] Intramolecular hydrogen bonds between silanol (SiOH) groups is known to lower the cluster energy and contribute to structure stabilization. Figure 5(b) shows linear tetramer-like structure which has intramoleular hydrogen bond between silanol groups. Figure 5(c) shows entangled ring-like structures which have branching monomers and intramolecular hydrogen bond between silanols.

Figure 6 shows the 3 ring-like structure in SW system. Water molecules form hydrogen bond to Si(OH)$_4$ so they exclude the attack of other Si(OH)$_4$ monomers toward the 3 ring-like structure. The 3 ring-like structures starts to form as pressure and temperature increases as shown in Fig. 4. Si(OH)$_4$ is a fully hydrolyzed molecule from the TEOS monomer, so the SW system corresponds to excess water condition ($H_2O/TEOS \geq 8$) if we neglect the H$_2$O as byproduct after water-producing condensation between two Si(OH)$_4$. Figures 4 and 6 shows that Si(OH)$_4$ ring-like structure formation is inhibited by the presence of excess water and this is analogous to retardation of gelation in TEOS due to excess water.

CONCLUSIONS

To study the role of excess water in acidic sol–gel polymerization of TEOS, we performed simple MD simulations of model S and SW systems at various temperatures and pressures. The intermolecular interaction distance determined from the radial distribution function agrees well with other MD results [18,19]. In the S system, the number and relative occupancy of large ring-like structures increases with pressure under all temperature conditions. In the SW system, the formation of

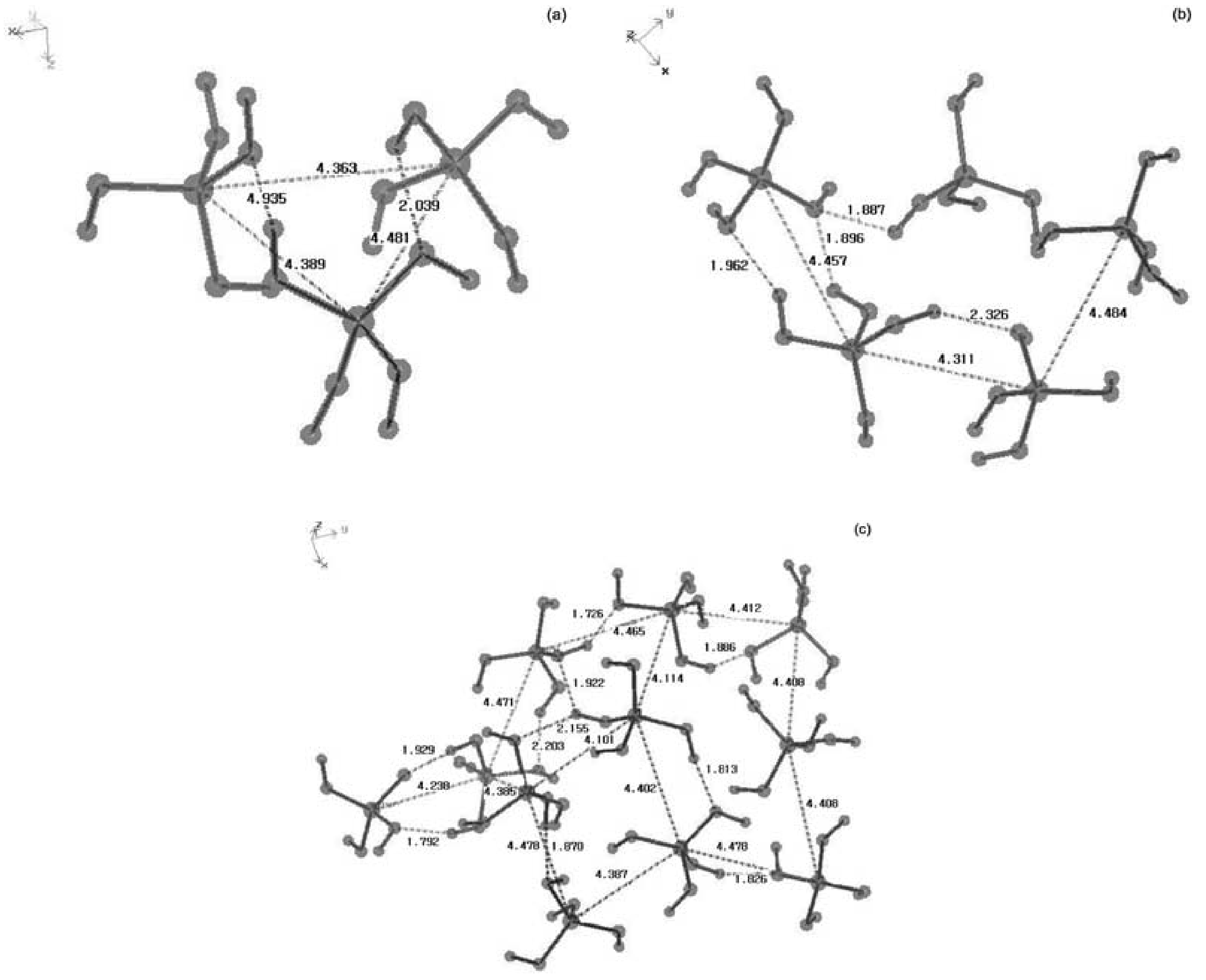

FIGURE 5 (a) 3 ring-like structure in S system under $P = 10\,\mathrm{kbar}$, $T = 298\,\mathrm{K}$ (b) Linear tetramer-like structure in SW system under $P = 1\,\mathrm{bar}$, $T = 298\,\mathrm{K}$ (c) Entangled ring-like structure in S system under $P = 10\,\mathrm{kbar}$, $T = 323\,\mathrm{K}$.

ring-like structures is less apparent under all temperature and pressure conditions. Although we have considered only ring-like structures, the role of excess water in condensation has been clarified by comparing the two systems.

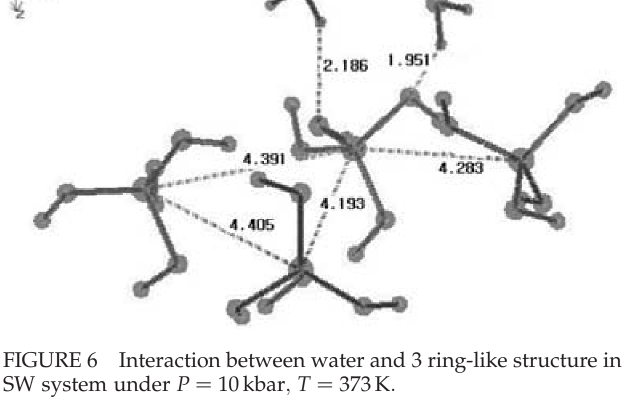

FIGURE 6 Interaction between water and 3 ring-like structure in SW system under $P = 10\,\mathrm{kbar}$, $T = 373\,\mathrm{K}$.

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