Small-Angle X-Ray Scattering Study on Sol-Gel Transition of Mixtures of Colloidal Silica and Organic Polymer

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Sol-gel transition of mixtures of colloidal silica-water soluble organic polymer (sodium polystyrenesulfonate) has been investigated by the small-angle X-ray scattering technique. With proceeding gelation, an increase of the intensity at small-angle regions was observed and the values of radius of gyration (R_g) were estimated by the Guinier method. The addition of polymer increased the initial increase of R_g with gelation, i.e., sol-gel transition was accelerated by the presence of the polymer. This observation is not in contradiction to the prediction of micro-phase separation into silica-rich phase and polymer-rich phase proposed by Nakanishi and Soga. The fractal analyses predicted that the geometrical structure of the gel finally formed is similar to those of random coil linear polymer and swollen branched polymer.

The sol-gel route to glass or ceramic materials is attracting increasing attention. The main advantage of this method is that the materials can be made at fairly low temperatures compared with conventional methods.1) For the alkoxy-derived silica system, the sol-gel reaction has been suggested to consist of two steps, i.e., the formation of primary silica particles by hydrolysis of alkyl silicate by water and the gel-network formation by aggregation of primary particles.2) The structure and properties of the gel-derived materials have been investigated by electron microscopy (EM),3) BET method,4) etc. while its mechanism has been studied by Raman scattering,5) NMR,6) and so on. Dynamical properties of sol-gel transition of tetramethoxysilane have been well-investigated by a variety of experimental techniques.7) Very recently, Nakanishi and Soga have found by EM that the glass finally obtained by the sol-gel method from mixtures of alkylsilicate and organic polymer has an interconnected porous structure in the micron-range.8) The production of glass materials with well-controlled porosity (in size and in its fraction) would have immeasurable value in materials science. The mechanism producing the porous structure has been considered to be microphase separation in the sol-gel system: silica-rich phases and polymer-rich phases are formed in the system whose size determines that of porosity.8) Porous structures of the glass finally obtained are clearly seen by EM. In addition, the same kind of porous gel can be obtained when colloidal silica is used as a silica source.8b) However, the mechanism and the structural change in sol-gel process for such systems are not yet clear. In this study, we applied the small-angle X-ray scattering (SAXS) technique to investigate the sol-gel process (from reaction mixture to wet gel with coexistence of an organic, water-soluble polymer). In this study, we used colloidal silica dispersion as a reaction material instead of alkyl silicate, since we can observe only the second step (aggregation of primary silica particles to form gel network). The SAXS technique has been shown recently to be useful9) to investigate the sol-gel process and the fractal structure10) of the gel formed.

Experimental

Colloidal silica used was SNOWTEX S kindly supplied by Nissan Chemical Co. (Tokyo, Japan). The diameter was found to be 6.65 nm by the Guinier method.11) The mother suspension was dialyzed against 10^{-4} NaOH solution to avoid aggregation until the NaOH solution shows a constant conductivity. The conductivity was checked by a Wayne-Kerr Auto Balance Precision Bridge (Model B331, Surry, England) with a glass conductivity cell with platinum electrodes. The organic polymer used was sodium polystyrenesulfonate (NaPSS) purchased from Pressure Chemical Co. (Pittsburgh, PA) whose molecular weight was 88000 by the supplier. NaPSS was also purified by dialysis against high quality Milli-Q water. The end point of dialysis was also determined by the conductivity method. The dialysis tube used both for colloidal silica and NaPSS was made by Union Carbide Corp. (Chicago, IL). The water used for sample preparation and for dialysis was obtained by the Milli-Q system (Millipore, Bedford, MA).

The SAXS apparatus used was made by Rigaku Corporation (Tokyo, Japan) the details of which have been described fully elsewhere.12) Since our SAXS system has a position sensitive proportional counter (PSPC), no angle-scanning is necessary. This enabled us to perform time-resolved measurements. The power of the X-ray generator was chosen to be 40 kV—100 mA because the strong scattering from the gel formed at high power condition is out of dynamic range of the detector. We used a Mark glass capillary (Diameter: 1.5 mm) as a SAXS cell. The SAXS cell was thermostatted at about 30 °C during measurements by circulating water from a temperature-controlled bath (Model K2R, Neslab, Newington, NH). The data obtained were corrected for slit smearing by Lake's method. The preparation of reaction mixture was as follows: an NaPSS solution at various concentrations was added into a purified colloidal silica suspension (4.0 vol%). An NaCl solution (0.2 M, M=mol dm^{-3})

Table 1. Component of Colloidal Silica-NaPSS Mixtures

[Silica]/vol%	[NaCl]/M	[NaPSS]/g dm^{-3}
4.0	0.2	0.0
4.0	0.2	0.1
4.0	0.2	0.5
4.0	0.2	1.0
4.0	0.2	2.0
4.0	0.2	6.0
4.0	0.2	12.0

Table 2. Component of Colloidal Silica and NapTS Mixtures

[Silica]/vol%	[NaCl]/M	[NapTS]/g dm^{-3}	[NapTS]/M
4.0	0.2	0.095	4.9X10^{-3}
4.0	0.2	0.94	4.8X10^{-2}
4.0	0.2	6.0	3.1X10^{-1}

was then added into the mixture to trigger gelation. Table 1 shows the composition of reaction mixtures at the onset of the reaction.

We used sodium *p*-toluenesulfonate (NapTS, Wako Chemicals Co., Osaka, Japan) as a monomer analog of NaPSS. The purification of NapTS was kindly done by Mr. Naoki Tanaka of our laboratory by recrystallization. Table 2 shows the compositions of NapTS systems. The concentrations of NapTS were determined to be comparable to the monomer concentration of NaPSS systems.

Results

Figure 1 shows the SAXS curves for a colloidal silica-NaPSS mixture at various gelation times. The time when salt solution was added into the system was defined as the gelation time zero. The abscissa q is the scattering vector ($q=4\pi\sin\theta/\lambda$, 2θ: scattering angle, λ: wavelength of X-ray (1.542 Å) and the ordinate is the relative intensity of scattered X-rays. It is clear that, with proceeding gelation, the intensity at very small-angle regions increases remarkably.

Figure 2 shows a comparison of the scattering behavior at three different NaPSS concentrations. The increase of scattered intensity at small-angle regions becomes significant and is rapid for higher NaPSS concentration systems.

Figure 3 shows a similar comparison for the NapTS systems. There was no significant difference at various concentrations.

Discussion

Guinier Analyses of Small-Angle Regions. In the small-angle regions called Guinier region, the scattering behavior follows a well-known Guinier law:[11]

$$I(q)=N\exp[(-1/3)R_g^2q^2] \quad (1)$$

where R_g is the apparent radius of gyration of scatterer and N a constant depending on the apparatus and the concentration. In $\ln I(q)$ vs. q^2 plot (Guinier

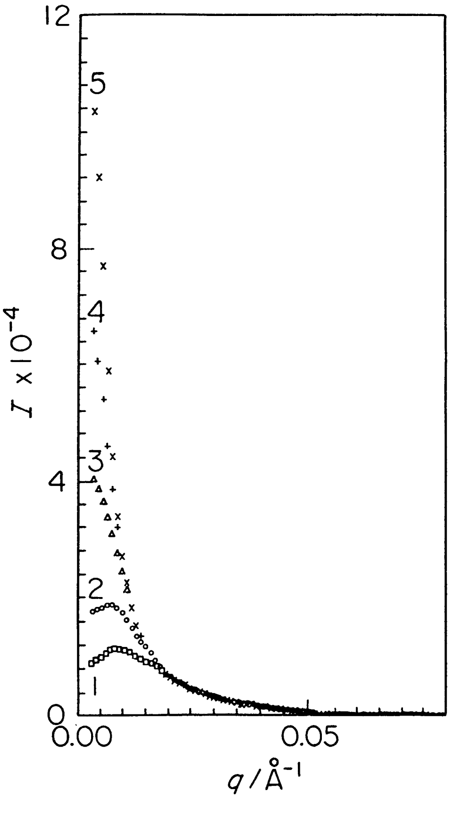

Fig. 1. Small-angle X-ray scattering (SAXS) curves for the gelation of a colloidal silica-NaPSS mixture. [silica]=4.0 vol%; [NaPSS]=1.0 g dm^{-3}; [NaCl]=0.2 M. Time/h: 1) 0.42, 2) 2.92, 3) 5.42, 4) 9.42, 5) 23.

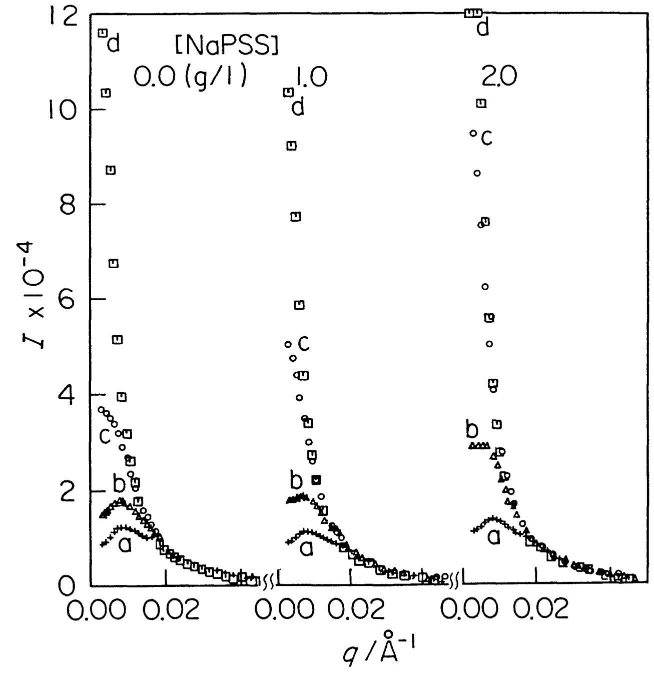

Fig. 2. Comparison of SAXS curves for gelation of colloidal silica at different NaPSS concentrations. [silica]=4.0 vol%; [NaCl]=0.2 M; Gelation time/h: a) 0.42, b) 2.9, c) 6.3, d) 20.

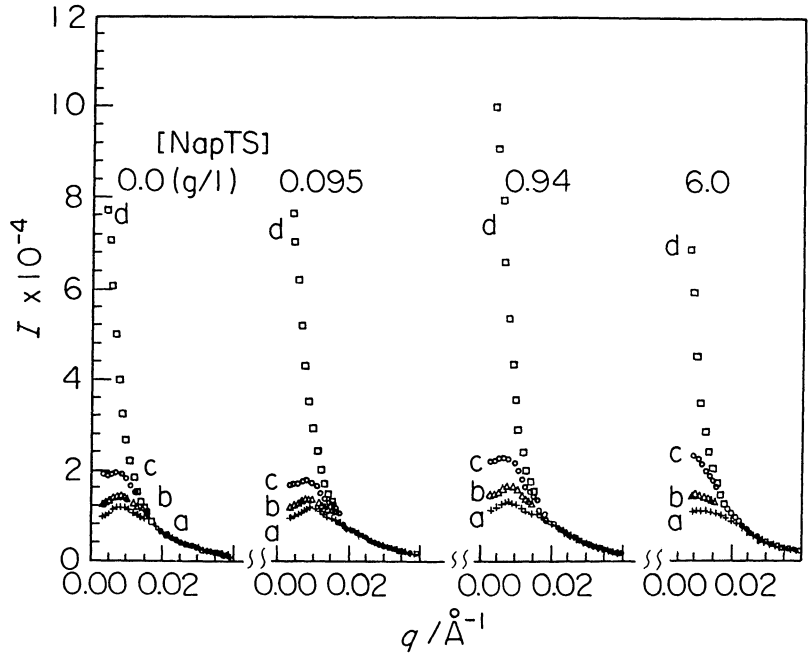

Fig. 3. SAXS curves for gelation of colloidal silica at different NapTS concentrations. [silica]=4.0 vol%; [NaCl]=0.2 M; Gelation time/h: a) 0.42, b) 2.9, c) 6.3, d) 23.

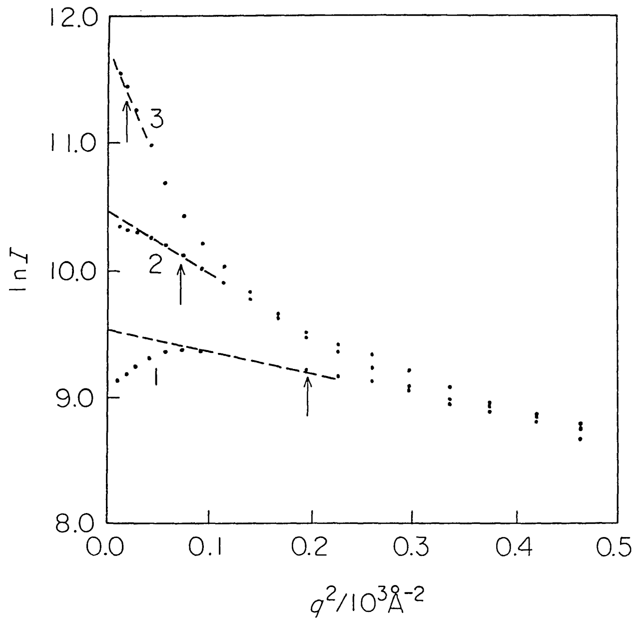

Fig. 4. Guinier plots for the gelation of a colloidal silica-NaPSS mixture. [silica]=4.0 vol%; [NaPSS]=1.0 g dm^{-3}; [NaCl]=0.2 M; Gelation time/h: 1) 0.42, 2) 4.6, 3) 23. The arrows mean the limit of Guinier region for the R$_g$ values obtained from the slope of the straight line.

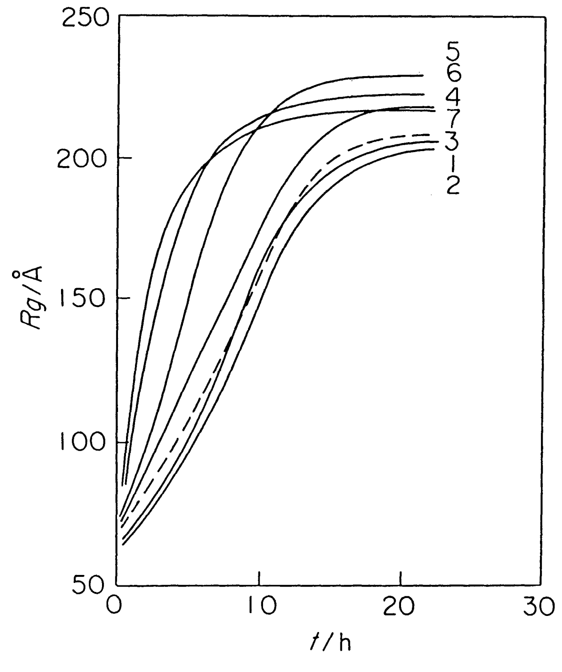

Fig. 5. Changes of the radii of gyration with gelation of colloidal silica dispersion at different NaPSS concentrations. [silica]=4.0 vol%; [NaCl]=0.2 M; [NaPSS]: 1) 0.0, 2) 0.1, 3) 0.5, 4) 1.0, 5) 2.0, 6) 6.0, 7) 12.0 g dm^{-3}.

plot), a linearity should appear in this region and R_g can be calculated from the slope of the straight line. Figure 4 shows typical examples of the Guinier plots, and the R_g values thus obtained are plotted against gelation time in Fig. 5 for different NaPSS concentrations. In general, the R_g value increased rapidly with proceeding gelation and reached constant values. The larger the NaPSS concentration, the steeper and faster the initial increase of R_g value. This tendency can be explained by invoking the concept of phase separation proposed by Nakanishi and Soga:[8] When a microphase separation occurs, silica-rich phases and polymer-rich phases are formed. The sol-gel process, i.e. aggregation of silica particles occurs in silica-rich phase in which the silica concentration is larger than the average concentration. Due to the higher silica concentration, the aggregation process and hence the sol-gel process is accelerated. A similar phase separation phenomenon has recently been reported by Furusawa et al. for a mixture of polystyrene-based polymer latex and NaPSS systems.[13]

Another possible interpretation of the acceleration phenomena described above may be adsorption of polymer: one linear polymer molecule adsorbed on surfaces of two or more silica particles bringing the particles closer and hence accelerate the aggregation reaction (enhanced collision). This phenomenon is called a bridging effect.[14] However, for our systems, the surface of the silica particles are negatively charged under these conditions (pH=8.9) and NaPSS is, of course, anionic. Adsorption of anionic polymer on negatively charged surface would be implausible due to the electrostatic repulsive interaction between them. In fact, Furusawa et al. reported that no adsorption occurred between NaPSS and polystyrene based, negatively charged polymer latex particle although these two consisted of the same material.[13]

If simple ionic salt is added into the system, the gelation process may be accelerated by the shielding effect of the salt; ionic impurities in the medium reduce the electrostatic repulsive interaction between silica particles, making the contact of the particles easier. Since NaPSS is also ionic, it may act as an ionic impurities and have a shielding effect. However, for our systems, the amount of NaPSS is 0.06 M at maximum, which can be considered to be much smaller than that of simple salt (NaCl, 0.2 M). Moreover, the results for NapTS systems (Fig. 6) clearly rule out this possibility. When compared at the same "monomer" concentration NapTS had nearly no acceleration effect (only at a NapTS concentration of 6.0 g dm^{-3} NapTS, a slight acceleration effect may be seen). Thus it is probable that the acceleration is due to a microphase separation, although the exact mechanism of separation phenomena is not clear at this stage. Further detailed experiments with polymers of various molecular weights are now in progress, and the results will be described in a forthcoming paper.

A few words are necessary on the physical meaning of R_g value. It would be highly possible that, just at the start point of gelation, R_g means the mean size of the colloidal silica particle and that, at the early stage of the reaction, R_g reflects the average size of small (isolated) aggregates of silica particles. However, at a certain point in the middle or late stages of the reaction, a cross-linking reaction should occur to form gel network. Hence, at least, at the final stage of the reaction, R_g should reflect the size of the network (or a correlation length of the network), or the size of "hole" in the network when we take into account the famous Babinet principle in optics.[15] Brinker et al.[16] proposed an interpretation of the meaning of R_g value for both cases of acid and base-catalyzed sol-gel transitions of tetraethoxysilane (TEOS) by a dilution technique. They claimed that the R_g for these two cases should be different; only for the acid case, an increase of R_g by dilution was observable indicating that R_g reflected the network size, while negligibly small changes of R_g for the base case indicated R_g to reflect the mean size of aggregates. However, since the possibility of swelling of the gel by dilution should be taken into account, their proposal of the interpretation might not be universal. For our case, what R_g means is not very clear at this stage. However, we can say that the size of aggregate, the network size, and the phase size in the system if a phase separation occurs, are important factors influencing R_g value.

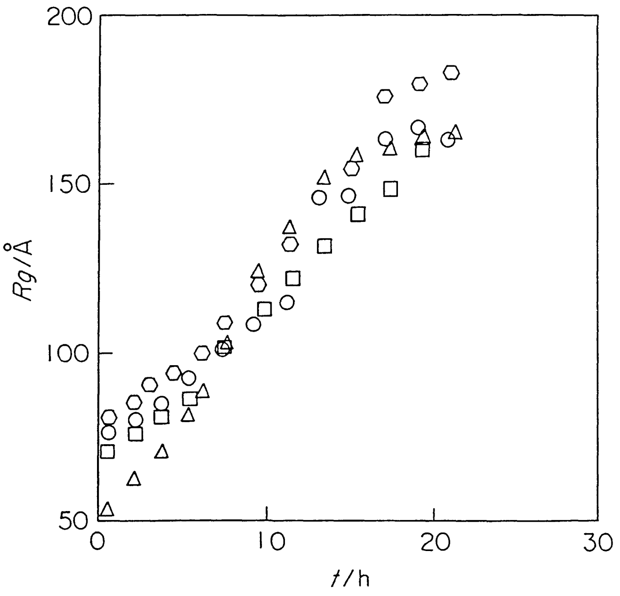

Fig. 6. Changes of radii of gyration with gelation of colloidal silica dispersion at different NapTS concentrations. [silica]=4.0 vol%; [NaCl]=0.2 M; [NapTS]: ○: 0.0, □: 0.095, ⬡: 0.94, △: 6.0 g dm^{-3}.

Fractal Analyses at the Middle and Large Angle Regions. In relatively higher angle regions, it is well-known that the scattering behavior follows a power law,[17] namely

$$I(q) \propto q^{-\alpha} \tag{2}$$

Hence, the double logarithmic plot of $I(q)$ and q (Porod plot) shows linearity and its slope α is called the Porod slope. When $3<\alpha\leqslant 4$ holds, α reflects the geometrical structure of the surface of the scatterer and α can be related to the surface fractal dimension D_s by $D_s=6-\alpha$.[9] When the surface is perfectly smooth, α

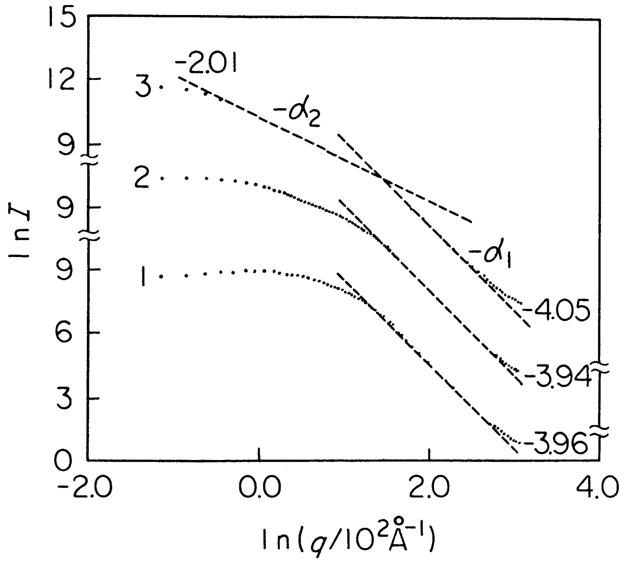

Fig. 7. Porod plots for the gelation of a colloidal silica-NaPSS mixture. [silica]=4.0 vol%; [NaPSS]=1.0 g dm^{-3}; [NaCl]=0.2 M; Gelation time/h: 1) 0.42, 2) 4.6, 3) 23.

should be equal to 4, and this relation had been well-known as a Porod law[18] much before Mandelbrot proposed the concept of fractal.[10] When α is less than or equal to 3, α reflects the geometrical structure of the scatterer itself and α can be related to the volume fractal dimension D_v by $\alpha=D_v$.[9] For both cases, the q range, in which the linearity holds, depends on the dimension of the scatterer which has a fractal character.

Figure 7 shows examples of the Porod plot at three different gelation times. At any gelation time, an excellent linearity is seen at relatively high angle regions. For middle angle region, no linearity is observed at the early stage of the reaction. But as gelation proceeds, linearity appears and at the end of the gelation also excellent linearity holds. The Porod slopes thus obtained for both large (α_1) and middle (α_2) regions are summarized in Table 3. The average radius of the units of the structure, R_u and a correlation length of the gel, R_c obtained from a low q-limit of the linearity for α_1 and α_2, respectively, are also shown in Table 3. The average values of α_1 and α_2 were 4.02 and 1.98, respectively. As mentioned above, it is most reasonable to conclude that α_1 and α_2 reflect the surface and the geometrical structure of the scatterer, respectively. Since the linearity whose slope gives α_1 is already observed at the early stage of the gelation, α_1 reflects the surface structure of colloidal silica particles. The result that R_u values are smaller than the radius of the silica particle corroborates our interpretation. $\alpha_1=4$ means that its surface is smooth (Porod law). The α_2 value, about 2, means the geometrical (fractal) structure of aggregates of primary particles and/or of the gel network formed.

Table 3. Properties of Gels of Colloidal Silica-NaPSS Mixtures

[NaPSS]	Porod slope		Average radius	Correlation
g dm^{-3}	α_1	α_2	R_u/Å	length R_c/Å
0.0	3.99	1.94	24.7	168
0.1	4.02	1.94	25.2	143
0.5	4.00	1.95	25.7	144
1.0	4.05	2.01	23.7	168
2.0	4.06	2.01	22.5	172
6.0	4.01	2.02	23.5	179

[Silica]=4.0 vol%, [NaCl]=0.2 M. $R_u=1/q_u$: q_u is the q value at the crossover point of two straight lines for α_1 and α_2. $R_c=1/q_c$: q_c is the low-q limit of the linearity for α_2.

Since the linearity for α_2 is observed in the angular range between those for the Guinier region and for α_1 linearity, it may be most reasonable to conclude that α_2 reflects the geometrical structure of silica aggregate if R_g reflects the size of the gel network. According to Schaefer,[19] the slope of -2 may be obtained for α at least two geometrical structures, a linear polymer (random coil) and swollen branched polymer. Hence, the structure of the aggregates and/or gel network observed in the present work would be very similar to those of linear polymer or swollen branched polymer, although it is not clear which is correct at the moment. We also observed that the α_2 value increases with increasing polymer concentration, although very slightly. This may reflect the possibility of the control of gel structure by addition of polymer. However, since the change is small, experiments in a much larger polymer concentration range and with other polymers are necessary for further detailed discussion and for study on the relation to the porous structure of final materials, and now are in progress.

Conclusion

Sol-gel transition of a colloidal silica suspension was accelerated by addition of water soluble polymer (NaPSS in this study). This acceleration may have been due to microphase separation between the colloidal silica and polymer, which is not in contradiction with the model proposed by Soga and Nakanishi. The geometrical structure of the gel formed had a fractal nature, and its (volume) fractal dimension was about 2, which is very close to those of linear polymer and swollen linear polymer. The fractal dimension of the gel was slightly affected by the concentration of the coexisting polymer, which makes it feasible to control a gel structure by addition of polymer.

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