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Phase Separation in Silica Sol–Gel System Containing Poly(ethylene oxide). I. Phase Relation and Gel Morphology

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Phase separation and gelation behaviors have been studied for the acid-catalyzed, alkoxide-based silica systems containing poly(ethylene oxide) (PEO) with an average molecular weight of 100000. Gels with micrometer range interconnected porous morphology were obtained similarly to the systems containing other water-soluble polymers, in which the structure development by the spinodal decomposition and the gel forming process take place concurrently. In spite of the morphological similarity, the thermogravimetric analysis revealed that the reacting solution decomposed into phases one rich in PEO and the other rich in solvent. Macropore volume of gels depended mainly on the amount of solvent phase.

In preceding papers, we reported phase separation and gelation in alkoxide-based silica sol–gel systems containing water-soluble ionic organic polymers such as poly(sodium styrenesulfonate)(NaPSS) and poly(acrylic acid)(HPAA).[1,2] When the starting composition and reaction temperature were appropriately adjusted so as to induce phase separation and sol–gel transition concurrently during the polymerization reaction of silica, various transitional structures developed by a phase separation process were fixed as morphologies of gels. Poly(ethylene oxide) is one of nonionic water-soluble polymers. It exhibits strongly exothermic interaction between water, and is known to adsorb onto the surfaces of colloidal silica especially under low pH conditions.[3] The purpose of the present study is to compare the phase separation and gelation behaviors of the system containing PEO with those reported previously.[1,2] The investigation was carried out for the system containing PEO having molecular weight of 100000 and tetramethoxysilane (TMOS) or tetraethoxysilane (TEOS) under strongly acidic conditions. The effect of starting composition on the morphology of gels is studied in comparison with the systems containing ionic polymers. The results are discussed mainly focusing on the phase relation of ternary system composed of PEO, silica, and solvent, and on the role of PEO in the sol–gel reaction.

Experimental

TMOS and TEOS, products of Shin-Etsu Chemical Co., were used as silica sources without further purificaiton. Poly(ethylene oxide) (PEO) with an average molecular weight of 100000, product of Aldrich Chemical Co., was used as a polymer component. Poly(acrylic acid) (HPAA) with an average molecular weight of 250000 was also used to compare the thermal decomposition behavior. Nitric acid was used as a catalyst for hydrolysis.

The sample gels were prepared by hydrolyzing TMOS or TEOS with acidic aqueous solutions containing various amount of organic polymer as was reported previously.[1] The typical starting compositions adopted are listed in Table 1. Gelation and aging were conducted under tightly sealed conditions in an air circulating oven at 40 °C. The gelation time, t_g, was determined by simply tilting the container as the time at which the bulk fluidity of the solution was lost. In the case that a solution exhibited a macroscopic two-phase appearance due to precipitation, the time at which the solution became turbid was recorded as the onset time of phase separation, t_ps, instead of t_g.

For the thermogravimetric analysis (TAS-100, Rigaku Corp.), a sample solution was divided into a "gel phase" and a "fluid phase" after the gelation of precipitated phase. In the case that bulk gelation took place, the syneresis liquid was extracted after an appropriate aging period. Evaporation of the solvent components was carried out at 80 °C, and the solid residue was roughly crushed and subjected to the analysis.

For the morphology observation with a scanning electron microscope (SEM; Hitachi-S510), after exchanging the solvent phase with 1 M HNO_3 aq by repeated immersions, wet gels were finally dried at 60 °C ($1\ \mathrm{M}=1\ \mathrm{mol\,dm^{-3}}$). The sizes of interconnected domains in the dried gels (expressed by L) are defined as the half of the sum of thickness of a silica skeleton plus width between the adjacent pore wall, and were evaluated by averaging more than twenty directly measured values on the SEM photographs. The linear drying shrinkage ratios varied little among the samples (about 60% of original dimension on average), so that as-measured values of L for dried samples were used to make comparison of their morphologies.

Results

Gel Formation Behavior. Figure 1 shows the dependence of t_g or t_ps on the incorporated amount of PEO with the starting composition of PO10-EP8 shown in Table 1. In a low concentration range up to 0.40 g, a polymerizing solution became turbid at t_ps, followed by the precipitation of dispersed phase, finally gave a distinct two-phase appearance. The as-precipitated phase exhibited fluidity, and transformed into a gel in a period depending on the PEO concentration. Although it was difficult to unambiguously determine the gelation time of highly visicous precipitated phase, the time lag of the onset of precipitation and subsequent gelation became shorter with an increase of PEO

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Table 1. Typical Starting Composition of Samples (Unit: g[a)])

Sample	Polymer	(M.W.)	H_2O	60%HNO_3 aq	Alkoxide	
PO10-EP8	PEO	0—1.50 (100000)	8.0	0.81	TEOS	6.51
PO10-ES8	PEO	1.00 (100000)	8.0	0.81	TEOS	4.65—8.37
PA25-E8	HPAA	0.30 (250000)	8.0	0.81	TEOS	6.51
PO10-MP10	PEO	0—1.80 (100000)	10.0	1.02	TMOS	5.15

a) In the text and figures, the weight of each component is represented by $m_{\mathrm{component}}$.

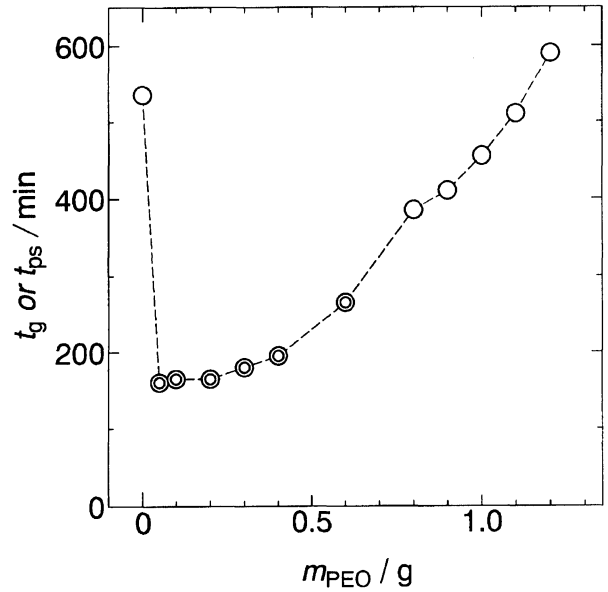

Fig. 1. Dependence of gelation time, t_g (○), or phase separation time, t_{ps} (◎), on incorporated amount of PEO, m_{PEO}. Starting composition is PO10-EP8 in Table 1, and reaction temperature is 40 °C.

concentration. The supernatant phase also gelled later, and the lag of the gelation times of precipitated and supernanant phases increased steeply with PEO concentration. The value of t_{ps} increased only gradually, whereas the amount of the precipitated layer increased roughly in proportion to the incorporated amount of PEO. At the PEO amount of 0.60 g, the supernatant phase no more gelled but spherical particles of silica in micrometer range were observed under SEM after the evaporation of solvent. When the amount of PEO was increased to 0.80 g, the solution first became turbid and gelled without precipitation. With a further increase of PEO the increase of turbidity was observed parallel to bulk gelation, whereas t_g increased monotonously. These observations are by good contrast with the system containing HPAA, which exhibited a monotonous decrease of t_g and an earlier occurrence of phase separation with respect to gelation with an increase of HPAA concentration. Hereafter, the precipitated or homogeneously gelled part is denoted as a "gel phase", and the supernatant liquid or that squeezed-out form a gel by the syneresis is denoted as a "fluid phase".

Thermal Analysis of Decomposed Phases. Table 2 shows weight ratios of "fluid phase" and "gel phase" together with that of drying residue of the "fluid phase". All the ratios are presented relative to the total weight of the starting solution. A monotonous increase of gel phase with increasing PEO concentration is recognized. While the sample containing 0.30 g of PEO gave a distinct two-phase appearance, that containing 0.60 g of PEO yielded much more precipitated phase and less supernatant. When 0.90 g of PEO was used, completely homogeneous gelation was observed, so that the fluid phase wholly consisted of syneresis liquor in this case.

When the dried gel and fluid phases were continuously heated at the rate of 10 °C min^{-1} up to 1000 °C, evaporation of residual solvent components took place below 200 °C, and large weight losses due to the decomposition of PEO were observed between 200 and 300 °C (see Fig. 2(a)). Thus the ratio of weight loss of each gel above 200 °C against the weight at 200 °C is directly correlated to the weight ratio of PEO to silica. The weight ratios calculated from the data are listed in Table 3. In the gel phase, either precipitated or homogeneously gelled, the ratio of PEO increases with initially added amount, and seems to approach a limiting value above 0.90 g. On the other hand, in the fluid phase, the ratios are lower than those in the gel phase at PEO additions of 0.30 and 0.60 g. However, at 0.90 g, more than half of the drying residue is composed of PEO.

From these results, it is expected that a large fraction of incorporated PEO exist in the gel phase, and that a considerable amount of silica component is distributed to the fluid phase when the PEO amount is small. With an increase of initial PEO concentration, the absolute amount of gel phase increases, and consequently, larger fraction of silica is distributed to the gel phase. With the PEO amount of 0.90 g, most of silica is distributed to the gel phase with PEO, which accounts for the high fraction of decomposed compo-

Table 2. Weight Ratios of Gel Phase and Fluid Phase

m_{PEO}[a)]/g	$F^{\mathrm{W}}_{\mathrm{Gel}}$[b)]	$F^{\mathrm{W}}_{\mathrm{Fluid}}$[b)]	$F^{\mathrm{D}}_{\mathrm{Fluid}}$[b)]
0.30	0.45	0.55	0.054
0.60	0.66	0.34	0.013
0.90	0.82	0.18	0.008

a) Starting composition is PO10-EP8 in Table 1.
b) Weight ratio relative to the total weight of starting solution. Superscripts W and D denote "wet" and "dried" states, respectively.

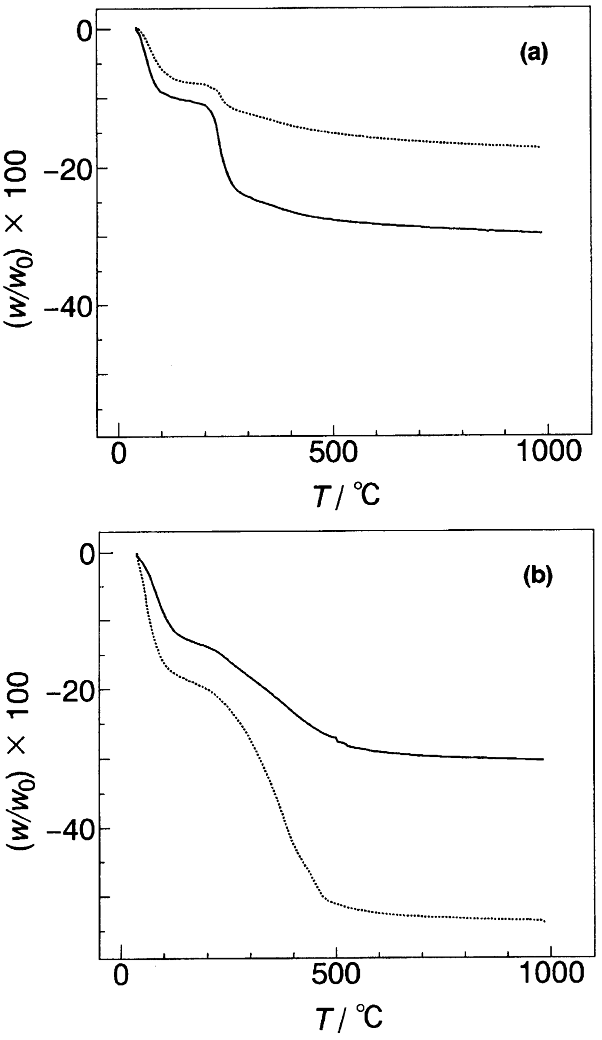

Fig. 2. Thermogravimetric curves of the sample prepared with (a) PO10-EP8 composition with $m_{\rm PEO}$= 0.30 g, and (b) PA25-E8. Values of sample weight, w relative to that after drying at 80 °C, w_0, at elevated temperatures, T, are plotted. Solid and dotted lines denote gel and fluid phases, respectively.

Table 3. Weight Fraction of Thermally Decomposed Component above 200 °C

$m_{\rm PEO}$/g	$f^{\rm TD\,a)}_{\rm Gel}$	$f^{\rm TD\,a)}_{\rm Fluid}$
0.30	0.22	0.09
0.60	0.28	0.17
0.90	0.32	0.54

a) Ratio of weight decrease above 200 °C relative to the sample weight at 200 °C.

nent, PEO, in the fluid phase. This phase relation is again by contrast with HPAA system (Fig. 2(b)) which decomposed into silica- and HPAA-rich phases with the solvent being distributed between them.

Dependence of Domain Size and Morphology on Starting Composition. Figure 3 shows the morphology of dried gels prepared with different amount of PEO in the starting composition of PO10-EP8 in Table 1. In the case of Fig. 3(a), since the solution gave a macroscopic two-phase appearance as described above, only the precipitated gel phase is shown. The morphology with isolated pores in a continuous gel matrix was a common feature which was observed in the samples of macroscopic two-phase. With the PEO amount of 0.80 g, the morphology turns into that with interconnected gel skeletons and pores with dimensions of few tens micrometers. Further additions of PEO made the interconnected structure finer to the length scale of submicrometer, and at last, although not shown in the photographs, the gel structure became that without detectable inhomogeneity under SEM. The domain size, L, determined from the photograph is plotted against PEO amount in Fig. 4. The steep decrease of L with PEO amount is contrasted with the results of previously studied systems in which the value L almost always increased with incorporated amount of polymer.[1,2)]

Figure 5 shows the morphology of dried gels prepared from PO10-ES8 compositions. In the case of Fig. 4(a), the morphology is in-between the "particle aggregates" and "interconnected structure". With an increase of TEOS under the constant amount of the other constituents, the morphology gradually turned into that with interconnected skeletons and pores with smoother surfaces and larger sizes. In the case of Fig. 5(e), however, the pores lose their connectivity and become dispersed in a continuous gel matrix. Although both the increase of PEO and that of TEOS increase the volume fraction of gel phase, they affect on the domain size in completely reversed ways.

Figures 6 and 7 respectively show the relation between calculated solution composition and resultant gel morphology for systems with TEOS and TMOS. In each triangle, the end component at the top corner is the sum of water, nitric acid, and alcohol. Since the amount of water in the starting compositions were at least 7 times the mol of alkoxide, the composition at the time of phase separation and gelation was calculated by assuming that the alkoxide is completely hydrolyzed and polycondensed. This assumption corresponds to the consumption of 2 mol of water and generation of 4 mol of alcohol per unit mol of alkoxide from the starting composition. It should be noted that the alcohol/water ratio in the solvent mixture increases with silica concentration. Although the alcohol/water ratio plays an important role in determining the domain size as discussed below, the three component expression is presented here to emphasize the contribution of respective end components to the volume fractions of gel and fluid phases.

The morphologies of "macroscopic two-phase" and "particle aggregates" tend to be formed when the volume fraction of a gel phase is considerably lower than that of a fluid phase. On the contrary, those of "isolated macropores" and "nanopores" (without observ-

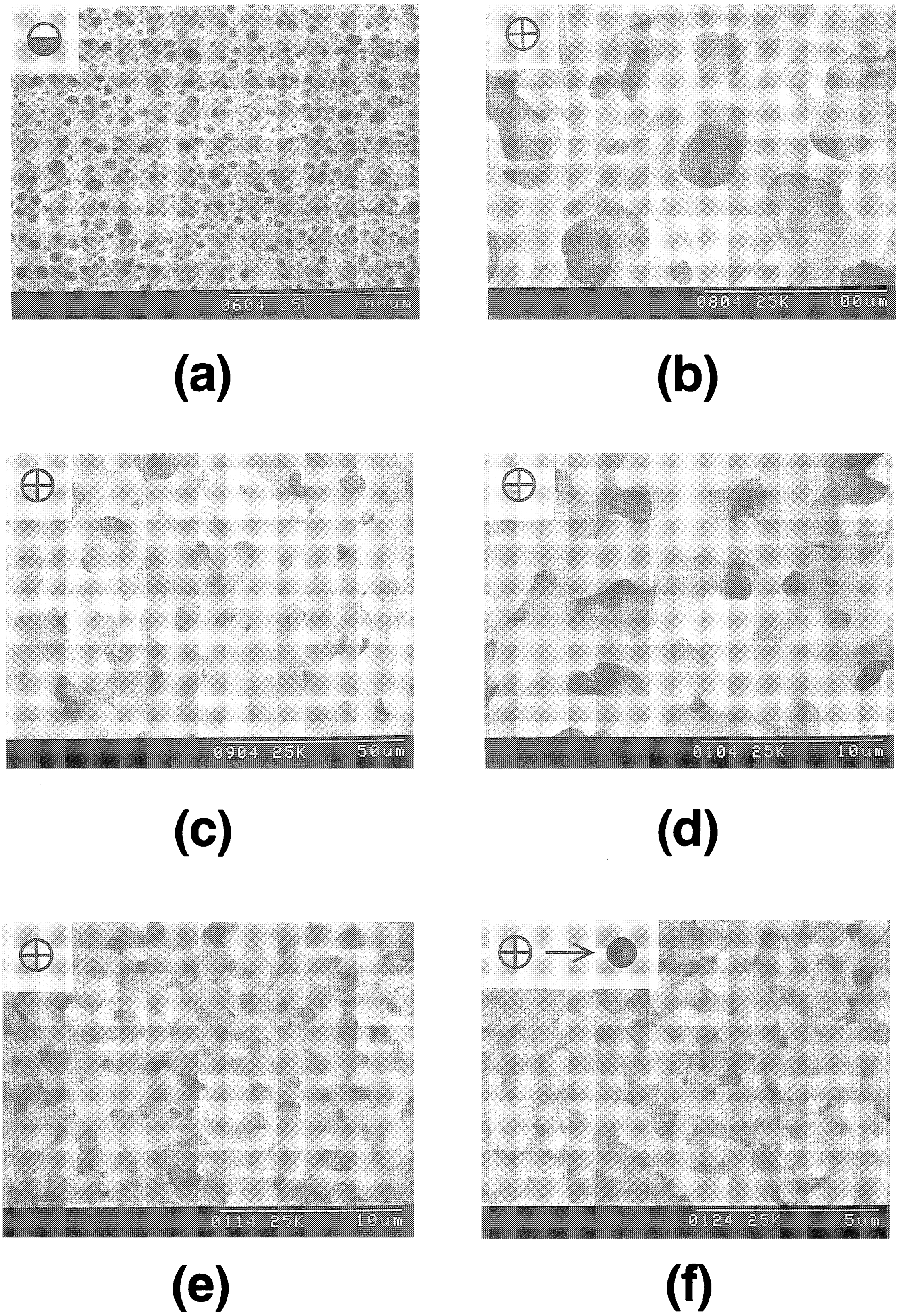

Fig. 3. SEM photographs of dried gel samples prepared with PO10-EP8 composition at 40 °C; $m_{\rm PEO}$=(a) 0.60 g, (b) 0.80 g, (c) 0.90 g, (d) 1.0 g, (e) 1.1 g, (f) 1.2 g.

able structure under SEM) are formed when the volume fraction of a gel phase becomes higher than that of a fluid phase. The resultant morphologies shown in Figs. 6 and 7 clearly show that the volume fractions of

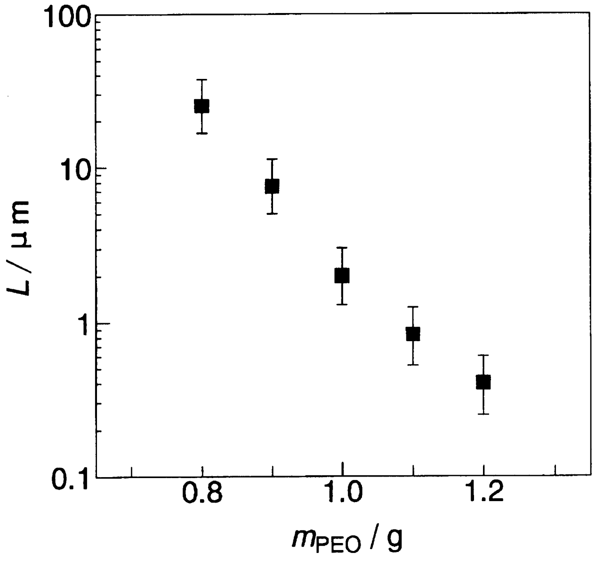

Fig. 4. Dependence of domain size, L of dried gels on m_{PEO} with PO10-EP8 composition. The morphology of gels prepared with $m_{\mathrm{PEO}}<0.80$ g was macroscopic two-phase, and that with $m_{\mathrm{PEO}}>1.2$ g was nanopores.

gel and fluid phases are respectively estimated by the weight fractions of "silica and PEO" and "solvent". For example, the increase of TEOS corresponds to the left downward shifting on Fig. 6, and the volume fraction of gel phase increases as shown in Fig. 5. On the other hand, a series of addition of PEO corresponds to the right downward shifting on the diagram, and it also increases the volume fraction of the gel phase.

In order to extract the effect of solvent phase composition on domain size, gels prepared with fixed PEO/alkoxide ratios and varied water amount were compared for TEOS and TMOS systems. The domain size and weight fraction of alcohol in the solvent are plotted in Fig. 8 for the samples prepared with the compositions on the broken lines in respective diagrams. With an increase of solvent fraction caused by the increase of water amount, both the fractions of ethanol and methanol decrease only slightly reflecting the high fraction of water in the starting composition. The domain size, however, changes drastically in TMOS system. This result indicates that the fraction of methanol strongly affects the phase separation and domain formation process, while that of ethanol does little.

Discussion

Phase Relation of Silica–PEO–Solvent System. In the polymer-incorporated silica systems reported previously,[1,2] the main components of "gel phase" and "fluid phase" are silica and organic polymer, respectively. The volume fraction of fluid phase, roughly estimated by the macropore fraction of a dried gel, is mainly determined by the incorporated amount of the organic polymer. In the present system incorporated with PEO, however, the phase relation is completely different form those; the amounts of PEO and solvent predominantly determine the fractions of gel and fluid phases, respectively. Silica is preferentially distributed to the gel phase rich in PEO, but can remain also in the fluid phase when the amount of PEO is small. The phase relation deduced from the thermal analysis suggests that the phase separation is driven by the repulsive interaction between the PEO molecules adsorbed or complexed on silica oligomers and the solvent mixture. In the following discussion, we try to explain the experimental results by assuming a kind of complex formation of PEO on polycondensing silica oligomers.

It is well-known that PEO strongly adsorbs on a hydrophilic surface of colloidal silica from hydrophobic media,[3] and that even in an aqueous medium PEO works as an efficient flocculant of colloidal silica dispersion.[5,6] Thus, it seems probable that ether oxygens in PEO chains form hydrogen bonds with surface silanols of alkoxy-derived silica oligomers. Although the fluocculation of colloids is often caused by weakening the electrostatic repulsive interaction between dispersed particles which leads to the aggregation and sedimentation of high-density dispersions, the alkoxy-drived silica oligomers carry less surface charge and have considerably lower density than colloidal silica. Hence the precipitation of silica oligomers in the presence of PEO can possibly be treated analogously to the exsolution of hydrogen-bonding polymers by complexing with PEO in an aqueous medium.

On the destablization or exsolution of water-soluble polymeric species in an aqueous medium, the complex formation between PEO, as well as PEO based nonionic surfactants, and polycarboxylic acids in a low pH range has been investigated.[7,8] In a typical case, PEO and HPAA molecules form a hydrogen-bonded complex which is insoluble in water by destroying respective hydrated structures. It is also known that insoluble complex can be formed only when the molecular weights of both polymers are higher than certain critical values depending on their respective concentrations and solution pH.[8] If we assume the adsorption of PEO on silica oligomers analogously to this complex formation, a PEO chain will form hydrogen bonds only on continuously distributed silanols belonging to a large enough oligomer. When there exist only silica oligomers with low molecular weight in the solution, it will be unfavorable for the long PEO molecule to destroy its hydrated structure to form a limited number of hydrogen bonds. With an increase of the degree of polymerization of silica oligomers, more continuous silanol sites become available, on which greater fraction of PEO molecule can form hydrogen bonds, and as a result, the PEO–silica complex forms which is less soluble in the solvent. If the polymerization is strongly hindered by the adsorption of PEO, the silica oligomers will physically agglomerate and form precipitates in any cases. The experimental facts show that, however, the adsorbed

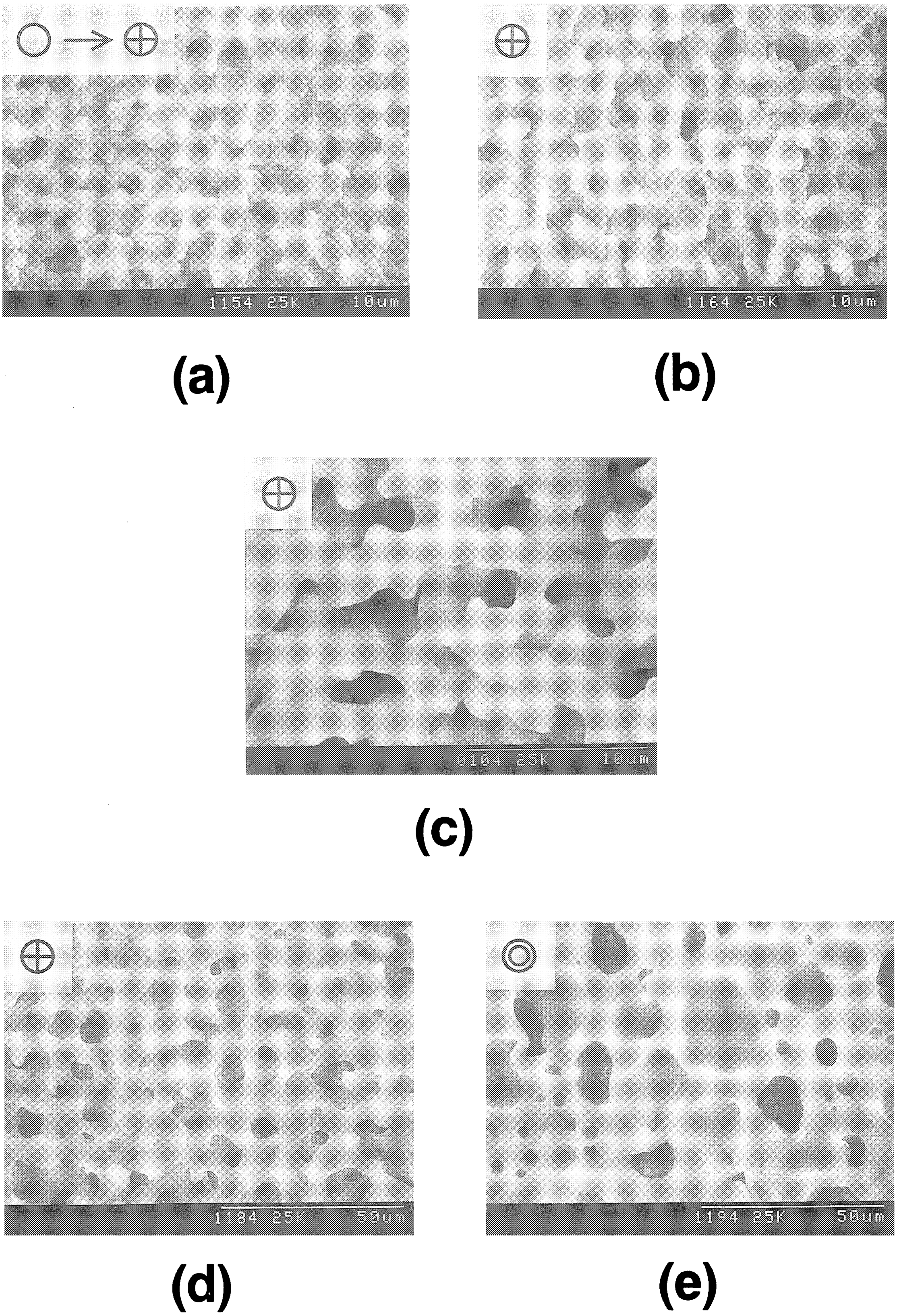

Fig. 5. SEM photographs of dried gel samples prepared with PO10-ES8 composition at 40 °C; m_{TEOS}=(a) 4.65 g, (b) 5.58 g, (c) 6.51 g, (d) 7.44 g, (e) 8.37 g.

oligomers are not readily excluded from the solution but continue to polymerize. It is probably due to the loose configuration of PEO molecules adsorbed on the surface of oligomers, which leaves a substantial number of free

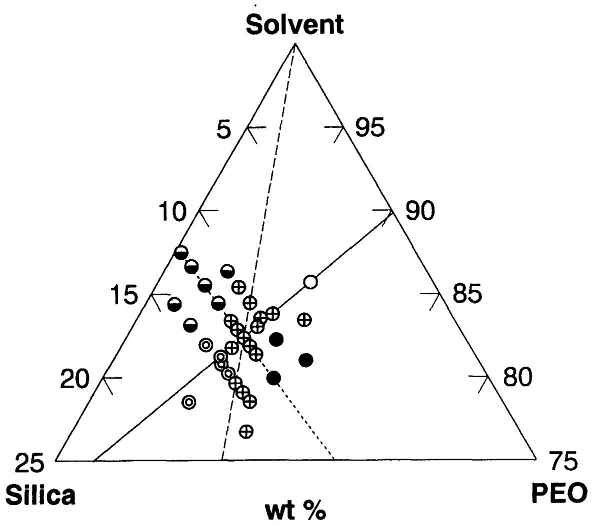

Fig. 6. Relation between calculated solution composition and resultant gel morphology in PEO–TEOS system; ◒ : macroscopic two-phase, ◎ : isolated macropores, ⊕ : interconnected macropores, ○ : particle aggregates, ● : nanopores. Dotted line corresponds to the PO10-EP8 compositions with varied m_{PEO}. Solid line corresponds to the PO10-ES8 compositions with varied m_{TEOS}. The calcnlation of composition is described in the text.

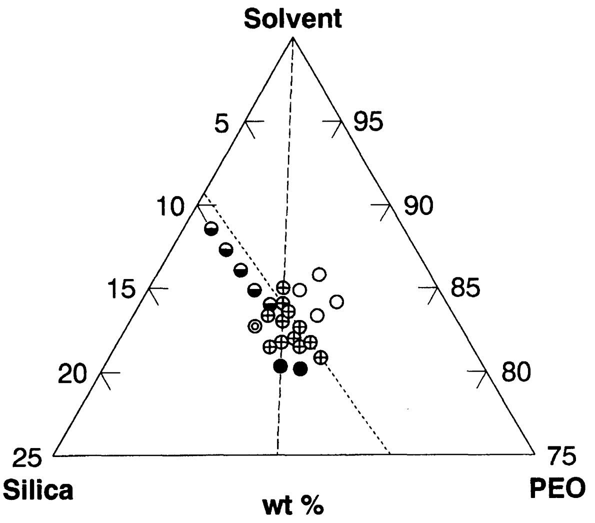

Fig. 7. Relation between calculated solution composition and resultant gel morphology in PEO–TMOS system; Symbols are the same as in Fig. 6. Dotted line corresponds to the PO10-MP10 compositions with varied m_{PEO}.

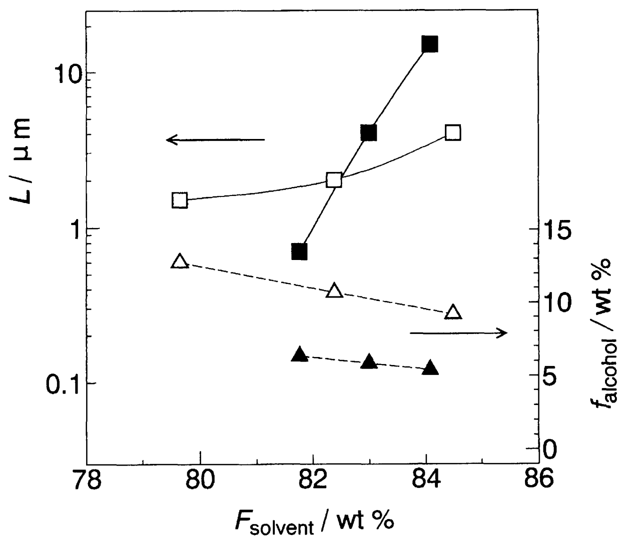

Fig. 8. Dependence of domain size, L, on solvent fraction in the calculated composition, F_{solvent} (denoted by squares), and variation of weight fraction of alcohol in the solvent mixture, f_{alcohol}, with F_{solvent} (denoted by triangles). Open and closed symbols respectively denote PEO–TEOS and PEO–TMOS systems, and compositions are varied along the broken lines in Figs. 6 and 7, respectively.

silanols available for further polymerization reactions. As a result, the competition of macroscopically homogeneous gel formation and precipitation is observed by adjusting the starting compositional parameters.

Mechanism of Morphology Formation. In the systems containing water-soluble polymers such as poly(sodium styrenesulfonate) or poly(acrylic acid), the formation of interconnected gel morphology has been consistently explained by the concurrent occurrence of phase separation and sol-gel transition induced by the polymerization of alkoxide-based silica.[1,2] The free energy change caused by mixing chemically different polymeric species can be expressed by the Flory–Huggin's formula as follows;[9]

$$\Delta G \approx RT\{(\phi_1/P_1)\ln\phi_1 + (\phi_2/P_2)\ln\phi_2 + \chi_{12}\phi_1\phi_2\} \quad (1)$$

where ϕ_i and P_i (i=1, 2) respectively denote the volume fraction and degree of polymerization of the component i, and χ_{12} the interaction parameter, R the gas constant, T the temperature. The first two terms in the bracket, both have negative values, represent contributions of mixing entropy and their absolute values decrease when the corresponding component polymerizes, i.e. P_i increases. If the value of χ_{12} is positive, which corresponds to a repulsive interaction between the components, a polymerizing system would exhibit an upward convex binodal line moving toward higher temperature in a composition-temperature diagram. In other words, an initially homogeneous solution may phase-separate as either component polymerizes. The origin of phase separation could be well explained by this entropic factor in the cases of NaPSS and HPAA where the solution decomposes into phases one rich in silica and the other rich in organic polymer with the solvent components being distributed to both phases.

In the present system containing PEO, the situation is even more complicated. The reacting solution contains polymerizing silica oligomers, PEO, and solvent mixture. The solution decomposes into phases one rich in PEO and the other rich in solvents, with the silica component being distributed to both phases by a proportion which depends on the PEO-silica ratio. As discussed in the previous section, the origin of phase separation is assumed to be the decreased affinity (increased repulsive interaction) of PEO molecule adsorbed on silica oliogomers against the solvent mixture. It implies that the enthalpic interaction parameter between PEO and solvents increases with the progress of polymerization reaction of silica. The experimental results show that, with a small amount of incorporation of PEO, the phase separation which causes precipitation of a PEO–silica phase took place long before the gelation of the reference sample without PEO. This fact suggests that, although the polymerization of silica is inevitably linked with the whole process, its entropic contribution to increase the free energy of the system is not essential to cause the phase separation observed in the present study.

For any reason, when the initially homogeneous system is thrust into the thermodynamically unstable region, i.e. within the spinodal line in the phase diagram, the spinodal decomposition can take place.[10] The domain formation process of spinodal decomposition is known to be divided into successive three stages.[11] In the initial stage, concentration fluctuation with a particular dominant wavelength grows only in amplitude exponentially with time. In the following intermediate stage, both the wavelength and amplitude of the fluctuation increases. And after the concentration difference between conjugated domains reached to the equilibrium value, the coarsening process driven by the interface instability follows, and this is called the late stage. The characteristic interconnected phase structure can develop when the volume fractions of the conjugate phases are comparable.

On the other hand, the present system forms a gel network by an irreversible polymerization reaction of silica. The sol–gel transition is the process in which the mobility of a fluid is frozen from the longer length scale to smaller. When the sol–gel transition occurs concurrently with the structure development by the spinodal decomposition, the transient structures can be frozen-in in various stages described above. Provided that respective kinetics of domain formation and sol–gel transition do not influence on each other, the earlier occurrence of phase separation relative to the sol–gel transition necessarily results in the more coarsened morphology frozen-in in a gel (See Fig. 9). Our recent light scattering experiments evidently support the above mechanism of morphology formation.[12]

Dependence of Gel Morphology on Compositional Parameters. According to the discussion of the previous section, the change of reaction parameters which retard the gel formation, or those enhance the occurrence of phase separation, can increase the domain size of resultant gel morphology. That is, any change of compositional parameters should be related to the resultant domain size through its effects on both the solubility of PEO–silica complex and the rate of polymerization reaction.

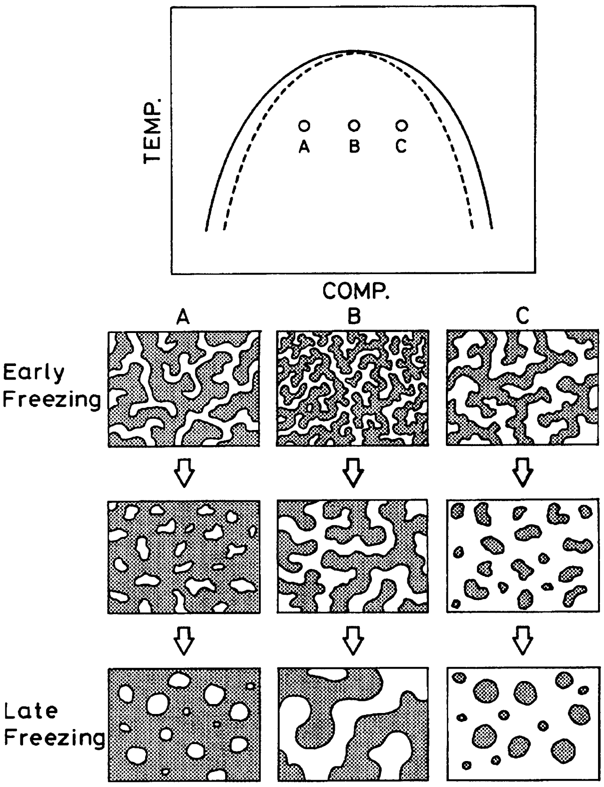

Fig. 9. Schematic drawings of transient structures developed by a spinodal decomposition with varied proportions of conjugated phases. Symmetric binodal and spinodal lines are assumed for simplicity. With the composition B, the critical composition, the interconnected (bicontinuous) structure coarsens with elapse of time. Earlier freezing of the transient structure results in the finer morphology.

The change of domain size along the compositions at constant PEO/silica ratio, shown in Fig. 8, reflects the dependence of solubility of PEO–silica complex in the solution on its solvent fraction and alcohol/water ratio. The steeper change of domain size in TMOS than TEOS system indicates that the solvent composition has larger effect than that of solvent fraction on the solubility of PEO–silica complex. The difference between TMOS and TEOS systems can be interpreted from the viewpoint of effect of corresponding alcohols on the stability of PEO–silica complex in an aqueous solution. It is reported that the presence of alcohols generally hinders the formation of polymer–polymer complex such as PEO–HPAA.[8,13] Since the stability of such type of polymer–polymer complex is influenced by both the hydrophilic and hydrophobic interactions between polymer chains, amphiphilic small molecules such as alcohols tend to disturb the complexation reaction, and the strength of this disturbing effect is expected to decrease with decreasing amphiphilic character of alcohol which is roughly estimated by the length of its alkyl chain. That is, it is expected that methanol enhances the dissolution of PEO–silica complex more effectively than ethanol. As a result, the dependence of gel morphology on alcohol/water ratio becomes stronger in TMOS than in TEOS system.

The effect of PEO/silica ratio would be better discussed based on the data of TEOS system which exhibited weaker dependence of morphology on solvent fraction or alcohol/water ratio. Following the sequence of phase separation discussed above, it is possible for the sol–gel transition to take place earlier than the detectable aggregation and sedimentation of PEO–silica complex when the PEO/silica ratio is very low. Furthermore, there should exist a certain PEO/silica ratio at which the PEO–silica complex is most stable and phase separates fastest from the solvent. Although not presented in this report, adoption of PEO with lower molecular weight or of higher reaction temperature indeed gave nanoporous translucent gels similar to those obtained with high PEO/water ratio, as well as a more definite minimum in the gelation time vs. PEO/silica relation. Details of the systems with extended molecular weight and reaction temperature ranges are reported in the forthcoming paper.[14)]

On the composition line which the solvent fraction is fixed at ca. 83% in Fig. 6, the resultant morphology changed from macroscopic two phase, through interconnected structures with decreasing domain size, finally to nanoporous gel matrix. Since the PEO/silica ratio at which the PEO–silica complex is most stable is very low in the present system, the increase in PEO/silica ratio decreases the stability of the complex, that is, to retard the occurrence of phase separation, monotonously. Although the overall gelation process is also retarded with an increase of PEO/silica ratio, the morphological change shown in Fig. 6 clearly indicates that the onset of phase separation becomes later and finally crosses over the sol–gel transition in the intermediate PEO/silica ratio. In addition, from the comparison of morphologies shown in Figs. 3 and 5, the changes of domain size and of volume fractions of phases can be controlled independently.

Conclusion

Silica gels with micrometer range interconnected pores could be prepared by the polymer-incorporated sol–gel process using PEO having the average molecular weight of 100000 at 40 °C. It was found that silica oligomers associated with PEO molecules form the gel phase, and that the volume fraction of pores was determined mainly by the amount of solvent mixture. This phase relation distinguished the present system from those with poly(sodium styrenesulfonate) and poly(acrylic acid), where the conjugated phases are polymer-rich and silica-rich with the solvent being distributed in appropriate proportions. The variation of resultant gel morphology with compositional parameters was consistently explained by assuming the concurrent occurrence of spindal decomposition and sol–gel transition, and by considering the effect of composition on the solubility of PEO–silica complex.

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