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Phase Separation in Silica Sol–Gel System Containing Poly(ethylene oxide) II. Effects of Molecular Weight and Temperature

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Phase separation and gelation behaviors have been studied for acid-catalyzed, alkoxide-based silica systems containing poly(ethylene oxide), PEO. In order to clarify the role of PEO in a phase-separating sol–gel system, the effects of the molecular weight of PEO and the reaction temperature were investigated in detail. The PEO concentration of the highest phase-separation tendency slightly increased along with a decrease in the molecular weight, suggesting that the phase-separation behavior is mainly governed by an interaction between PEO and the solvent mixture. The reaction temperature affected the morphology-composition relationship mainly by its effect on the sol–gel transition kinetics.

The sol–gel process is generally recognized to be a new route for preparing dense, porefree ceramic or glass materials from homogeneously mixed precursor solutions.[1)] A great deal of effort has been made to control the size and distribution of pores in gels in order to avoid cracking and fracturing during the drying and calcination stages, during which fragile gel networks are sintered into dense, strong ceramic bodies.

Another possibility of the sol–gel process, which has been exploited by us in alkoxy-derived systems, is that porous structures can be designed in a similar manner to polymer alloying, i.e. by making use of the structure formation caused by phase separation.[2)] A broad range of well-defined macroporous structures has been demonstrated in preceding studies of systems including, polymer–silica–solvent,[2—4)] surfactant–silica–solvent,[5)] and simpler silica–polar solvent[6)] systems.

Among others, those systems containing poly(ethylene oxide), PEO, and derivative surfactants exhibit unique phase relations in which polymerized silica and PEO become major constituents of one of the conjugate phases due to the formation of strong hydrogen bonds between the poly(oxyethylene) units and silicate oligomers.[4)] The other coujugate phase, mainly comprising of solvent mixtures, determines the macropore fraction of the phase separated gels. The present paper describes the effects of the molecular weight of PEO and reaction temperature on the structure formation behavior in an alkoxy-derived silica system, and discusses the role of PEO in inducing phase separation along with the progress of the polycondensation of silica oligomers.

Experimental

Tetraethoxysilane, TEOS, a product of Shin-Etsu Chemical Industry Co., was used as a silica source without further purification. Poly(ethylene oxide), PEO, with average molecular weights of 100000, 10000, and 8300, products of Aldrich Chemical Co. and Hayashi Pure Chemicals Co., Ltd., were used as polymer components. These PEOs with different molecular weights are respectively denoted as PO10, PO1, and PO08, hereafter. Nitric acid was used as a catalyst for hydrolysis.

The sample gels were prepared by hydrolyzing TEOS with acidic aqueous solutions containing various amount of PEO, as previously reported.[4)] The typical starting compositions adopted are listed in Table 1. Gelation and aging were conducted under a tightly sealed condition in an air-circulating oven at 40, 60, and 80 °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 the phase separation (t_{ps}) instead of t_g.

For a morphology observation with a scanning electron microscope (SEM; Hitachi-S510), after exchanging the solvent phase with 1 M (1 M = 1 mol dm^{-3}) HNO_3 aq by repeated immersions, wet gels were finally dried at 60 °C.

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

Sample	PEO (MW)	H_2O	60%HNO_3 aq	TEOS
PO10-EP8	0—1.20 (100000)	8.0	0.81	6.51
PO1-EP8	0—1.00 (10000)	8.0	0.81	6.51
PO08-EP8	0—0.70 (8300)	8.0	0.81	6.51

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

Results

Effect of Temperature. Figure 1 (a)—(c) illustrate the dependence of the resultant gel morphology on the calculated solution composition at varied temperatures in a system incorporated with PEO10. 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 was at least 7-times larger than the alkoxide in moles, the composition at the time of phase separation and gelation was calculated by assuming that the alkoxide was completely hydrolyzed and polycondensed. This assumption corresponds to the consumption of 2 mol of water and the generation of 4 mol of alcohol per unit mol of alkoxide from the starting composition. At 40 °C, the interconnected structure, denoted by the circle with a cross, was observed in the composition region of 80—85 mass% solvent and a PEO/silica ratio of around 1 : 2. Macroscopic two phases or particle aggregates were observed in the region of higher solvent fraction, and isolated macropores or structures with only nanopores were observed

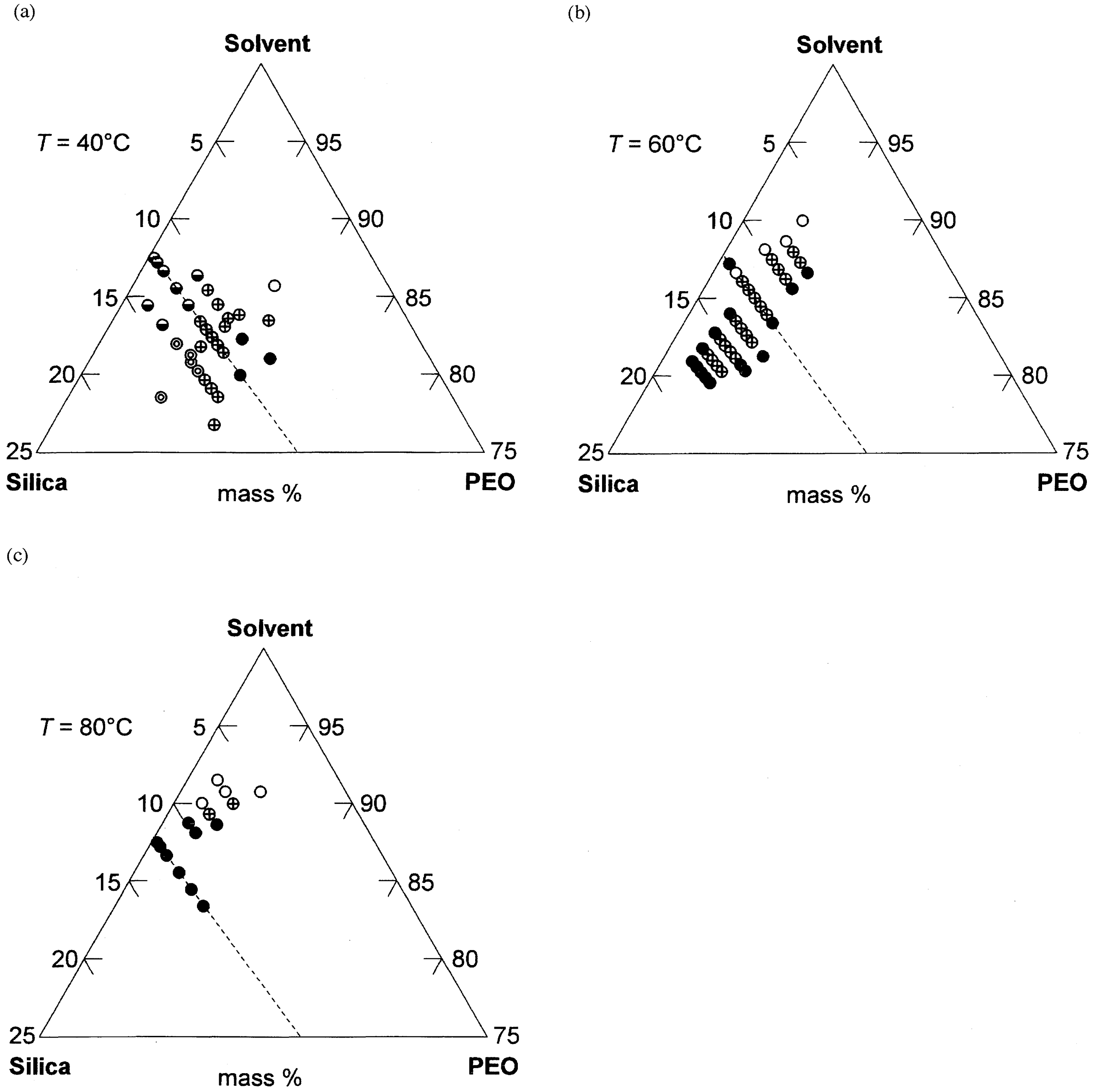

Fig. 1. Relation between calculated solution composition and resultant gel morphology in PEO10–TEOS system at varied temperatures (a) 40 °C, (b) 60 °C, (c) 80°C; ◓ :macroscopic two-phase, ◎ :isolated macropores, ⊕ :interconnected macropores, ○ :particle aggregates, ● :nanopores. Dotted line corresponds to the PO10-EP8 compositions with varied m_{PEO}. The calculation of composition is described in the text.

in the region of lower solvent fraction. These variations in the gel morphology have been consistently explained by assuming that the "gel phase" mainly comprised polymerized silica and PEO, and that the "fluid phase", which was observed as macropores after drying, mainly comprised the solvent mixture. This type of phase relation was also confirmed by a thermogravimetric analysis of macroscopically phase separated samples.[4] At 60 °C, the compositions which resulted in the interconnected structure shifted to a lower PEO/silica ratio, ca. 1 : 4, and a slightly solvent-rich region. The morphologies of isolated macropores and macroscopic two phases could not be observed. At 80 °C, the composition region which gave a phase separated morphology shifted to a much higher solvent fraction of ca. 90 mass%. The interconnected structure was observed only in a limited region between nanoporous gels and particle aggregates.

Figure 2 shows the dependence of the phase separation time (t_{ps}) or gelation time (t_g) on the PEO concentration in the PO10-EP8 composition at varied temperatures. With the PO10-EP8 composition at 40 °C, the phase separation took place much earlier than the gelation from a very small addition of PEO to $m_{PEO} = 0.6$, resulting in macroscopically separated fluid and gel phases. When the temperature was increased to 50 °C, a clear minimum with the resultant morphology of particle aggregates was observed in t_g at $m_{PEO} = 0.2$, and no macroscopic phase separation was observed at lower PEO concentrations. This indicates that the gelation of the whole solution took place earlier than the phase separation also at lower PEO concentrations. The formation of particle aggregates at $m_{PEO} = 0.2$, 60 °C, although not exactly a minimum in t_g, supports the idea that phase separation is best enhanced relative to gelation around $m_{PEO} = 0.2$. On the other hand, at 80 °C all of the starting solutions with PEO10-EP8 composition gelled without any obvious phase separation, as is graphically presented in Fig. 1(c). The gelation time was around 50 min and hardly depended on the PEO concentration.

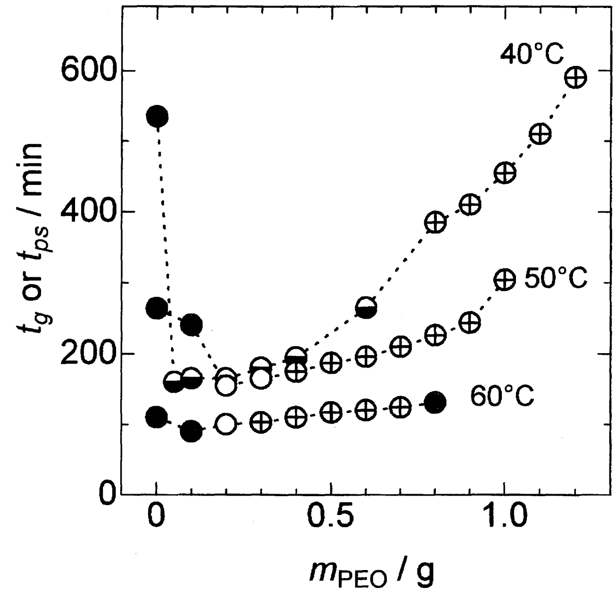

Fig. 2. Dependence of gelation or phase separation time and morphology on incorporated amount of PEO, m_{PEO} at 40, 50, and 60 °C. Data points also represent respective resultant morphology as in Fig. 1. Starting composition is PO10-EP8 in Table 1.

Effect of the Molecular Weight. Figure 3 shows the dependence of the resultant gel morphology on the starting composition in a system incorporated with PEO1 at 40 °C. Compared with the PEO10 system (Fig. 1(a)), the interconnected structures were observed with a somewhat lower and narrower range of the PEO/silica ratio. No macroscopic two-phases were observed, even at very low PEO concentrations. These differences are directly reflected to the dependence of t_{ps} or t_g on the PEO concentration in the respective EP8 compositions shown in Fig. 4. Even a relatively small difference in the molecular weight between PEO1 and PEO08 makes a clear difference in the phase separation-gel formation behavior. Any composition containing PEO1 or PEO08 exhibited no obvious phase separation at temperatures higher than 60 °C. It should be noted that with these lower molecular weight PEOs the phase separation seems best enhanced at around $m_{PEO} = 0.3$ to 0.4. Several examples of dried-gel morphology prepared from PEO1-EP8 compositions at 40 °C are shown in Fig. 5.

Discussion

As discussed in the previous papers, the various morphologies in the gel structure are formed due to the occurrence of phase separation during the polycondensation reaction of hydrolyzed alkoxysilane.[7] Various transient structures of phase separation can be frozen-in as a permanent gel morphology, depending on the time relation between the onset of phase separation and gel formation. The interconnected structure was observed when an onset of the phase separation and

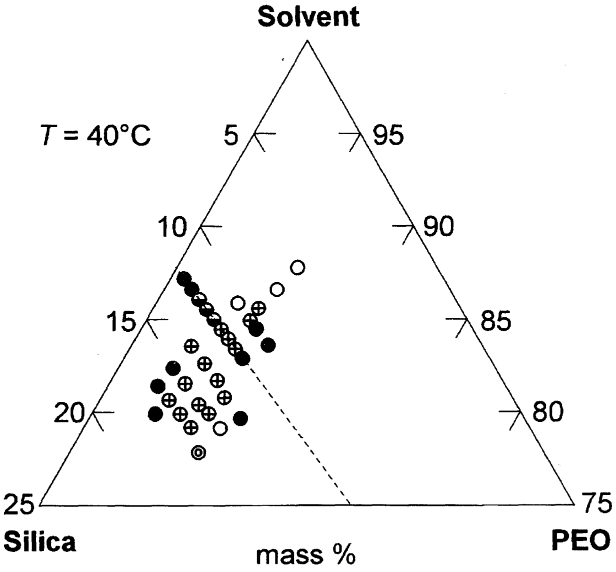

Fig. 3. Relation between calculated solution composition and resultant gel morphology in PEO1-TEOS system at 40 °C. Symbols are the same as in Fig. 1. Dotted line corresponds to the PO1-EP8 compositions with varied m_{PEO}.

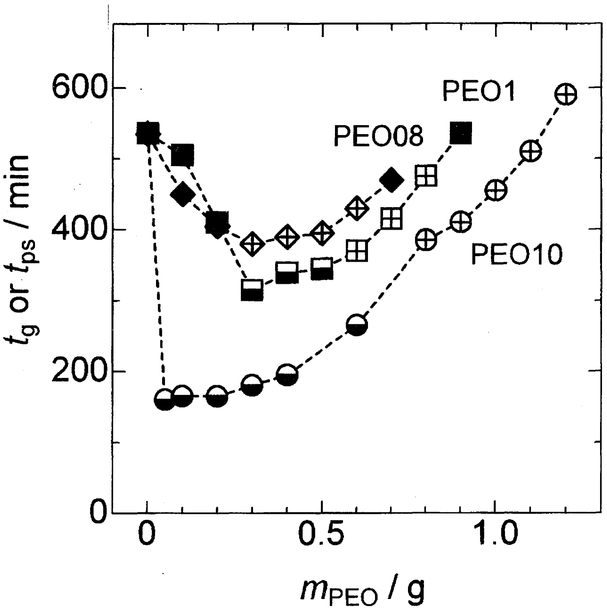

Fig. 4. Dependence of gelation or phase separation time on incorporated amount of PEO, m_{PEO}. Starting compositions are those shown in Table 1, and reaction temperature is 40 °C.

structure freezing by gel formation almost coincide with each other. Particle aggregates and isolated macropores resulted from an earlier onset of phase separation relative to the gel formation, under which condition a prolonged coarsening including fragmentation of the phase domains took place. The macroscopic two-phases were observed when the phase separation took place much earlier than gel formation, whereas gels having only nanometer range pores were obtained in the opposite case.

The effect of the reaction temperature can be mainly interpreted as that of accelerated gel formation. Within the composition range adopted in the present study, the gelation rate depended only weakly on the silica/solvent ratio in the absence of PEO.[8] Thus, the variation in the resultant morphology was mainly due to the composition dependence of the phase-separation tendency at specified temperatures. The decrease in the apparent t_g with small additions of PEO, typically seen at 40 °C, was due to the earlier occurrence of phase separation and subsequent sedimentation of the primarily formed gel phase. Along with an increase in the reaction temperature, the phase-separation tendency decreased and the polycondensation was accelerated. Although a substantial decrease in the magnitude of phase-separation tendency was expected, the composition region of highest phase-separation tendency hardly varied, as suggested by the results shown in Fig. 2. The gelation took place progressively earlier, and the phase separation tended to onset later at higher temperatures, which suppressed the growth and coarsening of phase domains to a macroscopic scale. Consequently, at a higher temperature the interconnected morphology was formed in the composition region where the coarsened, i.e. fragmented or sedimented, morphology had been formed at a lower temperature, and the composition region of the interconnected structure at a lower temperature turned into that of nanoporous structure at higher temperatures.

In Fig. 2, the prevention of macroscopic phase separation at 50 °C at $m_{PEO} = 0.1$ is mainly due to the reduced phase-separation tendency because the gelation time, itself, is longer than t_{ps} at 40 °C. The narrowing of the composition range of the interconnected structure from 50 to 60 °C is evidently due to the accelerated gel formation. The same interpretation can be applied to the results shown in Fig. 1(a) and (b). The composition which resulted in the interconnected structure shifted to the region of lower PEO/silica ratio and slightly higher solvent fraction when the reaction temperature was increased from 40 to 60 °C. This again implies that at higher temperature the starting compositions, which allowed an earlier onset of phase separation, became suitable to form interconnected structures and to freeze them in as permanent gel morphologies.

At the highest temperature of 80 °C, the macroporous morphology, such as an interconnected structure and particle aggregates, was observed only in the region of very high solvent fraction, where the polycondensation rate is low and the coarsening of structure of gel phase occurs rapidly. This kind of sharp transition from nanoporous to macroporous morphology is commonly observed when the volume fraction of the "gel phase" is substantially lower than 50 %, similar to the cases of incorporation of lower molecular weight surfactants[5] or polar solvent[6] in the hydrolysis of alkoxysilane.

A clear difference in the formation of phase separated structures in the systems of weakly hydrogen-bonding polymers, such as poly(acrylic acid), HPAA, and of strongly hydrogen-bonding PEO, exists in that the coarsened mophology tends to form at higher solvent fractions in the latter system. In a system containing HPAA, the solvent phase comprising water, alcohol and catalyst works as a mediater of the phase-separation tendency into polymer-rich and silica-rich domains. In a system containing PEO, however, the role is completely reversed due to the repulsive interaction between the silica oligomers adsorbed by PEO and the solvent mixture. This difference can be favorably utilized in designing the macropore structure of silica gels. While the pore size can be controlled by changing the PEO/silica ratio, the pore volume can be modified, though not completely, independently of the pore size, by changing the volume fraction of the solvent mixture.

The main effect of the varied molecular weight of PEO is a change in the composition dependence of the phase separating tendency in the hydrolysis and polycondensation reaction of alkoxysilane. It has recently been proven by SAXS that the PEO molecule affects the growth behavior of silica from a very early stage of polycondensation.[9] At a low concentration of PEO, corresponding to $m_{PEO} < 0.2$, the sedimentation of a viscous phase rich in PEO and silica was observed in a PEO10 sample within a short time, whereas nanoporous gels with only microscopic phase separation were obtained for PEO1 and PEO08 samples.This difference in the phase-separation behavior may be due to the molecular-weight de-

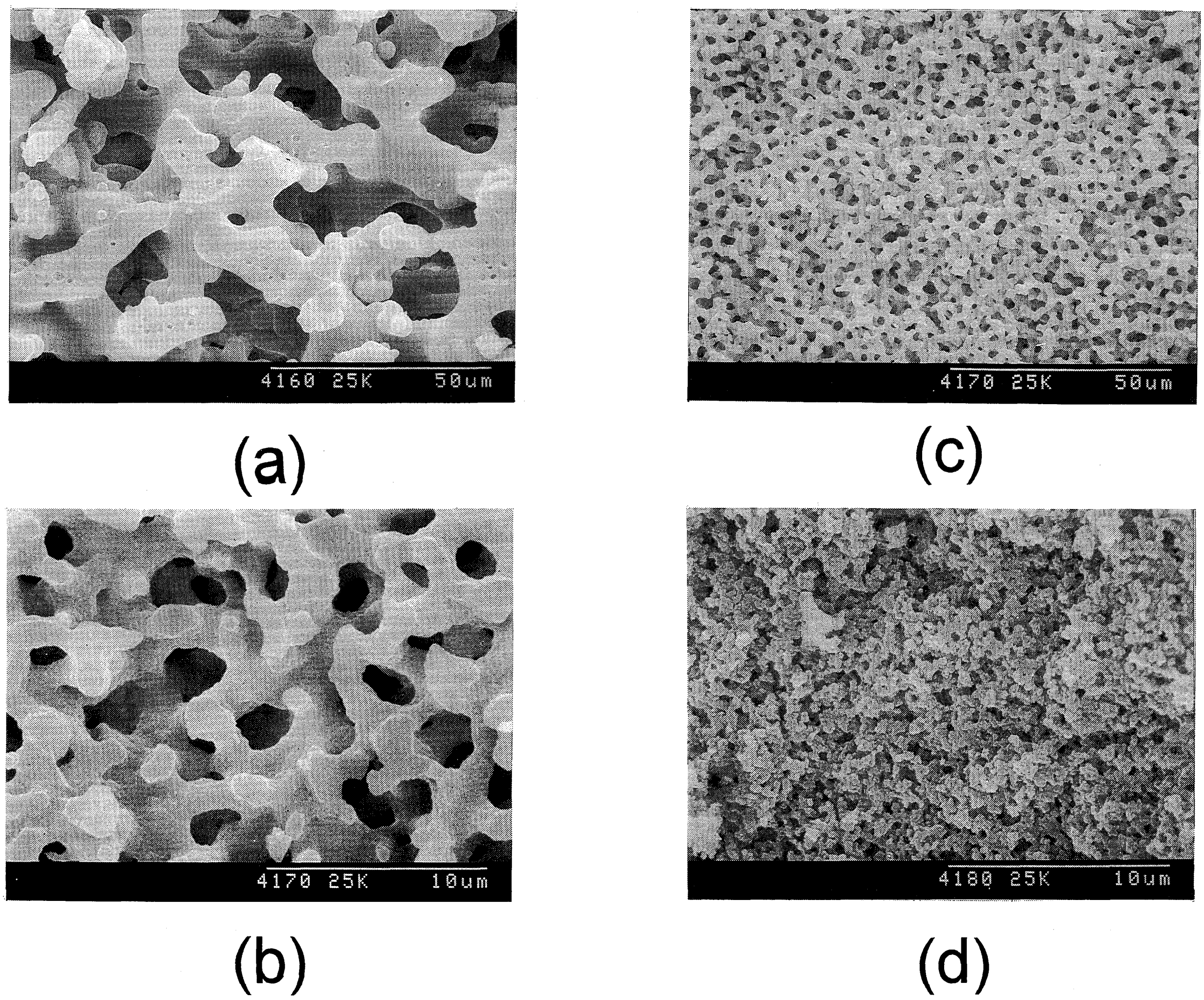

Fig. 5. SEM photographs of dried gel samples prepared with PO1-EP8 composition at 40 °C. (a) $m_{\mathrm{PEO}}=0.60$, (b) $m_{\mathrm{PEO}}=0.70$, (c) $m_{\mathrm{PEO}}=0.70$ (lower magnification), (d) $m_{\mathrm{PEO}}=0.80$.

pendence of the adsorption strength of PEO onto silica and/or the solubility of a PEO chain partly adsorbed on silica. As shown in Fig. 2, the PEO/silica ratio of the highest phase-separation tendency in a PEO10 sample seems to exist at around $m_{\mathrm{PEO}}=0.2$, whereas those for PEO1 and PEO08 exist at around $m_{\mathrm{PEO}}=0.3$—0.4. Since the amounts of the solvent mixture and silica are fixed for all samples, the lower PEO/silica ratio designates the lower PEO concentration in the whole solution. The molecular-weight dependence of phase equilibria in a PEO–water binary system has been reported by Saeki et al.,[10] and the LCST (lower critical solution temperature) type phase diagram clearly shows a decrease in the critical concentration and temperature along with an increase in the molecular weight of PEO. In addition, the change in the critical concentration and temperature of PEO is marked up to a molecular weight of about 20000, in which range the energy change on dissolution into water varies steeply with the molecular weight.[11] These facts suggest that the observed phase-separation tendency of PEO–silica–solvent systems is mainly determined by the solubility of PEO chains partly adsorbed onto silanols of silica oligomers, and that their dependence on the molecular weight can be simply interpreted based on the phase diagram of PEO–water binary systems.

Concerning the origin of the phase-separation tendency in the present system, we will go into more details. The formation of the hydrogen bond between the silanols and ether oxygens of PEO has been assumed to be a main cause of the phase separation.[4] It is well known that most hydrogen-bonded interpolymer complexes consist of a simple integer complexation ratio of monomeric units having proton-donating and -accepting abilities, and that the ratio does not depend on the respective molecular weights only if they are higher than certain critical values.[12] The tendency of exsolution due to complex formation becomes highest when the maximum number of monomer–monomer pairs are formed. The observed PEO amount of the maximum phase-separation tendency in PEO10-EP8 composition was $m_{\mathrm{PEO}}=0.2$. It was shown that, however, about 30% of silica was distributed to the fluid phase at $m_{\mathrm{PEO}}=0.3$, and that the fraction of silica distributed to the gel phase continued to increase along with an increase in the m_{PEO} value. That is, the composition with $m_{\mathrm{PEO}}=0.2$ does not correspond to the maximum interaction between PEO and silica oligomers. This suggests that the strength and manner of the hydrogen bond between silanols and ether oxygens are essentially different from those in water–insoluble organic interpolymer complexes. The observed molecular-weight dependence of the PEO concentration of the highest phase-separation tendency (Fig. 4) also supports this idea. Although the hydrogen bond plays a key role in the interaction between PEO and silica oligomers, complex formation was not responsible for the instability of the silica oligomers adsorbed by PEO in the present system in a strict sense.

Alternatively, it is better to assume that the partial adsorption of PEO chain on silanols reduces the number of effective hydrophilic or hydrogen-bonding sites, ether oxygens in the present case, and creates hydrophobic moieties around the adsorbed site. This kind of interaction would be chemically equivalent to the partial substitution of polyoxyethylene units with more hydrophobic ones. Such modified PEO's are reported to exhibit a lower cloud point (approximately LCST), depending on the substituted fraction.[13] In the present case, since a lowering of the solubility limit is caused by the polycondensation of silica, the longer and less soluble PEO chains will exsolute more easily together with the adsorbed silica oligomers. When the molecular weight of PEO is low enough and/or the reaction temperature is high enough to keep the system in a macroscopic single phase near to the sol–gel transition point, the transient structures of the phase separation can be frozen-in in the crosslinking silica network stiffly hydrogen-bonded with the incorporated PEO molecules.

Conclusions

Concerning the phase-separation behavior of an alkoxy-based silica sol–gel system incorporated with PEO with varied molecular weight and at different reaction temperatures, the following has been revealed: (1) the overall phase-separation tendency of the PEO–silica–solvent system could be consistently interpreted by considering the lowered solubility of PEO partly adsorbed onto silica oligomers in an aqueous solvent mixture; the higher the molecular weight became, the phase separation was induced at a lower concentration of PEO during an earlier stage of the polycondensation reaction of silica. The composition and molecular-weight dependence of the phase-separation tendency can be reasonably compared to that in PEO–water binary systems. (2) The increase in the reaction temperature simply reduces the phase-separation tendency, and increases the polycondensation rate. The composition range in which the phase separated macropore morphology is obtained shifted toward a solvent-rich and lower PEO/silica ratio region, where the phase-separation tendency is higher.

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