Effects of Homopolymers on the Gel Formation in Aqueous Block Copolymer Solutions

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ABSTRACT: The gel formation in aqueous EO_{99}–PO_{65}–EO_{99} solutions has been studied (EO and PO being ethylene oxide and propylene oxide, respectively). In particular, the effects of the homopolymers (i.e., PEO and PPO) were investigated in detail. It was found that PEO of intermediate molecular weight causes the gel to "melt", at an amount of homopolymer which depends on the copolymer concentration. The efficiency of PEO in inducing the gel melting increases with its molecular weight, but at very high PEO molecular weights, phase separation, rather than gel melting, occurs. The gel melting behavior was found also for a cationic polyelectrolyte (PDADMAC). PPO, on the other hand, tends to increase the stability region of the gel, depending, however, on the PPO molecular weight. These findings are reported by means of rheological data and detailed phase diagrams, and discussed in terms of the temperature-dependent micellization occurring in this copolymer system.

Introduction

Like many low molecular weight surfactants,[1] several block copolymers form micelles at low concentrations,[2,3] whereas at higher concentrations, liquid crystalline regions may occur.[4] A similar behavior is displayed by many EO_a–PO_b–EO_c block copolymers (EO and PO being ethylene oxide and propylene oxide, respectively). Thus, at low concentrations, micelles are formed, but only at higher temperatures.[5-11] With increasing temperature, the critical micellization concentration (cmc) decreases, whereas the micellar size and aggregation number increase, as evidenced by both experimental and theoretical studies.[5-11] This is in line with the general behavior displayed by low molecular weight nonionic surfactants, e.g., of the oligooxyethylene alkyl ether (C_mE_n)[1] type.

At higher concentrations, a gel region is found in a certain temperature range in many of these systems.[12-20] Although the existence of the gel region has been known for quite some time, and although the gels are of potential importance in especially pharmaceutical applications,[17,18] the level of understanding is still unsatisfactory. However, a few studies have treated the structure of the gels and the mechanisms of their formation. From these studies it has been inferred, based, e.g., on small-angle neutron scattering (SANS), that the gels consist of cubically close-packed block copolymer micelles.[12,13]

In a preceding paper, we studied the temperature-dependent micellization of EO_{99}–PO_{65}–EO_{99} both experimentally and theoretically.[11] A good agreement was obtained between experimental findings and model calculations regarding the decrease in the cmc and the increase in the micellar size and aggregation number with increasing temperature. Furthermore, the phase behavior of aqueous EO_{99}–PO_{65}–EO_{99} solutions was investigated in detail.[19] It was found that a gel region occurs at polymer concentrations above approximately 18 wt %, but only at intermediate temperatures (Figure 1). Thus, even a concentrated solution is relatively low-viscous at low and high temperatures. The upper temperature gel boundary was found to be significantly lower than the lower consolute temperature. Moreover, the stability region of the gel is markedly affected by the presence of cosolutes, e.g., inorganic salts and hydrocarbons. Furthermore, the state of hydration in these systems was investigated by NMR self-diffusion measurements and the cell diffusion model.[20] The most important finding in this study was that the state of hydration is essentially uncorrelated to the phase behavior, and in particular, no dramatic dehydration occurs at gel formation, which has previously been suggested.[13,15]

During our work with the phase behavior, we observed pronounced and unexpected effects of homopolymers on the gelation in this block copolymer system. We therefore decided to investigate these in somewhat more detail, not the least considering the importance of homopolymer impurities in block copolymer systems.

Experimental Section

Material. In the experiments we used a specially purified sample of Pluronic F127, which was kindly supplied by BASF Wyandotte, U.S.A. This polymer has a total molecular weight of 12 500, and consists of approximately 70 wt % EO; i.e., the approximate formula is EO_{99}–PO_{65}–EO_{99}. NMR spectra confirm that the ratio EO/PO is approximately 70/30. No impurities were observed in the NMR spectra. The water content of the dried sample is estimated to be less than 3 wt %. Homopolymers were obtained from Merck, Germany (PEO 20 000), Serva, Germany (PEO 600, PEO 6000, PEO 200 000), Fluka, Germany (PPO 400, PEO 400, PEO 4000), and Polysciences, U.S.A. (PPO 4000). PDADMAC [poly(diallyldimethylammonium chloride)] of an approximate molecular weight of 2×10^6, was obtained from Allied Colloids Inc., U.K. All polymers were used without further purification.

Procedure. Samples for the phase diagrams were obtained by weighing a suitable amount of copolymer, homopolymer, and water, and then allowing equilibration for approximately one week. The gels formed are optically transparent. Instead, the boundaries of the gel region were determined from the abrupt change in viscosity on gelation. The lower concentration and temperature boundaries of the gel region are very sharp, and are easily determined with good accuracy (±1 wt % and ±1–2 °C, respectively). The upper temperature boundaries are somewhat more difficult to determine accurately, and some hysteresis (±3–4 °C) exists. The upper boundaries were obtained on heating.

Rheological Measurements. In the rheological measurements, we used a Bohlin VOR rheometer system (Bohlin Rheology, Sweden). Throughout, a concentric cylinder configuration was used. The instrument is equipped with a temperature control unit, allowing a temperature accuracy of about 0.1 °C. All oscillatory measurements were performed within the range of linear viscoelasticity. Furthermore, care was taken to avoid wall-slipping effects.

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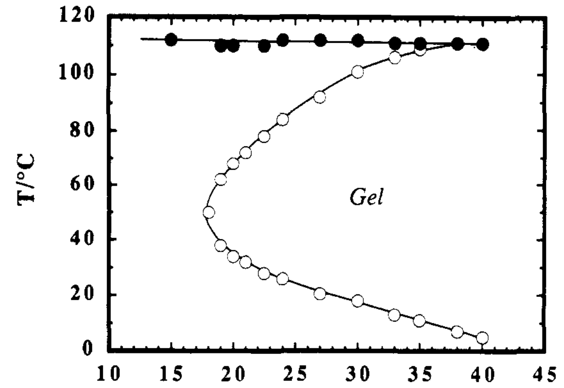

Figure 1. Phase behavior of the EO_{99}–PO_{65}–EO_{99}/water system. The solid circles refer to the cloud point (CP).[19]

Results and Discussion

Like many other block copolymers, Pluronic F127 forms micelles in dilute solutions, but only at higher temperatures.[5-11] The driving force for the micellization is primarily the poor solvency conditions of PPO in water, particularly at higher temperatures.[11,21] Increasing the temperature is found to result in a decrease in the critical micellization concentration and an increase in the size and aggregation number of the micelles. At higher concentrations, and at intermediate temperatures, a "gel" region appears in the phase diagram.[19] As can be seen in Figure 1, the gel region exists at copolymer concentrations above 18 wt %, but only at intermediate temperatures, the latter depending on the copolymer concentration.

Although the structure of the gels and the mechanisms of their formation are not well established to date, compelling evidence from both Wanka et al.[13] and Mortensen et al.[12] seems to indicate that they consist of a close-packed array of block copolymer micelles. Thus, at concentrations below the overlap concentration for the solvated micelles, no gel is formed, irrespective of temperature. Furthermore, no gelation is observed at low temperatures, since no micellization occurs under these conditions. [In fact, the lower temperature gel boundary seems to be coincident with, or close to, the critical micellization temperature at a given copolymer concentration.[19]] At intermediate temperatures, micelles form and order, and thus the gel occurs. At even higher temperatures, however, the micelles contract,[19] thus disrupting the lattice and lowering the viscosity. Considering this, it is not unexpected that the stability region of the gels depends strongly on low molecular weight cosolutes, which influence either the micellization process or the size of the micelles.[19]

In order to briefly quantify the mechanical properties of the copolymer solutions and gels, we performed some rheological measurements, the results of which are shown in Figures 2 and 3. As can be seen in these figures, the viscosity of the block copolymer solutions is fairly low, even at quite high copolymer concentrations. The gels, in turn, display a significant elasticity. For example, a 20 wt % EO_{99}–PO_{65}–EO_{99} sample at 50 °C is characterized by $G' \approx 20\,000$ Pa and $G'' \approx 1000$ Pa, independent of the oscillation frequency over a wide frequency range. The transition region from the low-viscous solution to the stiff gel is found to be only about 5 °C (results not shown).

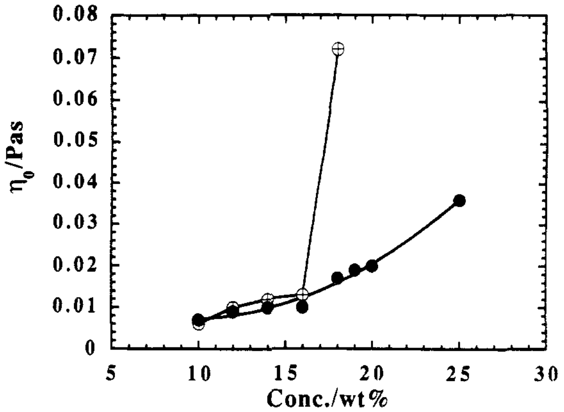

Figure 2. Zero-shear viscosity (η_0) versus copolymer concentration at 15 °C (solid circles) and 40 °C (crossed circles).

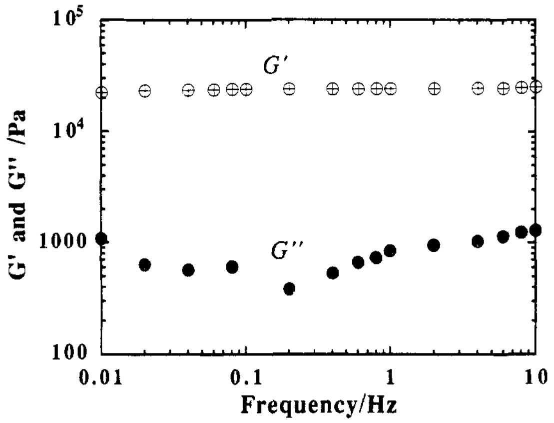

Figure 3. Frequency-dependent elastic modulus (G', crossed circles) and loss modulus (G'', solid circles) of a 20 wt % EO_{99}–PO_{65}–EO_{99} gel. The temperature was 50 °C.

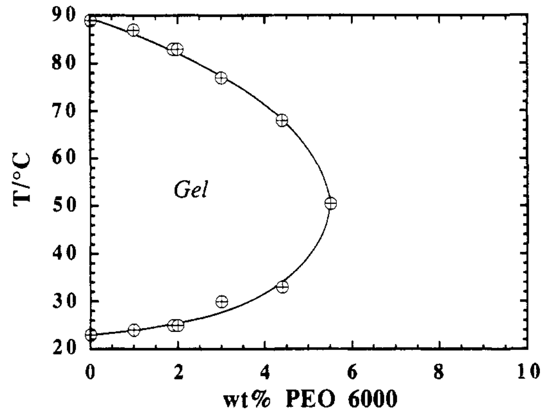

Figure 4. Effects of PEO 6000 on the gel behavior of the EO_{99}–PO_{65}–EO_{99}/water system. The copolymer concentration was 25 wt %.

It is interesting to compare these findings with those from previous studies on the same and similar systems. Thus, Wanka et al.[13] found the viscosity of aqueous EO_{99}–PO_{65}–EO_{99} solutions to be quite low, although strongly increasing on approaching the gel boundary. Also quantitatively, the data from Wanka et al. agree reasonably well with the present results. Furthermore, the gels are characterized by a high elastic modulus and a low loss modulus. Wanka et al. obtained $G' \approx 40\,000$ Pa and $G'' \approx 4000$ Pa for a 25 wt % sample at 30 °C, which is in reasonable agreement with the present results ($G' \approx 20\,000$ Pa and $G'' \approx 1000$ Pa for a 20 wt % sample at 50 °C). Furthermore, the transition from low-viscous solutions to stiff gels occurs over a temperature range of 5–10 °C. Analogous results were obtained for a similar system by Brown et al.[14]

As can be seen in Figure 4, a surprising result was obtained when adding a comparably small amount of a medium molecular weight PEO to the EO_{99}–PO_{65}–EO_{99}/water system. Thus, at addition of PEO of an intermediate

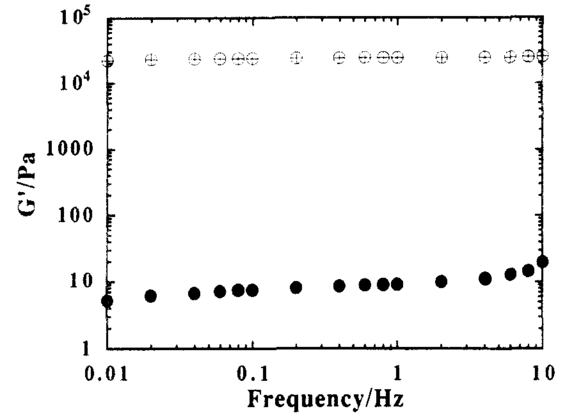

Figure 5. Elastic modulus (G') for a 20 wt % EO_{99}–PO_{65}–EO_{99} solution in the presence (solid circles) and absence (crossed circles) of 4 wt % PEO 20 000. The temperature was 50 °C.

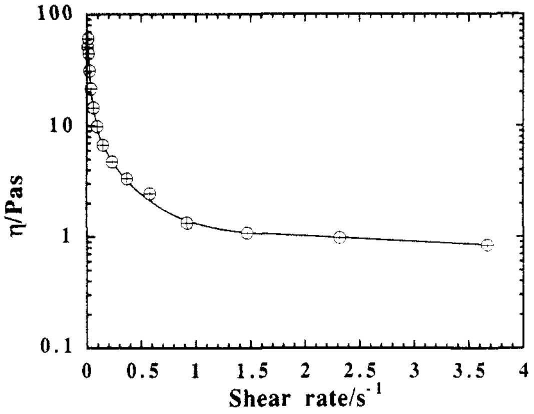

Figure 6. Shear rate dependent viscosity for a sample containing 20 wt % EO_{99}–PO_{65}–EO_{99} and 4 wt % PEO 20 000. The temperature was 50 °C.

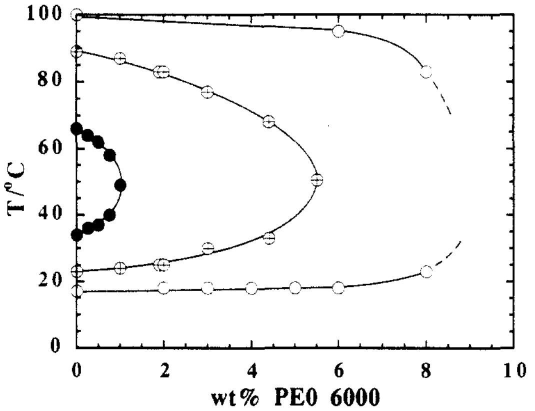

Figure 7. Effects of PEO 6000 on the gel behavior of the EO_{99}–PO_{65}–EO_{99}/water system at a copolymer concentration of 20 wt % (solid circles), 25 wt % (crossed circles), and 30 wt % (open circles).

molecular weight, the gel region decreases, and finally vanishes at a sufficiently high PEO concentration. [As can be seen in Figures 5 and 6 the presence of a few percent of PEO reduces the elastic modulus by more than 3 orders of magnitude. In fact, at shear rates above approximately 1 s^{-1}, the system behaves almost as an Newtonian fluid of a comparably low viscosity (Figure 6).] It was found that a higher PEO concentration was needed to accomplish the melting at a higher copolymer concentration (Figure 7).

In principle, one could imagine that the effect of intermediate molecular weight PEO on the gel behavior of EO_{99}–PO_{65}–EO_{99} is due to the decrease in the effective

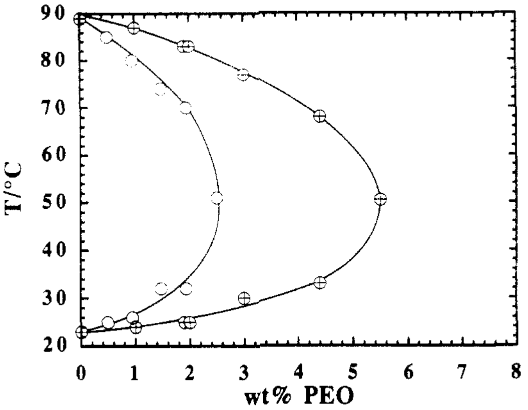

Figure 8. Effects of PEO on the gel behavior of the EO_{99}–PO_{65}–EO_{99}/water system at a PEO molecular weight of 6000 (crossed circles) and 20 000 (open circles). The copolymer concentration was 25 wt %.

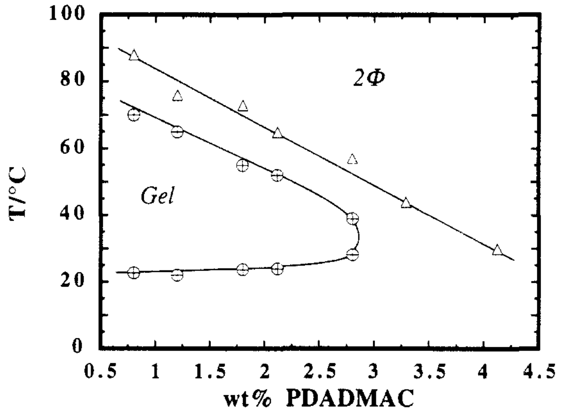

Figure 9. Effects of PDADMAC on the gel behavior of the EO_{99}–PO_{65}–EO_{99}/water system. The open triangles refer to the cloud point (CP). The copolymer concentration was 25 wt %.

solvent polarity in the presence of PEO, since this is expected to preclude micelle formation and thus decrease the stability region of the gel. [The driving force for micellization is the poor solvency conditions for PPO in water (the lower consolute temperature for PPO 400 is about 53 °C in water; results not shown).[21] Decreasing the solvent polarity increases the solubility of PPO, and thus counteracts micellization and gel formation.]

In order to investigate whether this is the case or not, we performed two sets of experiments. In the first, we compared the effects of PEO fractions of different molecular weights on the gelation and found that PEO 20 000 is more efficient than PEO 6000 in melting the gel (Figure 8), whereas PEO 400 and PEO 600 only affect the gelation behavior very little. It should be noted, that a high molecular weight PEO ($M_w \approx 200\,000$) induces phase separation, rather than gel melting (results not shown). Since we would expect the effects of PEO on the effective "solvent polarity" to be the same, irrespective of the PEO molecular weight, this finding clearly shows that solvent polarity effects are of minor importance.

Furthermore, a cationic polyelectrolyte, PDADMAC, also results in a gel melting, despite this polyelectrolyte strongly *increasing* the solvent polarity (Figure 9). [The reason for choosing a cationic polyelectrolyte rather than an anionic one is that the latter often forms insoluble complexes in water with nonionic polymers containing ether groups.[22]] Again, it seems clear, that the gel melting is *not* due to simple solvent polarity effects.

Another possible explanation is that the presence of the homopolymer precludes micellization due to a conformational and translational entropy effect, which would also explain the concentration and molecular weight dependencies. Thus, low molecular weight PEO's are smaller that the average gel mesh size, and do not experience much restrictions in their conformational and translational freedom. Consequently, the stability region of the gel is not markedly affected by the presence of a low molecular weight PEO. As soon as the homopolymer is of roughly the same size as the average mesh size of the gel (i.e., of the order of the micellar size), however, the restrictions become severe. There are, in principle, two choices for the system in this case, i.e., either the lattice is disrupted (e.g., by preclusion of micellization (lower temperature gel boundary) or by a micellar contraction (upper temperature gel boundary)) or the system phase separates. For low molecular weight homopolymers, the former is preferred, since the entropy loss of forming a separate phase is comparably large. For high molecular weight homopolymers, on the other hand, phase separation is less unfavorable. An analogous molecular weight dependence is found, e.g., for phase separation in binary polymer-solvent systems or for polymer incompatibility.[23] Furthermore, the higher the copolymer concentration, the higher the energy gain on micellization and structure formation, and consequently, the higher the homopolymer concentration needed to (over)compensate for this.

A third possible explanation to the observed effect of homopolymers is based on the (inhomogeneous) distribution of the homopolymer molecules in the system. Thus, one might consider the copolymer micelles as semipermeable regions, unattainable for (especially larger) homopolymers (cf. steric stabilization). This gives rise to an osmotic pressure gradient, which acts to increase the cmc (lower gel boundary) and decrease the micellar size (upper gel boundary). The molecular weight dependence can be explained by considering that the distribution becomes more inhomogeneous and the osmotic pressure gradient larger with an increasing homopolymer molecular weight.

It is interesting to note that an analogous effect has been found previously. Thus, Ito et al.[24] found that PEO induces a shrinking of Sephadex gel beads. Furthermore, the higher the PEO molecular weight and the higher the degree of Sephadex cross-linking (i.e., the smaller the average mesh size), the stronger the effect. This is expected, since a higher PEO molecular weight and/or a smaller average mesh size gives rise to a more pronounced inhomogeneity, i.e., a stronger osmotic pressure gradient. It is important to note, however, that the comparison between a block copolymer micelle and a cross-linked polymer particle is far from obvious a priori, since in the former case, the aggregation number may vary, at least in principle, e.g., with the homopolymer concentration. The present results therefore seem to suggest that aggregation number adjustments are of minor importance in the present system.

The effect of the PDADMAC homopolymer on the gel behavior is more complex. Thus, in a polyelectrolye system, the translational and conformational entropy contribution from the polymer backbone itself is dwarfed by the translational entropy of the counterions. Although the PDADMAC polymer experiences some entropy restrictions in the gel, this effect may be of only limited importance, provided that the counterions are not too restricted. Thus, the possible significance of the mechanism based on entropy effects clearly depends on the (unknown) counterion distribution in the gels. However, considering charge neutrality conditions, it is likely that these will enhance possible osmotic pressure gradients, as described above.

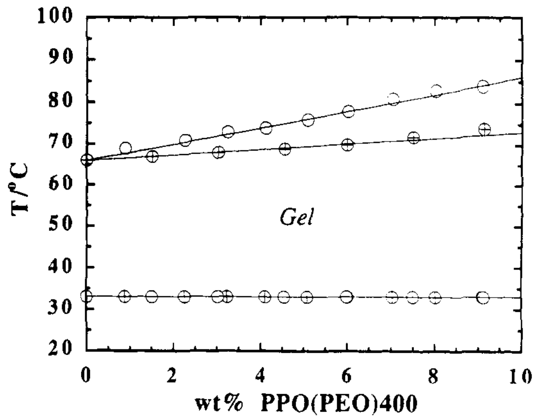

Figure 10. Effects of PPO 400 (open circles) and PEO 400 (crossed circles) on the gel behavior of the EO_{99}-PO_{65}-EO_{99}/water system. The copolymer concentration was 20 wt %.

Furthermore, one should not disregard simple solvency effects in the case of PDADMAC, since this polyelectrolyte lowers the cloud point (CP) of the block copolymer system strongly (Figure 9). For example, it has previously been found that NaCl lowers CP, as well as displaces the gel stability region to lower temperatures.[19] It is interesting to note that the "salting out" effects (tending to enhance micellization) and the "polymer" effects (tending to preclude micellization) are of equal magnitude, resulting in the lower temperature gel boundary being essentially independent of the PDADMAC concentration, while the upper temperature gel boundary decreases dramatically.

The effects of PPO on the stability region of the gel must be discussed in a completely different way, since the solubility of this homopolymer in water is limited. Thus, PPO 400 is infinitely soluble in water at room temperature, but has a lower consolute temperature of 53 °C (results not shown).[21] Since PPO 400 is soluble in water at low temperatures, we would not expect it to be located in the micellar core to any large extent under these conditions, due to the entropy loss on solubilization. Thus, the finding that PPO 400 does not markedly influence the lower temperature gel boundary (Figure 10) is expected. At higher temperatures, however, the PPO is solubilized in the copolymer micelles. This is evident from the finding that CP in the presence of 10 wt % PPO is 105 °C, as compared to 110 °C for the binary copolymer/water system and to 53 °C of a 10 wt % aqueous PPO solution. Thus, the solubilization of PPO 400 at higher temperatures is essentially complete, even at this high PPO concentration. The solubilization of the PPO in the micellar core gives rise to micellar growth. Since the upper temperature gel boundary is sensitive to the micellar size,[19] the finding that this increases in the presence of PPO is expected. PEO 400, on the other hand, only weakly influences the upper temperature gel boundary by a general polymer concentration effect, in analogy with PEO 600 (Figure 10).

In the case of PPO 4000, the solubility is low at all temperatures, which means that this polymer strives toward either solubilization or phase separation at all temperatures. Surprisingly enough, it was found that a 20 wt % block copolymer solution was unable of solubilizing even 1 wt % PPO 4000. This indicates that the solubilization of PPO 4000 is precluded, e.g., due to steric hindrance. It is interesting to note that for surfactant systems, the solubilization of an oil is more difficult the longer the hydrocarbon chain length,[25] which is analogous to the present results, and which seems to emphasize the importance of chain entropy effects for solubilization.

It is interesting to note that the effects of homopolymer on the rheology and stability of concentrated copolymer systems have been studied previously. For example, Watanabe et al. previously studied ordering phenomena of polystyrene–polybutadiene block copolymers in selective solvents (e.g., *n*-tetradecane) and found that the lattice formed in these systems can be disordered by addition of homopolybutadiene. These findings were discussed in terms of micellar "softness" and concentration fluctuations.[26-29] Although there appears to be a close correlation between the present findings and these previous results, a detailed comparison is still difficult. The reason for this is that the micellization in the PEO–PPO–PEO/water system appears to differ from that, e.g., in the polystyrene–polybutadiene/tetradecane system in that the micellization properties and even the compatibility between the PEO and PPO blocks seem to depend more strongly on both temperature and composition.[11,30] Moreover, the detailed understanding of the micellization and the lattice formation in the present system is still insufficent for such a comparison.

Summary

The effects of homopolymers on the gelation in aqueous EO_{99}-PO_{65}-EO_{99} solutions have been studied. In particular, detailed phase diagrams and some rheological data are reported. It is found, that PEO "melts" the gel formed in the binary copolymer system. The gel-melting capacity of PEO increases with increasing PEO molecular weight, until, at high PEO molecular weights, phase separation occurs. Furthermore, the higher the copolymer concentration, the higher the PEO concentration needed for melting the gel. A similar behavior is obtained with a cationic polyelectrolyte. Simple solvent polarity effects do not suffice in explaining these effects. Instead, the translational and conformational entropy of the homopolymers, as well as osmotic pressure gradients, have to be considered. Low molecular weight PPO, on the other hand, increases the stability region of the gel, which is a consequence of the solubilization of the latter in the block copolymer micelles, especially at higher temperatures.

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