Improved Micellar Hydration and Gelation Characteristics of PEO−PPO−PEO Triblock Copolymer Solutions in the Presence of LiCl

2 AUTHORS:

Rajib Ganguly
Bhabha Atomic Research Centre
61 PUBLICATIONS **918** CITATIONS

SEE PROFILE

Vinod K Aswal
Bhabha Atomic Research Centre
392 PUBLICATIONS **4,901** CITATIONS

SEE PROFILE

Improved Micellar Hydration and Gelation Characteristics of PEO−PPO−PEO Triblock Copolymer Solutions in the Presence of LiCl

R. Ganguly*,† and V. K. Aswal‡

Chemistry and Solid State Physics Divisions, Bhabha Atomic Research Center, Mumbai 400 085, India

Received: December 7, 2007

LiCl-induced changes in the micellar hydration and gelation characteristics of aqueous solutions of the two triblock copolymers F127 ($EO_{100}PO_{70}EO_{100}$) and P123 ($EO_{20}PO_{70}EO_{20}$) (where EO represents the ethylene oxide block and PO represents the propylene oxide block) have been studied by small-angle neutron scattering (SANS) and viscometry. The effect of LiCl was found to be significantly different from those observed for other alkali metal chloride salts such as NaCl and KCl. This can be explained on the basis of the complexation of hydrated Li^+ ions with the PEO chains in the micellar corona region. The interaction between the chains and the ions is more significant in the case F127 because of its larger PEO block size, and therefore, micelles of this copolymer show an enhanced degree of hydration in the presence of LiCl. The presence of the hydrated Li^+ ions in the micellar corona increases the amount of mechanically trapped water there and compensates more than the water molecules lost through the dehydration of the PEO chains in the presence of the Cl^- ions. The enhancement in micellar hydration leads to a decrease in the minimum concentration required for the F127 solution to form a room-temperature cubic gel phase from 18% to 14%. Moreover, for both copolymers, the temperature range of stability of the cubic gel phase also increases with increasing LiCl concentration, presumably because of the ability of the Li^+ ions to reduce micellar dehydration with increasing temperature. Viscosity studies on a poly(ethylene glycol) (PEG) homopolymer with a size equivalent to that of the PEO block in F127 (4000 g/mol) also suggest that the dehydrating effect of the Cl^- ion on the PEG chain is compensated by its interaction with the hydrated Li^+ ions.

Introduction

Polyethylene oxide−polypropylene oxide−polyethylene oxide (PEO−PPO−PEO) triblock copolymers, with their rich structural polymorphism and an extensive range of applications, are an important class of nonionic amphiphilic compounds.[1–15] The self-assembly characteristics of these copolymers show a strong dependence on temperature in aqueous medium mainly because of the temperature-dependent solubilities of their constituent blocks in water. Both of these polymers are soluble in water at low temperature, and the copolymer molecules remain in their aqueous solutions as unimers. At a characteristic temperature called the critical micellar temperature (CMT), the PPO block becomes insoluble, and the copolymer molecules form micelles with a hydrophobic core comprising the insoluble PPO blocks and a hydrophilic corona comprising the hydrated PEO blocks.[2] At the cloud point, the copolymer molecules as a whole become insoluble and phase separation from water occurs.

At high concentrations, these copolymers can form a number of lyotropic liquid-crystalline phases with cubic, hexagonal, or lamellar structures. It has been shown that, in aqueous medium, a stiff and isotropic gel phase is formed when the volume fraction of the micelles reaches 53% at the critical gelation concentration (cgc) of the copolymers.[16–25] Interestingly, because of a large degree of hydration in the corona region of these copolymer micelles, the cgc values are much lower than 53%.[16–25] Understandably, the cgc values of these copolymers depend strongly on their PEO/PPO block size ratio, which can modulate the degree of hydration of the copolymer micelles. Small-angle neutron scattering (SANS) and small-angle X-ray scattering (SAXS) studies of these gel phases suggest that they are formed through the crystallization of spherical micelles[16–21] or through the entanglement of deformed micelles at their limiting micellar volume fractions.[22–25] These phases are stable in the temperature range between their lower and upper melting points, denoted as T_1 and T_2, respectively ($T_2 > T_1$). T_1 is defined the temperature at which the volume fraction of the micelles becomes sufficiently high that micellar close packing or entanglement leads to the formation of the gel. The melting of the gel at T_2 could result from a progressive decrease in the micellar hydration because of a decrease in the solubility of the copolymer molecules with increasing temperature.

The presence of different electrolytes, which can effectively modulate the solvent quality of water, has a significant influence on the aggregation and gelation characteristics of these copolymers in aqueous medium.[26–35] The water-structure-forming salts such as NaCl, Na_2SO_4, and Na_3PO_4 decrease the solubility of the copolymers (salting-out effect) and reduce their critical micellar concentrations, critical micellar temperatures, and cloud points. Moreover, these salts also reduce T_1 and T_2 and shrink the temperature range of stability of the cubic gel phase.[29] Alexandridis and Holzwarth showed that the anions play a more important role in determining the self-assembly behavior of these copolymers than the cations.[26] They showed that the effectiveness of the halide ions in reducing the solubility of the copolymers decreases with increasing size in the order $F^- > Cl^- > Br^- > I^-$, which agrees well with the decreasing ability of the ions to form water structures around them. In the case of alkali metal ions, on the other hand, the observed order was

---

* Corresponding author. E-mail: rajibg@barc.gov.in. Tel.: +91-22-25590286, Fax: + 91-22-25505150.
† Chemistry Division.
‡ Solid State Physics Division.

PEO–PPO–PEO Solutions in the Presence of LiCl

J. Phys. Chem. B, Vol. 112, No. 26, 2008 **7727**

found to be Na$^+$ > K$^+$ > Li$^+$, an unexpected trend considering that Li$^+$, as the smallest ion, has the maximum degree of hydration. In this article, we show that, despite the dehydrating effect of the Cl$^-$ ions on the copolymer molecules, the micellar hydration and gelation characteristics of the aqueous copolymer solutions are improved in the presence of LiCl. It has been suggested that the ability of hydrated Li$^+$ ions to form complexes with the ether oxygen of the PEO chains in the micellar corona region is responsible for this behavior.[36] Viscosity studies on a poly(ethylene glycol) (PEG) homopolymer also support this conjecture.

Experimental Section

The triblock copolymers EO$_{100}$PO$_{70}$EO$_{100}$ (F127) and EO$_{20}$PO$_{70}$EO$_{20}$ (P123) (where EO represents the ethylene oxide block and PO represents the propylene oxide block) were obtained from Sigma and Aldrich, respectively. Lithium chloride and sodium chloride were purchased from Merck, and 4000 g/mol PEG was purchased from Sysco Research Laboratory, Mumbai, India. The copolymer solutions were prepared by weighing required amounts of water, copolymer, and salt (when needed) and keeping them refrigerated in tightly closed glass-stoppered vials for about 1 week. PEG solutions were prepared by gentle stirring of the mixture of polymer, salt, and water at room temperature. The gelation points were measured in a temperature-controlled water bath by visual inspection of the flow of the solutions, similar to the approach reported in the literature.[37] The absolute viscosities of the solutions were measured at room temperature using calibrated Cannon Ubbelohde viscometers.[38]

SANS measurements were carried out on the samples prepared in D$_2$O at the SANS facility at the Dhruva reactor, Bhabha Atomic Research Centre (BARC), Trombay, India. The mean incident wavelength was 5.2 Å with $\Delta\lambda/\lambda = 15\%$. The scattering was measured in the scattering vector (q) range of 0.017−0.35 Å^{-1}. The measured SANS data were corrected for the background, the empty cell contributions, and the transmission and were placed on an absolute scale using standard protocols. Correction due to the instrumental smearing was taken into account throughout the data analysis.[39]

The differential scattering cross section per unit volume (dΣ/dΩ) of monodisperse micelles can be written as

$$d\Sigma/d\Omega = NF_{mic}(q)\,S(q) + B \tag{1}$$

In eq 1, N is the number density of the micelles, and B is a constant term that represents the incoherent background scattering mainly from the hydrogen atoms present in the sample. $F_{mic}(q)$ is the form factor characteristic of the specific size and shape of the scatterers, and $S(q)$ is the structure factor that accounts for interparticle interactions. The block copolymer micelles can be considered as core−shell particles with different scattering length densities for the core and shell. The structure of these micelles is described using a model consisting of PEO chains attached to the surface of the PPO core.[40,41] The form factors for spherical and ellipsoidal micelles were used as formulated by Pedersen.[41] In this model, the shell is described as consisting of noninteracting Gaussian polymer chains, and these chains are assumed displaced from the core (otherwise, the mathematical approximations will not work, as the chains overlap each other and the core); that is, a mushroom polymer configuration is assumed. Nonpenetration of the chains into the core region is mimicked by moving the center of mass of the chains a distance R_g away from the surface of the core, where R_g is the radius of gyration of the chains. The form factor of
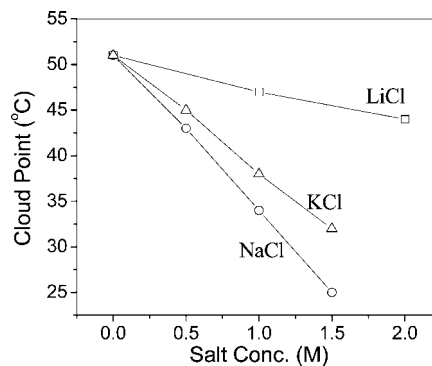

Figure 1. Variation with salt concentration of the cloud point of 20% P123 solutions.

the micelles, $F_{mic}(q)$, comprises four terms: the self-correlation of the core, the self-correlation of the chains, the cross term between core and chains, and the cross term between different chains. The interparticle structure factor, $S(q)$, for block copolymer micelles is usually captured from the analytical solution of the Ornstein−Zernike equation in the Percus−Yevick approximation, employing a hard-sphere potential.[42]

In the case of polydisperse micelles, eq 1 can be written as

$$d\Sigma/d\Omega = \int d\Sigma/d\Omega(q,R)\,f(R)\,dR + B \tag{2}$$

The polydispersity in the micellar core size (R_c) was taken into account by a Schultz distribution, as given by the equation

$$f(R_c) = [(z+1)/R_{cm}]^{z+1} R_c{}^z \exp[-(z+1)R_c/R_{cm}] \times$$
$$[1/\Gamma(z+1)] \tag{3}$$

where R_{cm} is the mean value of the distribution and z is the width parameter. The polydispersity of this distribution is given by $\Delta R/R_{cm} = 1/(z+1)^{1/2}$.

Results and Discussion

To understand the influence of different chloride-containing salts such as KCl, NaCl, and LiCl on the hydration properties of the copolymer micelles as a function of temperature, we measured the cloud point of 20% P123 solutions as a function of salt concentration (Figure 1). All of the solutions exhibited sharp cloud points, which were measured by dynamic light scattering as the temperatures at which a large increase in light scattering intensity was observed. As expected, because of the water-structure-forming properties of the ions present in the salts, the cloud points of the copolymer solutions decrease with increasing salt concentrations. It has been reported in the literature that, in the case of alkali metal halides, the salts containing smaller ions result in sharper decreases in the cloud point because of the higher water-structure-forming abilities of their ions.[26] Although this effect is significantly more prominent in the case of anions, the cations too follow the same rule, with Li$^+$ ion being one exception, probably because of its complex-formation abilities with PEO chains in the corona region.[26,36] As shown in Figure 1, the rate of decrease in the cloud point follows the order NaCl > KCl > LiCl, showing that, because of their complex-formation abilities, the Li$^+$ ions reduce the dehydrating effect of the Cl$^-$ ions and lead to the observation of a lower rate of decrease of the cloud point than for other alkali metal chloride salts.[36] In the later sections, we show that this property contributes to an enhancement in the temperature range of stability of the micellar gel phase.
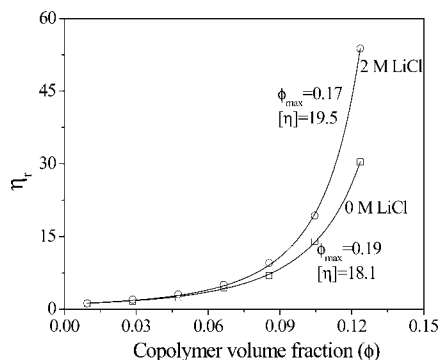
7728 *J. Phys. Chem. B, Vol. 112, No. 26, 2008*

Ganguly and Aswal

Figure 2. Relative viscosity (η_r) vs F127 volume fraction measured at 40 °C in the absence and presence of LiCl.
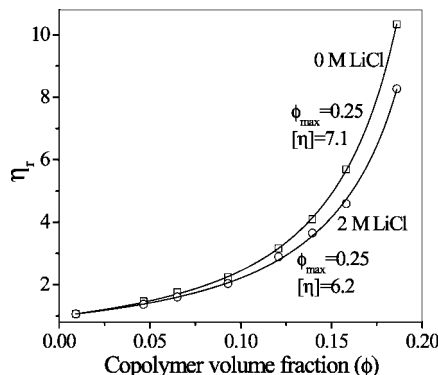

Figure 3. Relative viscosity (η_r) vs P123 volume fraction measured at 30 °C in the absence and presence of LiCl.

The effect of LiCl on plots of the relative viscosity vs copolymer (F127 and P123) volume fraction is shown in Figures 2 and 3, respectively. The volume fraction of the copolymer was calculated using copolymer-specific volumes of 0.95 and 0.93 for F127 and P123, respectively.[43,44] For F127, it was calculated from its density,[43] and for P123, it was in the form of partial specific volume in aqueous medium.[44] The relative viscosities of the F127 solutions were measured at 40 °C because, at low copolymer concentration, the CMTs of F127 solutions are close to room temperature and many of the F127 molecules remain as unimers at room temperature.[7] In the case of P123 solutions, on the other hand, viscosities were measured at 30 °C because the CMTs are much lower than room temperature at all of the measured copolymer concentrations.[7] At these measured temperatures, both copolymer molecules thus remain mostly as micelles, and the copolymer solutions can be represented as hard-sphere dispersions. The relative viscosities of the salt-containing copolymer solutions shown in the Figures 2 and 3 were calculated using the viscosity of the salt solution as the solvent viscosity. The plots in Figure 2 show that the addition of 2 M LiCl increases the relative viscosity of the F127 solutions at fixed copolymer concentration, with the increase being more conspicuous at higher copolymer concentrations. The low- and high-shear viscosities of the colloidal hard-sphere dispersions conform to the equation $\eta_r = (1 - \phi/\phi_{max})^{-[\eta]\phi_{max}}$, where ϕ is the hard-sphere volume fraction, ϕ_{max} is the limiting value at which the relative viscosity diverges, and $[\eta]$ is the intrinsic viscosity.[45,46] In the case of triblock copolymer solutions, $\phi_{max} = 0.53$, as such solutions form isotropic gel phases at this limiting volume fraction.[16] Because of the high degree of hydration in the corona region of the micelles, the divergence in the relative viscosity occurs at copolymer volume fractions much lower than 53%. Zhou et al. showed that the divergence in relative viscosity occurs at a lower copolymer

concentration at room temperature for copolymer P105 ($EO_{37}PO_{58}EO_{37}$) than for copolymer L64 ($EO_{13}PO_{30}EO_{13}$), where the former has a larger ethylene oxide chain.[47]

The results in Figure 2 indicate that, in the presence of 2 M LiCl, the divergence in relative viscosity of the copolymer solution occurs at lower copolymer concentration than in the case of pure copolymer solutions. Fitting of the relative viscosity data shown in Figure 2 according to the above-mentioned equation for η_r indeed shows that, upon addition of 2 M LiCl, the ϕ_{max} value decreases from 0.19 to 0.17. The lower ϕ_{max} value in the case of the copolymer solutions containing 2 M LiCl suggests that, in the presence of 2 M LiCl, the formation of the gel phase should occur at a lower copolymer concentration. As discussed in the next section, the formation of the cubic gel indeed occurs at lower copolymer concentration in the presence of 2 M LiCl. The enhancement of micellar hydration in the presence of LiCl is also reflected by an increase in the intrinsic viscosity, $[\eta]$, of the copolymer solutions from 18.1 to 19.5 cm^3/g. Both of these values are much higher than the Einstein value of 2.5 cm^3/g for hard-sphere dispersions in solution. This suggests that, in both cases, the copolymer micelles are hydrated to a significant extent and the extent of hydration is greater in the presence of 2 M LiCl.

The results for the P123 solutions in Figure 3 shows that, unlike in the case of F127, the LiCl-containing P123 solutions have lower values of relative viscosity than the pure solutions. Fitting of the data shows that the ϕ_{max} values are much higher than those observed in the case of F127 solutions because of the lesser degree of hydration of the P123 micelles. A significantly lower value of $[\eta]$ as compared to those observed for F127 solutions is also in accordance with this behavior. The observed decrease in relative viscosity upon addition of LiCl is accompanied by a decrease in the value of $[\eta]$ and essentially no change in the value of ϕ_{max}. A decrease in $[\eta]$ should result in an increase in ϕ_{max}, as a lower degree of micellar hydration requires a higher copolymer concentration for the gelation. The observed unchanged value of ϕ_{max} is probably because the intrinsic viscosity is determined by the hydration characteristics of the micelles at low copolymer concentrations, whereas ϕ_{max} is determined by the hydration characteristics of the micelles at high copolymer concentrations. The observed difference in the hydration characteristics at high and low P123 concentrations is possible because, for some block copolymers such as P123 and P85, the micellar structure undergo changes at high copolymer concentrations.[22,48] The opposite behavior shown by the P123 micelles vis-à-vis F127 suggests that the interaction between the Li$^+$ ions and the PEO chains becomes more prominent with increasing PEO block size.

Because the interaction between Li$^+$ ions and the ether oxygen of PEG chains[49] finds applications in solid-state lithium batteries in the form of solid electrolytes,[50–52] we also studied the effect of LiCl on the viscosity of aqueous solutions of 4000 g/mol PEG and compared the results with values observed for NaCl. PEG does not form micelles in aqueous medium because of its hydrophilic nature, and the size of its chain is equivalent to that of the PEO block in F127. The viscosity vs concentration data shown in the Figure 4 demonstrate that the rate of increase in viscosity with polymer concentration increases with increasing concentration of the polymer. The observed viscosity behavior in the dilute and semidilute regimes could be well depicted by equation proposed by Martin.[53,54] The concentrated regimes, which show a higher rate of increase in viscosity with concentration, are not governed by this equation, and only data up to a PEG concentration of 0.2 g/cm^3 were obtained.[54] The
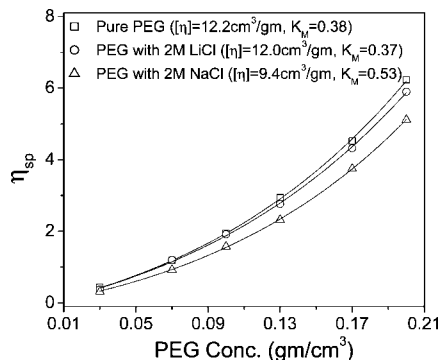
Figure 4. Specific viscosity ($\eta_{sp} = \eta_r - 1$) vs PEG (molecular weight 4000) concentration measured at 30 °C in the absence and presence of LiCl and NaCl. The solid lines are fits to the data obtained using the Martin equation.
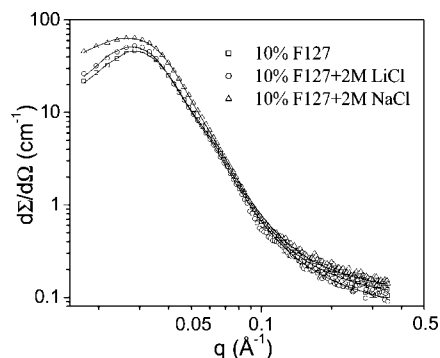

Figure 5. SANS data for 10% F127 solutions recorded at 40 °C in the absence and presence of salts. The solid lines are fits to the data obtained using a model for interacting hard-sphere colloids.

Figure 6. SANS data for 10% P123 solutions recorded at 30 °C in the absence and presence of salts. The solid lines are fits to the data obtained using a model for interacting hard-sphere colloids.

Martin equation contains an empirical parameter, K_M, called the Martin constant. and is given by

$$\eta_{sp} = C[\eta] \exp(K_M[\eta]C) \qquad (4)$$

where η_{sp} is specific viscosity ($\eta_r - 1$), C is the polymer concentration expressed in g/cm³, and $[\eta]$ is the intrinsic viscosity expressed in cm³/g. The results obtained from the fit to the data using this equation are shown in Figure 4. Low K_M values (≤0.5) in all three cases, i.e., in the absence and presence of LiCl and NaCl, show that water remains a good solvent for PEG even in the presence of the salts.[53,54] The influence of Li⁺, however, is evident from the fact that the K_M value remains almost constant upon addition of LiCl but it increases upon addition of NaCl. This is similar to the finding for the intrinsic viscosity ($[\eta]$), which shows only a marginal increase in the case of LiCl and more a significant increase in the case of NaCl. These results thus clearly suggest that complexation of the hydrated Li⁺ ions with the ether oxygen of the PEG chain
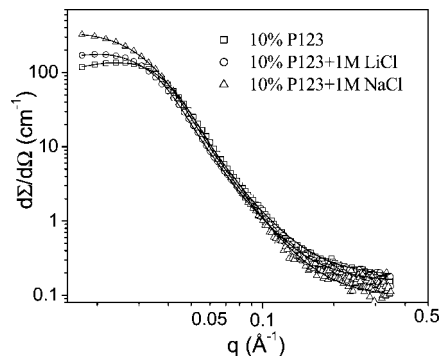
partially compensates for the dehydrating effect of the Cl⁻ ions. The difference in the behavior between LiCl and NaCl is also evident from the fact that the cloud point of the 10% PEG solutions decreases to 78 °C in the presence of 2 M NaCl, but it never falls below 100 °C for LiCl concentrations of as high as 6 M. These studies on PEG solutions thus relate well with the observed increase in the hydration of the F127 micelles because of the interaction of the Li⁺ ions with the ether oxygen of the PEG chains.

Results of SANS studies on the influence of LiCl on the structures of the F127 and P123 micelles are shown in Figures 5 and 6, respectively, and the micellar parameters obtained by fitting of the data based on spherical core–shell micelles are reported in Table 1. For both copolymers, the results are in agreement with the viscosity studies described in the previous section. The micellar volume fraction of the 10% F127 solution increases in the presence of LiCl (Table 1), and such an observation at fixed copolymer concentration can occur only because of an increase in the degree of hydration of the F127 micelles. Because the F127 solutions show a decrease in the micellar volume fraction in the presence of NaCl (Table 1), the role of the Li⁺ ions is clearly different from that of the Na ions. As explained earlier, an increase in the amount of water in the micellar corona as a result of complex formation between the hydrated Li⁺ ions and the PEO chains offsets the dehydrating effect of Cl⁻ ions on the PEO chains and leads to the observed increase in the degree of micellar hydration. Table 1 also shows that both salts increase the core radius and the aggregation number, which generally shows that the hydrophobic character of the copolymers increases in the presence of the Cl⁻ ions but the effect is less in the case of LiCl. The difference between the hard-sphere radius (R_{hs}) and the core radius (R_c), which signifies the micellar degree of hydration, increases marginally in the presence of LiCl but decreases upon addition of NaCl. The radius of gyration and the polydispersity in the micellar

TABLE 1: Core Radius (R_{cm}), Hard-Sphere Radius (R_{hs}), Aggregation Number (N_{agg}), Radius of Gyration (R_G), Volume Fraction (ϕ), and Polydispersity ($\Delta R_c/R_{cm}$) of the Micelles in 10% F127 (EO$_{100}$PO$_{70}$EO$_{100}$) Solutions at 40 °C and in 10% P123 (EO$_{20}$PO$_{70}$EO$_{20}$) Solutions at 30 °C with Different Salt Concentrations

| sample	core radius (R_c) (nm)	aggregation number (N_{agg})	radius of gyration (R_G) (nm)	hard-sphere radius (R_{hs}) (nm)	volume fraction (ϕ)	polydispersity ($\Delta R_c/R_{cm}$) (%)
10% F127						
pure	2.91 ± 0.02	15 ± 1	2.3 ± 0.1	11.5 ± 0.1	0.32 ± 0.01	32 ± 1
2 M LiCl	3.20 ± 0.02	21 ± 1	2.4 ± 0.2	12.0 ± 0.2	0.35 ± 0.02	29 ± 1
2 M NaCl	3.65 ± 0.01	30 ± 1	1.9 ± 0.1	10.9 ± 0.1	0.26 ± 0.01	29 ± 1
10% P123						
pure	4.53 ± 0.03	58 ± 1	1.1 ± 0.1	9.0 ± 0.1	0.21 ± 0.01	41 ± 2
1 M LiCl	4.87 ± 0.02	72 ± 1	1.1 ± 0.1	9.2 ± 0.2	0.19 ± 0.02	46 ± 2
1 M NaCl	5.02 ± 0.02	79 ± 1	1.3 ± 0.1	8.9 ± 0.2	0.15 ± 0.02	49 ± 2
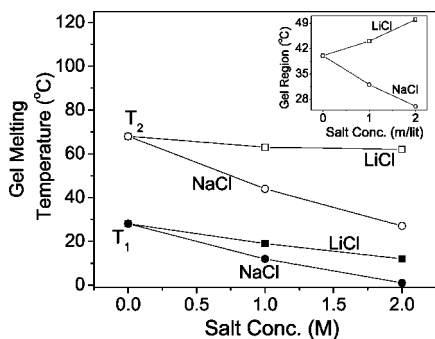
Figure 7. Lower (T_1) and upper (T_2) melting temperatures of 18% F127 gels as a function of salt concentration. The inset shows the temperature range of the gel phase ($T_2 - T_1$) as a function of salt concentration.

Figure 8. Lower (T_1) and upper (T_2) melting temperatures of 30% P123 gels as a function of salt concentration. The inset shows the temperature range of the gel phase ($T_2 - T_1$) as a function of salt concentration.
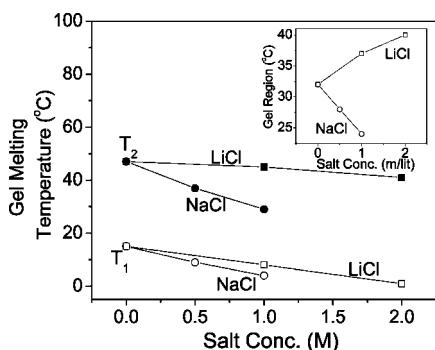
core radius, however, do not undergo any significant change in the presence of either salt. Unlike in the case of F127 solutions, the P123 solutions show a decrease in the micellar volume fraction upon addition of LiCl (Figure 6 and Table 1). This again is in agreement with the viscosity studies and indicates that the degree of hydration of the P123 micelles decreases in the presence of LiCl. The reduction in the volume fraction in the presence of LiCl, however, is less than that observed for NaCl. These results thus suggest that, although LiCl reduces the degree of hydration of the P123 micelles, because of the ability of Li$^+$ ions to form complexes in the micellar corona, the extent of reduction is less than that observed in the case of NaCl.

The changes in the degree of hydration of micelles with the addition of LiCl and NaCl are also reflected in the gel formation characteristics of the copolymer solutions (Figures 7 and 8). The absence of any birefringence in the gels when they are observed through crossed polarizing lenses under an optical microscope confirms their isotropic nature. These isotropic gels have two melting temperatures, T_1 and T_2. T_1 is defined as the temperature at which the volume fraction of the micelles reaches 53%. The volume fraction remains small at the critical micelle temperature (CMT), as only a fraction of the unimers form micelles. As increasing numbers of unimers are converted into micelles at increasing temperatures above the CMT, the micellar volume fraction increases progressively and reaches 53% at T_1.[16] The value of T_1 decreases with increasing copolymer concentration.[19] The melting of the gel phase at T_2 could result when the micellar volume fraction become less than the minimum volume fraction required for gel formation because of a progressive decrease in micellar hydration with increasing temperature.

The evolutions of the lower and the upper melting temperatures (T_1 and T_2) of the gels formed by the aqueous solutions of F127 and P123 are shown in the Figures 7 and 8, respectively. In the case of P123 solutions, the gel points were measured only up to 1.0 M NaCl concentration because the gel becomes cloudy at room temperature with higher NaCl concentrations. The figures show that both T_1 and T_2 decrease with increasing NaCl and LiCl concentrations, and the rate of decrease was found to always be higher in the case of NaCl. The decrease in T_1 can be correlated with a decrease in the critical micellar temperature in the presence of the water-structure-forming abilities of the chloride and alkali metal ions.[26] Because the PPO block becomes insoluble at the CMT, a lower rate of decrease in T_1 by LiCl suggests that complexation of the Li$^+$ ions with PEO blocks has a significant influence on the solubility of the PPO block as well, which becomes insoluble at the CMT. The variation of the upper melting temperature (T_2) with salt concentration shows a similar trend, and LiCl results in a much smaller decrease than NaCl. Because melting of the gel could be attributed to progressive micellar dehydration with increasing temperature, the results suggest that the presence of the Li$^+$ ions possibly reduces micellar dehydration at higher temperature.

Although the variations in both T_1 and T_2 show similar trends in the presence of LiCl and NaCl, the two salts show exactly opposite behavior with respect to the temperature range of stability of the gel phase, that is, the difference between the two melting temperatures ($T_2 - T_1$). For both copolymers, the addition of NaCl progressively reduces the temperature range of stability of the gel phase, but the addition of LiCl leads to an improvement in it (insets of Figures 7 and 8). The observed improvement in stability of the gel phase in the presence of LiCl results because of a lower rate of decrease in T_2 compared to that of T_1 with increasing LiCl concentration, opposite to what is observed in the case of NaCl. Moreover, LiCl also reduces the minimum copolymer concentration required for the F127 solution to form the room-temperature cubic gel phase from 18% to 14%. The pure 14% F127 solution does not form any gel phase, but in the presence of 2 M LiCl, it forms a room-temperature cubic gel phase with the lower and upper melting temperatures of 24 and 42 °C, respectively. However, the case is not the same with the P123 solution, as the presence of LiCl does not lead to a decrease in the minimum copolymer concentration required to form the cubic gel phase. This difference in the behavior of the two copolymers can be correlated with the results of viscosity and SANS studies: whereas the F127 solutions show an increase in the micellar volume fraction in the presence of LiCl, the P123 solutions show a decrease. These results thus highlight the importance of the hydrophilicity of the copolymers as well as the choice of the salts in determining the gelation characteristics of the copolymers in their aqueous salt solutions.

Conclusion

The micellar hydration and gelation characteristics of aqueous solutions of F127 ($EO_{100}PO_{70}EO_{100}$) and P123 ($EO_{20}PO_{70}EO_{20}$) have been studied in the presence of alkali metal chloride salts. The effect of LiCl was found to be different from those of the other alkali metal salts, as LiCl leads to an increase in the degree of hydration of the F127 micelles and an improvement in the gelation characteristics of the copolymer solutions. The results can be explained in terms of the complexation of hydrated Li$^+$ ions with the PEO chains in the micellar corona region. A comparison of the behavior of the two copolymers suggests that the interaction is more significant in the F127 micelles than in

PEO–PPO–PEO Solutions in the Presence of LiCl

J. Phys. Chem. B, Vol. 112, No. 26, 2008 **7731**

the P123 micelles because of the larger size of the PEO block in F127. Viscosity studies on poly(ethylene glycol) (PEG) with a size equivalent to that of the PEO block in F127 also suggest that the interaction between the Li^+ ions and the ether oxygen of the PEG chains plays a role in improving the hydration characteristics of the PEG chains.

References and Notes

(1) Chu, B. *Langmuir* **1995**, *11*, 414.

(2) Wanka, G.; Hoffmann, H.; Ulbricht, W. *Colloid Polym. Sci.* **1990**, *268*, 101.

(3) Holmqvist, P.; Alexdandridis, P.; Lindman, B. *J. Phys. Chem. B* **1998**, *102*, 1149.

(4) Schmolka, I. R. *J. Am. Oil Chem. Soc.* **1977**, *54*, 110.

(5) Pandit, N. K.; Wang, D. *Int. J. Pharm.* **1998**, *167*, 183.

(6) Hvidt, S.; Jorgensen, E. B.; Brown, W.; Schillen, K. *J. Phys. Chem.* **1994**, *98*, 12320.

(7) Alexandridis, P.; Holzwarth, J. F.; Hatton, T. A. *Macromolecules* **1994**, *27*, 2414.

(8) Mortensen, K.; Pedersen, J. S. *Macromolecules* **1993**, *26*, 805.

(9) Zhou, Z.; Chu, B. *J. Colloid Interface Sci.* **1988**, *126*, 171.

(10) Schillen, K.; Brown, W.; Johnson, R. M. *Macromolecules* **1993**, *27*, 4825.

(11) Lehner, O.; Lindner, H.; Glatter, O. *Langmuir* **2000**, *16*, 1689.

(12) Waton, G.; Michels, B.; Steyer, A.; Schosseler, F. *Macromolecues* **2004**, *37*, 2313.

(13) Duval, M.; Waton, G.; Schosseler, F. *Langmuir* **2005**, *21*, 4904.

(14) Ganguly, R.; Aswal, V. K.; Hassan, P. A.; Gopalakrishnan, I. K.; Yakhmi, J. V. *J. Phys. Chem. B* **2005**, *109*, 5653.

(15) Bahadur, P.; Pandya, K.; Almgren, M.; Li, P.; Stilbs, P. *Colloid Polym. Sci.* **1993**, *271*, 657.

(16) Mortensen, K.; Brown, W.; Norden, B. *Phys. Rev. Lett.* **1992**, *68*, 2340.

(17) Mortensen, K.; Schwahn, D.; Janssen, S. *Phys. Rev. Lett.* **1993**, *71*, 1728.

(18) Brown, W.; Schillen, K.; Almgren, M.; Hvidt, S.; Bahadur, P. *J. Phys. Chem.* **1991**, *95*, 1850.

(19) Malmsten, M.; Lindman, B. *Macromolecules* **1992**, *25*, 1282.

(20) Zhang, K.; Khan, A. *Macromolecules* **1995**, *28*, 3807.

(21) Robbins, M. O.; Kremer, K.; Grest, G. S. *J. Chem. Phys.* **1988**, *88*, 3286.

(22) Glatter, O.; Scherf, G.; Schillen, K.; Brown, W. *Macromolecules* **1994**, *27*, 6046.

(23) Pusey, P. N.; Van Megan, W. *Nature* **1986**, *320*, 340.

(24) Cabana, A.; Ait-Kadi, A.; Juhasz, J. *J. Colloid Interface Sci.* **1997**, *190*, 307.

(25) Yu, G.-E.; Li, H.; Fairclough, J. P. A.; Ryan, A. J.; McKeown, N.; Ali-Adib, Z.; Price, C.; Booth, C. *Langmuir* **1998**, *14*, 5782.

(26) Alexdandridis, P.; Holzwarth, J. F. *Langmuir* **1997**, *13*, 6074.

(27) Malmsten, M.; Lindman, B. *Macromolecules* **1992**, *25*, 5440.

(28) Bahadur, P.; Li, P.; Almgren, M.; Brown, W. *Langmuir* **1992**, *8*, 1903.

(29) Pandit, N. K.; Kisaka, J. *Int. J. Pharm.* **1996**, *145*, 129.

(30) Brown, W.; Schillen, K.; Hvidt, S.; Bahadur, P. *J. Phys. Chem.* **1992**, *96*, 6038.

(31) Bahadur, P.; Pandya, K. *Langmuir* **1992**, *8*, 2666.

(32) Su, T-I.; Liu, H-Z.; Wang, J.; Chen, J-Y. *Langmuir* **2002**, *18*, 865.

(33) Aswal, V. K.; Goyel, P. S.; Kohlbrecher, J.; Bahadur, P. *Chem. Phys. Lett.* **2001**, *349*, 458.

(34) Pandit, N. K.; Trygstad, T.; Croy, S.; Bohorquez, M.; Koch, C. *J. Colloid Interface Sc.* **2000**, *222*, 213.

(35) Thiyagarajan, P.; Chaiko, D. J. Jr. *Macromolecules* **1995**, *28*, 7730.

(36) Kumbhakar, M.; Ganguly, R. *J. Phys. Chem. B* **2007**, *111*, 3935.

(37) Hecht, E.; Mortensen, K.; Gradzielski, M.; Hoffman, H. *J. Phys. Chem.* **1995**, *99*, 4866.

(38) ASTM Standards D445-04 and D446-04; ASTM International: West Conshohocken, PA, 2004, and references therein.

(39) Aswal, V. K.; Goyel, P. S. *Curr. Sci.* **2000**, *79*, 947.

(40) Pedersen, J. S.; Gerstenberg, C. *Macromolecules* **1996**, *29*, 1363.

(41) Pedersen, J. S. *J. Appl. Crystallogr.* **2000**, *33*, 637.

(42) Percus, J. K.; Yevick, G. *J. Phys. Rev.* **1958**, *1*, 110.

(43) *Pluronic F127 Block Copolymer Surfactant Technical Bulletin*; BASF Corporation: Mount Olive, NJ, 2002; available at www.basf.com/performancechemical/pdfs/Pluronic_F127.pdf.

(44) Nolan, S. L.; Phillips, R. J.; Cotts, P. M.; Dungan, S. R. *J. Colloid Interface Sci.* **1997**, *191*, 291.

(45) De Kruif, C. G.; Van Iersel, E. M. F.; Vrij, A.; Russel, W. B. *J. Chem. Phys.* **1985**, *83*, 4717.

(46) Krieger, I. M. *Adv. Colloid Interface Sci.* **1972**, *3*, 111.

(47) Zhou, D.; Alexdandridis, P.; Khan, A. *J. Colloid Interface Sci.* **1996**, *183*, 339.

(48) Ganguly, R.; Aswal, V. K.; Hassan, P. A.; Gopalakrishnan, I. K.; Kulshreshtha, S. K. *J. Phys. Chem. B* **2006**, *110*, 9843.

(49) Londono, J. D.; Annis, B. K.; Habenschuss, A.; Borodin, O.; Smith, G. D.; Turner, J. Z.; Soper, A. K. *Macromolecules* **1997**, *30*, 7151.

(50) Berthier, C.; Gorecki, W.; Minier, M.; Armand, M. B.; Chabagno, J. M.; Rigaud, P. *Solid State Ionics* **1983**, *11*, 91.

(51) Gray, F. M. *Solid Polymer Electrolytes: Fundamentals and Technological Applications*; VCH Publishers, Inc.: New York, 1991.

(52) Scrosati, B. *Applications of Electroactive Polymers*; Chapman & Hall, London, 1993.

(53) Martin, A. F. Presented at the *American Chemical Society National Meeting, Memphis, TN*, April 1942.

(54) Durand, A. *Eur. Polym. J.* **2007**, *43*, 1744.

JP801940M