PEO-PPO-PEO Block Copolymer Micelles in Aqueous Electrolyte Solutions: Effect of Carbonate Anions and Temperature on the Micellar Structure and Interaction

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ABSTRACT: The structure and interaction of micelles formed by an amphiphilic triblock copolymer $P(EO)_{103}-P(PO)_{39}-P(EO)_{103}$ (F88) in aqueous electrolyte solutions of potassium carbonate have been investigated using small-angle neutron scattering as functions of temperature and salt concentration. Modeling the SANS data from the copolymer solutions using analytical expressions for the scattering intensity revealed the remarkable effects of carbonate anion concentration and the temperature on the self-assembly of F88 into spherical and cylindrical aggregates and subsequent phase separation. The critical micellization temperature (cmt) of 5 wt % F88 decreases with an increase in the salt concentration, and the cmt approaches ambient temperature at which the transition from spherical to cylindrical micelles occurs as well as the phase separation temperature of the copolymer from the solution. These observations clearly indicate that the evolution of the micellar structure and the phase separation are through gradual dehydration of the copolymer chains with an increase in the salt concentration. The effects of carbonate ions are quite dramatic when compared to those of monovalent ions as the published results on monovalent ions.

Introduction

Amphiphilic copolymers consisting of both hydrophilic and hydrophobic blocks have extensive applications in diverse areas such as pharmaceutical formulations, radiation-damaged cell repair and treatment, controlled drug delivery, bioseparation and extraction, nuclear waste processing, etc.^{1,2} Triblock copolymers composed of two different polymers, when in a solvent selective to one of the species, self-organize into different geometrical shapes to avoid direct contact between the solvent and the insoluble block(s).³⁻⁵ These self-associated structures exhibit a rich phase behavior such as micelles of various forms and sizes often with very different physical properties. Temperature, pressure, copolymer concentration, and chain architecture can be tuned to obtain tailored self-assembled structures with desired physical properties. Structures of these selfassembled aggregates have been studied extensively by means of small-angle neutron scattering (SANS), $^{6-12}$ small-angle X-ray scattering, 13,14 dynamic light scattering (DLS),^{15–18} differential scanning calorimetry,^{19–21} and Raman spectroscopy.²² The formation of micelles is a direct result of anisotropic interaction between water molecules and copolymer blocks. While PEO is soluble on a relatively wide range of temperatures (0-100 °C), PPO blocks can only be well dissolved at temperatures below 15 °C.⁴ Hence, in a dilute aqueous

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The effect of electrolytes on the micellization of PEO– PPO–PEO block copolymers has been investigated by a number of groups.^{12,19,20,27,28} The alkali-metal halides act as structure makers, leading to an increase in their self-hydration through hydrogen bonding, thereby re-

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ducing the copolymer solubility and decreasing both cmt and CP in the order $Cl^- > Br^- > I^-$ and $Na^+ > K^+ >$ Li⁺. On the other hand, salts such as NaSCN and (NH₂)₂CO act as structure breakers, reducing selfhydration and increasing the hydration of the copolymer, thus elevating both cmt and CP in the order of NaSCN > $(NH_2)_2CO.^{19}$ In the case of NaI, the cmt increases but CP decreases.¹⁹ The effect of several different salts, including some salts with divalent anions (SO_4^{2-}) , on the cloud point of pluronic L64/water system is available in the literature.²⁸ These authors²⁸ found that the SO₄²⁻ anion lowered the CP and attributed it to a "salting out" effect similar to the one described earlier for the halides. Anions seem to have a larger effect on both the cmt and CP than cations.¹⁹ The effect of potassium halides on the micellization of F88 has been investigated using SANS and found to be analogous to that of temperature.¹² Limited information^{19,28} is available on the behavior of triblock copolymers in aqueous solution in the presence of multivalent anions (e.g., carbonates, sulfates, phosphates). Previous investigations^{25,26} have shown that anions such as CO_3^{2-} , S O_4^{2-} , and PO_4^{3-} are more effective in modifying the solution structure of PEO than the halides, and the higher the salt concentration, the stronger the effect. Since a PEO-PPO-PEO triblock copolymer chain contains one PPO section and two PEO end blocks, the addition of multivalent salts to aqueous copolymer solutions is expected to produce dramatic effects on the micellization and structural transformations of the copolymers.

To understand the thermodynamics involved in the micellization and phase separation in PEO–PPO–PEO solutions, we carried out systematic SANS studies on the aqueous solution of Pluronic F88 [P(EO)₁₀₃–P(PO)₃₉–P(EO)₁₀₃] as a function of temperature and concentration of several potassium salts. In this paper we propose a modification to an existing formalism⁸ for the analysis of the SANS data and apply it to the case of potassium carbonate (K₂CO₃). The effect of other monovalent and multivalent anions will be the subject of a future publication.

Experimental Section

The Pluronic F88 (obtained from BASF Corp., New Jersey) was used as received. The solutions were prepared by dissolving 5 wt % polymer in D_2O (99.9% deuterium, Aldrich) containing measured amounts of potassium carbonate (purchased from Fisher Scientific). SANS experiments were carried out by using the time-of-flight small-angle neutron diffractometer (SAND) at the Intense Pulsed Neutron Source (IPNS), Argonne National Laboratory. This instrument provides data in the $Q(4\pi \sin \theta / \lambda)$, where 2θ is the scattering angle and λ is the wavelength of the neutrons) range of 0.004-0.8 Å⁻¹ in a single measurement by using a 40×40 cm² position-sensitive ³He gas detector and neutrons with wavelengths in the range of 0.5-14 Å ($\Delta\lambda/\lambda = 0.05$ at each λ). Copolymer solutions were sealed in Suprasil cylindrical cells with 1 mm path length for the SANS measurements. A liquid flow thermostat was used to control the temperature to within ± 1 °C. The scattering data were corrected for empty cell and solvent scattering, detector sensitivity, and sample transmission. The differential scattering cross section I(Q) was placed on an absolute scale in the units of cm⁻¹ by using secondary standards whose absolute scattering cross sections are known.

SANS Data Analysis

The scattering intensity for a monodisperse system of particles can be written as

$$I(Q) = (\Delta \rho)^2 N_{\rm s} F(Q) S(Q) + I_{\rm inc}$$
(1)

where $(\Delta \rho)^2$ is the contrast factor, N_s is the number density of the scattering particles, F(Q) is the single particle form factor, S(Q) is the interparticle structure factor, and I_{inc} is the incoherent scattering background.

Since the $[P(EO)_{103}P(PO)_{39}P(EO)_{103}]$ copolymers exist as unimers in 5 wt % solution at ambient temperature, the SANS data can be modeled using the form factor for a single polymer coil obeying Gaussian statistics. With an increase in temperature and/or salt concentration, the copolymers tend to aggregate, forming micelles with a spherical hydrophobic core and a corona consisting of Gaussian chains. The micellar structure can be described using a modified version of the form factor given by Pedersen and Gerstenberg⁸ for micelles formed by a diblock copolymer. The form factor for a spherical micelle consists of four parts, two self-correlation terms, one for the spherical core and the other for the Gaussian chains in the corona; and two cross-correlation terms, one between the spherical core and the attached chains and the other between the different chains.

The form factor $F_s(Q)$ for a sphere of radius *R* is given by the square of the scattering amplitude A(Q,R),

$$A(Q,R) = \frac{3[\sin(QR) - QR\cos(QR)]}{(QR)^3}$$
(2)

The form factor for the Gaussian chains with a radius of gyration $R_{\rm g}$ in the corona, $F_{\rm c}$, is given by

$$F_{\rm c}(Q, R_{\rm g}) = \frac{2[{\rm e}^{-z} - 1 + z]}{z^2}$$
(3)

where $z = Q^2 R_g^2$. The core–chain interference term S_{sc} is given by

$$S_{\rm sc} = A(Q,R) B(Q,R_{\rm s}) \sin(QR)/(QR)$$
(4)

and the chain-chain interference term is

$$S_{\rm cc} = [B(Q, R_{\rm g}) \sin(QR)/QR]^2 \tag{5}$$

where $B(Q, R_g)$ in eqs 4 and 5 is defined as

$$B(Q, R_{o}) = z^{-1}(1 - e^{-z})$$
(6)

According to Pedersen and Gerstenberg,⁸ the form factor for a spherical micelle formed by a diblock copolymer of aggregation number N is

$$F_{\rm mic} = N^2 b_{\rm s}^2 F_{\rm s} + N b_{\rm c}^2 F_c + N(N-1) b_{\rm c}^2 S_{\rm cc} + 2N b_{\rm s} b_{\rm c} S_{\rm sc}$$
(7)

where b_s and b_c are the excess scattering lengths of the portion of the copolymer in the core and in the corona, respectively. Equation 7, derived for a diblock copolymer,⁸ needs to be modified for a triblock with identical end branches. To take into consideration the presence of two blocks in the corona for every block in the core, N in the last three terms of eq 7 has to be replaced by 2N, leading to

$$F(Q) = N^{2} b_{s}^{2} F_{s} + 2N b_{c}^{2} F_{c} + 2N(N-1) b_{c}^{2} S_{cc} + 4N b_{s} b_{c} S_{s}$$
(8)

The structure factor S(Q) of the spherical micelles in eq 1 is estimated using the Percus–Yevick approximation for the case of hard spheres in the Ornstein– Zernicke equation.^{29,30}

$$S(Q) = \frac{1}{1 + 24\phi G(y,\phi)/y}$$
(9)

where $y = 2QR_{hs}$, R_{hs} is the hard-sphere interaction radius, and ϕ is the volume fraction and

$$G(y,\phi) = (\alpha/y^2)[\sin(y) - y\cos(y)] + (\beta/y^3)[2 y\sin(y) + (2 - y^2)\cos(y)] + (\gamma/y^5)[-y^4\cos(y) + 4\{((4y^2 - 6) \times \cos(y) + (y^3 - 6y)\sin(y) + 6)\}] (10)$$

The functions α , β and γ are

$$\alpha = (1 + 2\phi)^2 / (1 - \phi)^4$$

$$\beta = -6\phi (1 + \phi/2)^2 / (1 - \phi)^4$$

$$\gamma = \alpha \phi/2$$

The scattering curves can be fitted using a least-squares routine to eq 8, yielding the parameters R, R_g , N, R_{hs} , and ϕ . We held the excess scattering lengths of the polymer in the core and the corona as constants at $b_s =$ -0.0222 Å and $b_c = -0.0429$ Å by assuming that only PPO chains are in the core and PEO chains in the corona. But it does not preclude the presence of some PEO in the core at higher temperatures.¹⁰ Furthermore, SANS cannot distinguish between PEO and PPO segments in the micelles in D₂O solutions as the neutron scattering lengths for PEO and PPO are very close to each other.

Results and Discussion

To assess the validity of our modification of the form factor for the interacting diblock copolymer micelles⁸ (eq 7) to describe the interacting triblock copolymer micelles (eq 8), we modeled the scattering data for F88 in pure D₂O at 73 °C using both eqs 7 and 8. While the difference at low $Q(Q < 0.1 \text{ Å}^{-1})$ is negligible, eq 8 provides a better representation of the entire data as shown by the value of reduced χ^2 (3.8 vs 15.1). In addition, the two fits yielded very different values for the radius $R_{\rm hs}$ and aggregation number N. The values of $R_{\rm hs}$ and \overline{N} derived from the fits can be used to calculate the concentration of F88 in solution. On the basis of a reasonable assumption that most of the F88 copolymers will exist in the micelles rather than as unimers in solution at 73 °C, the concentration of F88 can be calculated using

$$\operatorname{conc} = \frac{3\phi NM}{4\pi R_{\rm hs}^{3} N_{\rm A}}$$
(11)

where N_A is the Avogadro's number and M the molar mass of F88. The concentrations calculated using the fitted values for N and R_{hs} are 0.074 g/mL (eq 7) and 0.039 g/mL (eq 8) compared to the experimental sample concentration of 0.055 g/mL. We argue that the smaller concentration for F88 derived from eq 8 (0.039 g/mL) is more reasonable than that from eq 7 because of the following reasons. While deriving the F88 concentration using the fitted parameters, we assumed that the whole micelle is packed with F88 molecules, and we did not take into consideration of the fact the micelles also



Figure 1. SANS data of 5 wt % $P(EO)_{103}P(PO)_{39}P(EO)_{103}$ in pure D_2O solution at different temperatures. The markers are the experimental data points, and continuous lines are the theoretical fits corresponding to eq 3 for the unimer and eqs 1, 8, and 9 for the interacting micelles.

contain $D_2O.^{5,6}$ Since we attributed the whole miceller volume (based on $R_{\rm hs}$ from eq 8) to the polymers, we obtained a smaller F88 concentration of 0.039 g/mL. In reality, the presence of D₂O in the micelles will reduce the net volume occupied by the F88 molecules. Consequently, the reduction in the polymer volume in the micelle will lead to a larger concentration of F88 because the volume is a denominator in eq 11. Thus, the concentration of F88 derived from SANS should be lower than the actual concentration (0.055 g/mL) but cannot be higher as that from eq 7. Equation 8 thus provides better fits of the scattering data from the interacting micelles as well as reasonable parameters, one of which is the F88 concentration which is a well-known experimental parameter. Therefore, in this paper all the results presented are from fits using eq 8 for the scattering from the interacting spherical micelles.

SANS data of 5 wt % F88 in D₂O at different temperatures are shown in Figure 1. The scattering profile of the copolymer solution at 26 °C shows a relatively weak Q dependence, implying that the scattering objects are small. The scattering intensity can be fitted well using eq 3 for randomly distributed Gaussian coils. Thus, only unimers, not aggregates, are present in solution. This is consistent with the fact that the cmt (T_{c1}) of aqueous solution of 5 wt % F88 is about 31 °C.⁵ The radius of gyration R_g was found to be 26 Å, which is consistent with the published values of 21 Å from SANS¹² and the hydrodynamic radius of 29 Å measured using dynamic light scattering.17 As the temperature increases, I(Q) increases monotonically (Figure 1) due to the formation of micelles and their growth. The presence of broad peaks at $Q \sim 0.025~{
m \AA}^{-1}$ at higher temperatures reflects the strong interaction between the micelles. The peak height increases with temperature with only minimal changes in the peak position. The fits to the data shown in Figure 1 yield a good representation of the experiments, and the results are shown in Table 1.

The R_g of the polymer segments in the corona changes very weakly with temperature. A similar result for the thickness of the corona (given by $R_{hs} - R$) was obtained by Mortensen and Pedersen⁶ for F88 and Mortensen and Brown⁷ for the pluronics P85 (P(EO)₂₅P(PO)₃₉P(EO)₂₅), F87 (P(EO)₆₇P(PO)₃₉P(EO)₆₇), and F88, all having the

Table 1. Miceller Parameters from the Modeling of SANS Data of 5 wt % $P(EO)_{103}P(PO)_{39}P(EO)_{103}$ Solutions in D_2O

T (°C)	<i>R</i> (Å)	$R_{\rm g}$ (Å)	$R_{\rm hs}$ (Å)	N	ϕ
No Salt					
41	31.2 ± 0.5	28.1 ± 0.4	80.6 ± 0.6	18	0.12
52	$\textbf{37.8} \pm \textbf{0.1}$	28.6 ± 0.2	88.0 ± 0.2	28	0.18
63	41.5 ± 0.1	$\textbf{27.8} \pm \textbf{0.2}$	91.2 ± 0.2	36	0.17
73	44.0 ± 0.1	27.5 ± 0.2	91.9 ± 0.2	43	0.16
0.1 M K ₂ CO ₃					
26	12.3 ± 1.0	29.5 ± 1.7	$\tilde{84.2}\pm4.8$	6 ± 2	0.08 ± 0.03
42	41.9 ± 0.1	$\textbf{28.9} \pm \textbf{0.4}$	90.3 ± 0.4	33	0.18
52	44.9 ± 0.1	$\textbf{28.9} \pm \textbf{0.3}$	91.1 ± 0.4	44	0.15
0.3 M K ₂ CO ₃					
26	32.1 ± 0.9	29.5 ± 0.5	84.1 ± 0.9	21	0.09
41	44.6 ± 0.1	28.4 ± 0.3	84.3 ± 0.3	43	0.14
52	48.5 ± 0.2	30.8 ± 0.4	$\textbf{78.8} \pm \textbf{0.3}$	50	0.12
0.5 M K ₂ CO ₃					
26	43.9 ± 0.3	28.5 ± 0.2	78.1 ± 1.0	34	0.12

same number of PO units but decreasing PO to EO segment ratios. Increase in temperature shifts the equilibrium between unimers and micelles in favor of micelles. Hence, more unimers aggregate to form micelles, and the aggregation number increases from 18 at 41 °C to 43 at 73 °C (see Table 1). The micelle aggregation number for F88 obtained using DLS⁵ was 17 at 40 °C, in good agreement with our value of 18 at 41 °C. Furthermore, *R* increases to accommodate the increasing number of polymer chains in each micelle.

The volume fraction of the spherical micelles, ϕ , on the other hand, increases from 0.12 at 41 °C to 0.18 at 52 °C but remains nearly a constant at higher temperatures. Our results are consistent with the published data for F88,5,7 but not with those of Jain and coworkers.¹² It is believed that the saturation of the volume fraction indicates the near completion of the micellization^{6,7} and that the corresponding temperature (T_{c2}) depends on the number of EO units in the copolymer. In the region between T_{c1} and T_{c2} , both the micelles and the unimers are in thermodynamic equilibrium.^{5,6,15} As the temperature increases, the equilibrium shifts in favor of the micelles, and above T_{c2} the amount of unimers present in the system becomes negligible. The data in Table 1 show that the micellization process may be complete around 52 °C.

Jain and co-workers¹² carried out SANS studies on F88 in pure D₂O as well as in D₂O/monovalent salt solutions as a function of temperature and concluded that (i) the parameters $R_{\rm hs}$, ϕ , and N are temperature independent and (ii) the aggregation number is a constant (62) at all temperatures. However, we find that $R_{\rm hs}$, R, and N increase with increasing temperature (see Table 1), and this is consistent with the monotonic increase in scattered intensity at low Q with increasing temperature. The results from the present study and those from Mortensen and Brown⁷ significantly differ from those obtained by Jain and co-workers.¹²

The increase in the core radius R with temperature can be explained by a gradual dehydration mechanism wherein both PPO and PEO constitute the core, rather than PPO alone. The volume of a PO monomer in the dry PPO is 96 Å³ based on

$$V_{\rm PO}(\rm dry) = M_{\rm PO}/(\rho_{\rm PO}N_{\rm A})$$
(12)

where $M_{PO} = 58$ is the molar mass of a PO monomer, $\rho_{PO} = 1.01$ g/cm³ is the density of dry PPO, and N_A is Avogadro's number. If we assume that the micelle core



Figure 2. SANS data of 5 wt % $P(EO)_{103}P(PO)_{39}P(EO)_{103}$ in K_2CO_3 electrolyte solutions at different salt concentrations at ambient temperature (26 °C).

consists of only PPO blocks, then the average volume occupied by a propylene oxide (PO) monomer in the core is given by

$$V_{\rm PO} = \frac{(4\pi/3)R^3}{n_{\rm PO}N}$$
(13)

where *R* and *N* are the core radius and aggregation number derived from the fits and $n_{PO} = 39$, the total number of PO monomers in a PPO block. At 41 °C eq 13 yields $V_{PO} = 190$ Å³, which is much larger than that for dry PPO (96 Å³). The core is likely to contain only a small amount of D₂O, as it becomes anhydrous at the end of the micellization process.¹⁰ We believe that core volume is occupied by some partially dehydrated PEO segments in addition to the PPO segments. But for the purposes of calculating the amount of EO in the core, we will assume that the amount of D₂O in the core is negligible. The number of EO units in the core can be calculated by using

$$n_{\rm EO} = \frac{(4\pi R^3/3) - V_{\rm PO}({\rm dry})n_{\rm PO}N}{V_{\rm EO}({\rm dry})N}$$
(14)

where $V_{\rm EO}$, the volume of a ethylene oxide (EO) monomer in dry PEO, $V_{\rm EO}(dry) = M_{\rm EO}/(\rho_{\rm EO}N_{\rm A}) = 75$ Å³, $\rho_{\rm EO}$ = 1.01 g/cm³. Using the appropriate values of *R* and *N* at a given temperature, $n_{\rm EO}$ can be shown to increase from 48 to 64 as the temperature increases from 41 to 73 °C. These numbers must be taken as suggestive rather than absolute because of the likelihood of the presence of some D₂O in the core, especially at lower temperatures.

Effect of (CO₃)^{2–} Ions. SANS data of 5 wt % F88 in D₂O at different concentrations of K₂CO₃ at 26 °C are presented in Figure 2. The fitted parameters for the SANS profiles of F88 copolymer in K₂CO₃ solutions are also given in Table 1. The values of *R*, *N*, and ϕ increase considerably with salt concentration, but *R*_g and *R*_{hs} do not change significantly. The aggregation number varies from 6 at 0.1 M K₂CO₃ to 34 at 0.5 M K₂CO₃. Analogous to cmt and cmc for the phenomena of micelle formation, we propose a critical micelle salt concentration (cmsc) as the salt concentration at which the micelles begin to form. On the basis of the small aggregation number of 6 at 0.1 M K₂CO₃ and the absence of micelles in pure



Figure 3. SANS data of 5 wt % $P(EO)_{103}P(PO)_{39}P(EO)_{103}$ in 0.1 M K₂CO₃ electrolyte solution at different temperatures.

F88 solution at 26 °C, we propose that the cmsc for a 5 wt % F88 solution is close to 0.1 M K_2CO_3 . The cmsc's for the monovalent and many divalent ions are much larger than that for K_2CO_3 .

On the basis of a reasonable assumption that both PO and EO monomers in the micelle cores have the same volume as those in the dry PPO and PEO, the number of dehydrated EO monomers of a PEO block can be calculated for different concentrations using eq 14. For 0.3 M K₂CO₃, $n_{\rm EO} \approx 40$, and for 0.5 M K₂CO₃, $n_{\rm EO} \approx$ 94. That is, in the 0.3 M K₂CO₃ solution, there are 40 out of 206 EO monomers are dehydrated and become part of the micelle core. At 0.5 M concentration, the number of dehydrated EO monomers increases to 94, which is nearly half of the EO units becoming hydrophobic. Within the proposed model it would be difficult to calculate the amount of anions within the core and the corona. Hence, the above calculation does not include the anions, which are nonetheless present. Thus, the numbers quoted for the EO units in the core are probably an overestimation, which means that the number of EO units left in the corona should be larger than that calculated using the values obtained for the core. The discussion about the partial dehydration of PEO blocks is supported by other evidence as discussed below and also consistent with the picture that the growth of a micelle core is due to both fully dehydrated PPO blocks and partially dehydrated PEO blocks.^{5,9,10,22} Another interesting feature to be noted in Figure 2 is the data corresponding to a turbid solution in the presence of 0.7 M K₂CO₃ which exhibits a broad peak near Q = 0.049 Å⁻¹ but no coherent scattering in the low Q region. As described so far, the effects of temperature and the carbonate anion concentration at ambient temperature on the micellization and phase separation of copolymers in aqueous solution are qualitatively similar. It is thus possible to reach different regions of the phase map by varying either the temperature and/ or the concentration of K₂CO₃. The cmt and the CP will be much reduced depending on the salt concentration in solution and is similar to the behavior of CP in L64/ water²⁸ in the presence of SO_4^{2-} . Hence, it would be interesting to investigate the micellization and phase separation of F88 as a function of both the temperature and the concentration of K₂CO₃.

SANS data of 5 wt % F88 in D_2O at 0.1 M K_2CO_3 at different temperatures are shown in Figure 3. The coherent scattering intensity in the low Q region and



Figure 4. Modified Guinier plot for the rodlike particles of SANS data for F88/0.1 M K_2CO_3 solution at 73 °C.

the peak intensity monotonically increase with temperature up to 53 °C which reflects the increase in the aggregation number of copolymers (Table 1). However, in electrolyte solutions, both R and N increase much faster with temperature than in copolymer solution without salt. While scattering data retain the features of spherical micelles in copolymer/pure D₂O solution up to 73 °C (Figure 1), the scattering profile of the polymer near 60 °C in 0.1 M K₂CO₃ solution (Figure 3) clearly deviates from that of a spherical micelle. At these conditions the peak disappears, and the scattering intensity in the low Q region starts to increase, implying the beginning of aggregation of spherical micelles. At 73 °C, the scattering intensity in the low Q region exhibits a power law of Q^{-1} , and this can be interpreted to be due to the to the formation of rodlike particles. Schillen and co-workers¹⁶ have observed rodlike structures in P85/water system under similar temperature conditions. To further confirm the presence of rodlike micelles, we have carried out modified Guinier analysis for rodlike particles on the data at higher temperatures. A typical example of the modified Guinier plot of the data for F88 in 0.1 M K₂CO₃ solution at 73 °C is shown in Figure 4. The presence of a linear region with a negative slope is a clear indication of the presence of rodlike particles. However, the particles are strongly interacting as evidenced by the bend over in the low Q^2 region. The linear fit to the data in a Q^2 region where $Q_{\rm max}R_{\rm c} \leq 1.0$ provides a slope from which the crosssectional radius of gyration, $R_{\rm c}$, can be determined by using $R_c = (2 \cdot \text{slope})^{1/2}$. The radius of the rodlike micelles $is\sqrt{2}R_{c}$. The analysis of the data corresponding to rodlike micelles yielded an apparent radius of 40.9 ± 0.4 Å. It is well-known that in the presence of interaction only an apparent cross-sectional radius can be obtained by using Guinier analysis. The true dimensions of the rodlike micelles can be obtained only by using analytical expressions for the form factor and the structure factor for rodlike particles. At present, to our knowledge, there are no analytical expressions available for the structure factor for interacting rodlike particles. Given that we do not have the true radius of the rod, we only demonstrate the occurrence of the transformation from spherical to rodlike particles and refrain from discussing the organization of copolymers in those micelles.

Figures 5 and 6 present SANS data for the copolymer solutions containing 0.3 and 0.5 M K_2CO_3 as a function of temperature, respectively. It can be seen from Figure



Figure 5. SANS data of 5 wt % P(EO)₁₀₃P(PO)₃₉P(EO)₁₀₃ in 0.3 M K₂CO₃ electrolyte solution at different temperatures.



Figure 6. SANS data of 5 wt % P(EO)₁₀₃P(PO)₃₉P(EO)₁₀₃ in 0.5 M K₂CO₃ electrolyte solution at different temperatures.

5 that the coherent scattering signals for 0.3 M K₂CO₃ vary significantly with temperature when compared to that for 0.1 M K₂CO₃ (Figure 3). As expected, the micellization and transformation to rodlike particles occur at lower temperatures than that for lower salt concentrations. As discussed earlier, micelles exist even at 26 °C, and their aggregation number increases with increasing temperature up to 41 °C (Table 1). At 52 °C the peak disappears due to the onset of aggregation of micelles, and at 60 °C rodlike micelles are formed. At 73 °C the coherent scattering in the low *Q* region disappears, and a small broad peak is seen at *Q* = 0.049 Å⁻¹.

The rodlike micelles in 0.5 M K₂CO₃ solution are seen even at 42 °C (Figure 6). At 52 °C, the solution has already phase separated, and a clear gel is seen in the liquid. Neutron scattering from the solution with the gel exhibits a strong scattering peak at Q = 0.049 Å⁻¹, and the peak becomes stronger at higher temperatures. It is interesting to note that at this salt concentration the scattering in the low Q region at higher temperatures (>52 °C) seems to increase when compared to a flat scattering at 0.3 M K₂CO₃ (Figure 5). The occurrence of a peak indicates the formation of an ordered phase with a repeat distance of approximately 130 Å. The fact that the peak positions are at roughly the same Q value at various salt concentrations suggests the similarity of structure after phase separation. If we assume that the R_g of the polymer chains in the D₂Orich region remains the same as before, the contribution of the still hydrated EO units to the repeat distance would be in the range 65–80 Å. That would imply that the dehydrated portion of the copolymer consisting of both PO and EO would have a size between 50 and 65 Å, which is consistent with the parameters obtained at lower temperatures. At present we are not sure about the structure in the ordered phase. We plan to carry out synchrotron small-angle X-ray diffraction studies on the gels formed at different conditions which will be reported later.

The R_{g} of PEO homopolymer in a multivalent salt solution increases with salt concentration prior to the formation of biphase.²⁶ However, the R_g of the PEO blocks in the corona in all cases considered are nearly independent of both temperature and salt concentration. These contradicting features can be reconciled by our hypothesis that the size reduction expected from the gradual assimilation of some of the EO units into the core is compensated by a conformational change of PEO chains in the corona to become extended with increasing temperature and/or carbonate anions. By such a mechanism the $R_{\rm g}$ values of the PEO segments in the corona are conserved. One may argue that at higher temperatures it may not be correct to treat the PEO chains in the corona as Gaussian chains in eq 8 while modeling the SANS data from the micelles. However, we like to point out that the variation expected in the SANS signal for the micelles at Q > 0.05 Å⁻¹ from such conformational changes of PEO units in the corona is quite small, and that may be the reason for its less sensitivity in the fitting procedure. We believe that the uncertainties for all the parameters, except R_{g} , in Table 1 are correct. Given the uncertainty in the conformational distribution for PEO segments at different temperatures and carbonate concentrations, the uncertainty in the $R_{\rm g}$ determination may be slightly larger than that given in Table 1. We like to point out that using a form factor for the extended chains will increase the number of variables in the fitting procedure. Hence, the measured R_{g} values at higher temperatures and high carbonate ion concentrations for the PEO chains in the corona should be treated as approximate values. The chains in the corona can be considered as polymer coils grafted to a spherical surface, and the radius of gyration of these chains increases with an increase in the surface density of the chains due to the effect of excluded volume.³¹ Using the data for the no salt case in Table 1, it can be seen that the surface density ($\sim N/4\pi R^2$) does increase from 0.001 47/Å² at 41 °C to 0.001 77/Å² at 73 °C, imparting credibility to our hypothesis.

Conclusions

We have investigated the phenomena of micellization and phase separation of F88 in electrolyte solutions as functions of concentration of carbonate anions and temperature. Our studies show that multivalent salts like carbonates are much more effective in promoting micellization of triblock copolymer, $P(EO)_{103}P(PO)_{39}P(EO)_{103}$, than the monovalent salts such as KCl and KBr. At relatively low salt concentrations (or temperature), a small number of triblock copolymers start to aggregate due to the hydrophobicity of PPO blocks at ambient temperature. With the increase in carbonate concentration (or temperature), more PO monomers become hydrophobic, leading to the formation of spherical

micelles. The mechanism of the phase separation of F88 in aqueous solutions can now be outlined. We propose that first the spherical micelles form whose aggregation number increases with either increase in temperature or the concentration of carbonate anions. The transition from spherical to cylindrical micelles occurs when the size of a micelle becomes comparable to the hard sphere resulting from the dehydration of PEO blocks in the corona. When nearly all the PEO blocks are dehydrated, phase separation of the copolymers from the solution occurs. The temperature at which the phase separation occurs decreases with increasing carbonate anion concentration. From the application point of view of F88 the fascinating result is the ease of tunability of the system to attain different structural regions of the phase map by simply varying the temperature and/or carbonate concentration.

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