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# Effect of SDS on the Self-Assembly Behavior of the PEO–PPO–PEO Triblock Copolymer (EO)<sub>20</sub>(PO)<sub>70</sub>(EO)<sub>20</sub>

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The mixed micellar system comprising the poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide)-based triblock copolymer (EO)<sub>20</sub>(PO)<sub>70</sub>(EO)<sub>20</sub> (P123) and the anionic surfactant sodium dodecyl sulfate (SDS) has been investigated in aqueous media by small-angle neutron scattering (SANS) and viscosity measurements. The aggregation number of the copolymer in the micelles decreases upon addition of SDS, but a simultaneous enhancement in the degree of micellar hydration leads to a significant increase in the micellar volume fraction at a fixed copolymer concentration. This enhancement in the micellar hydration leads to a marked increase in the stability of the micellar gel phase until it is destroyed at very high SDS concentration. Mixed micellar systems with low and intermediate SDS concentrations form the micellar gel phase in much wider temperature and copolymer concentration ranges than the pure copolymer micellar solution. A comparison of the observed results with those for the copolymers (EO)<sub>26</sub>(PO)<sub>40</sub>(EO)<sub>26</sub> (P85) and (EO)<sub>99</sub>(PO)<sub>70</sub>(EO)<sub>99</sub> (F127) suggests that the composition of the copolymers plays a significant role in determining the influence of SDS on the gelation characteristics of the aqueous copolymer solutions. Copolymers with high PO/EO ratios show an enhancement in the stability of the gel phase, whereas copolymers with low PO/EO ratios show a deterioration of the same in the presence of SDS.

## Introduction

The self-assembly behaviors of poly(ethylene oxide) (PEO)–poly(propylene oxide) (PPO)–poly(ethylene oxide) (PEO)-based triblock copolymers have been studied quite extensively in view of their rich structural polymorphism and numerous applications in various industries.<sup>1–14</sup> The amphiphilic character of these copolymers arises from a difference in the hydrophobicities of the PEO and PPO blocks in polar and nonpolar solvents. In aqueous media, both of these blocks remain hydrated below a characteristic temperature of these triblock copolymers, called the critical micellar temperature (CMT). A dramatic decrease in the solubility of the PPO block at the CMT leads to the formation of micelles comprising PPO blocks as the core and hydrated PEO blocks as the corona.<sup>15</sup> The CMTs of these triblock copolymers are concentration-dependent and decrease with increasing copolymer concentration.<sup>16–18</sup> Above the CMT, an increase in temperature weakens the hydrogen bonding between the PEO chains and water and leads to a progressive dehydration of the PEO chains. At the cloud point (CP), the PEO chains become insoluble, and the copolymer and water phase separate. At high concentrations, these copolymers can form a number of lyotropic liquid-crystalline phases with cubic, hexagonal, or lamellar structures. For certain copolymers, the volume fraction of the spherical micelles in the copolymer solutions reaches the critical value for hard-sphere crystallization (53%)<sup>19–24</sup> at the critical gelation concentration (cgc), and stiff isotropic gels with a significant yield stresses are formed.<sup>19–29</sup> These gels are stable in a temperature range between their lower and upper melting points known as  $T_1$  and  $T_2$ , respectively ( $T_2$

$> T_1$ ).<sup>19–23</sup>  $T_1$  is defined as the temperature at which the volume fraction of the micelles becomes sufficiently high that micellar close packing or entanglement leads to the formation of a gel.  $T_2$  is not a simple function of the micellar volume fraction, and its origin is not yet clearly understood. In some cases, it coincides with a sphere-to-rod transition of the micelles, and it has been argued that such a micellar structural transition is the driving force for melting of the gel at  $T_2$ .<sup>19</sup> Interestingly, because of a large degree of hydration in the corona region of these copolymer micelles, aqueous solutions of these copolymers form micellar gels at copolymer volume fractions much lower than 53%.<sup>19–23</sup> An increase in the degree of hydration of the copolymer with increasing PEO chain weight fraction leads to a decrease in the critical gelation concentration (cgc).<sup>2</sup> Small-angle neutron scattering (SANS) and small-angle X-ray scattering (SAXS) studies suggest that these phases are formed as a result of the crystallization of the spherical micelles<sup>19–23</sup> or an entanglement of the deformed micelles at their limiting micellar volume fractions.<sup>30–33</sup>

In many applications, these block copolymers are used in combination with ionic surfactants such as SDS, CTAB (cetyl trimethyl ammonium bromide), etc. Detailed studies on the ionic surfactant–block copolymer mixed system in aqueous media show that, depending on their concentrations and temperature, interactions between them lead to the formation of either mixed micelles or different kinds of mixed aggregates.<sup>34–57</sup> At copolymer concentrations above the CMC, SDS–copolymer mixed micelles are formed, and the aggregation number of the copolymer decreases steadily with increasing SDS concentration.<sup>43–47</sup> At very high SDS concentrations, the micelles are destroyed, and the freed copolymer unimers form aggregates with the SDS micelles.<sup>44</sup> Copolymers with high PO/EO ratios [e.g., P123, (EO)<sub>20</sub>(PO)<sub>70</sub>(EO)<sub>20</sub>] show a significantly higher stability of the micelles against addition of SDS than copolymers

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with low PO/EO ratios [e.g., F127 (EO)<sub>99</sub>(PO)<sub>70</sub>(EO)<sub>99</sub>].<sup>40</sup> A study on the influence of SDS on the micellar gel phase formed by aqueous solutions of the copolymer F127 showed that the temperature and the concentration range of the stability of the gel phase are progressively reduced upon addition of SDS, leading ultimately to their complete destruction at high SDS concentration.<sup>43,55</sup> To the best of our knowledge, however, no studies have been reported that have examined the influence of SDS on the gelation characteristics of copolymers with high PO/EO ratios. Herein, we report SANS and viscosity studies on the triblock copolymer P123 [(EO)<sub>20</sub>(PO)<sub>70</sub>(EO)<sub>20</sub>] and SDS mixed surfactant system in aqueous media. The evolution of the structure and the degree of hydration of the copolymer micelles as a function of SDS concentration and their impact on the formation characteristics of the micellar gel phase have been studied. To understand the effect of copolymer composition on the influence of SDS, a comparative study of the gelation characteristics of another copolymer with a lower PO/EO ratio [P85, (EO)<sub>26</sub>(PO)<sub>40</sub>(EO)<sub>26</sub>] has also been carried out.

### Experimental Section

The triblock copolymers (EO)<sub>20</sub>(PO)<sub>70</sub>(EO)<sub>20</sub> (P123) and (EO)<sub>26</sub>(PO)<sub>40</sub>(EO)<sub>26</sub> (P85) were obtained from Aldrich and BASF, respectively. SDS was purchased from Sisco Research Laboratories, Mumbai, India; D<sub>2</sub>O was obtained from Heavy Water Division, Bhabha Atomic Research Center, Mumbai, India; and deuterated SDS was purchased from Cambridge Isotopes Laboratories. The copolymer solutions were prepared by weighing the required amounts of solvents, copolymer, and SDS (when needed) and keeping the mixtures in the refrigerator in tightly closed glass stoppered vials for 1 week. For solutions with high copolymer concentrations, the solutions were kept in the freezer for 1–2 days, and during this period, frequent intermittent stirrings for ~1–2 min were carried out to give well-equilibrated homogeneous solutions. The solutions were kept in the refrigerator because the rate of solubilization of these copolymers in water is enhanced quite significantly as the solution temperature decreases below room temperature. After solubilization, the samples were stored 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.<sup>43</sup> The results reported here are accurate to within  $\pm 0.5$  °C. The room-temperature (25 °C) relative viscosities of the solutions were measured using calibrated Cannon Ubbelohde viscometers.<sup>58</sup> The measured flow times of the solution were multiplied by the viscometer constant of the viscometers to obtain the absolute viscosities of the solutions. The relative viscosities ( $\eta_r$ ) were calculated by dividing the absolute viscosities of the solutions by the viscosity of water. The flow times were kept greater than 200 s to avoid the necessity of kinetic energy corrections.

SANS measurements were carried out on the samples prepared in D<sub>2</sub>O at the SANS facility at the DHRUVA reactor, Trombay, India.<sup>59</sup> The use of D<sub>2</sub>O as a solvent instead of H<sub>2</sub>O gives high contrast in the neutron scattering experiments. The incident wavelength was 5.2 Å with  $\Delta\lambda/\lambda = 15\%$ . The scattering intensity was measured in the scattering vector ( $q$ ) range of 0.02–0.3 Å<sup>-1</sup>. The measured SANS data were corrected for the background, the empty cell contributions, and the transmission and were converted to an absolute scale using standard protocols.<sup>59</sup> Correction due to the instrumental smearing was taken into account throughout the data analysis.

The differential scattering cross section per unit volume ( $d\Sigma/d\Omega$ ) for monodisperse micelles can be written as

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

where  $N$  is the number density of the micelles and  $B$  is a constant term that represents the background incoherent scattering, coming mainly from the hydrogen molecules present in the sample.  $F_{\text{mic}}(q)$  is the form factor characteristic of 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 a spherical core–shell particle with different scattering length densities of the core and the shell. The structure of these micelles is described by following model proposed by Pedersen and Gerstenberg.<sup>60</sup> The form factor,  $F_{\text{mic}}(q)$ , of the micelles according to this model can be defined as

$$F_{\text{mic}}(q) = N_{\text{agg}}^2 b_s^2 F_s(q, R) + 2N_{\text{agg}} b_c^2 F_c(q, R_g) + 2N_{\text{agg}} (2N_{\text{agg}} - 1) b_c^2 S_{\text{cc}}(q) + 4N_{\text{agg}}^2 b_s b_c S_{\text{sc}}(q) \quad (2)$$

where  $b_s$  and  $b_c$  are the excess scattering lengths of the core and chain, respectively, and  $N_{\text{agg}}$  is the aggregation number of the micelles.

$F_{\text{mic}}(q)$  comprises four parts: two self-correlation terms for the spherical core and Gaussian chains in the corona and two cross-correlation terms. The cross-correlation terms define the correlation between core and chain and the correlation between different chains in the corona. To describe the core radius ( $R_c$ ) we used a form factor for monodisperse spheres as<sup>61</sup>

$$F_s(q) = \{3[\sin(qR_c) - qR_c \cos(qR_c)]/(qR_c)^3\}^2 \quad (3)$$

For the Gaussian chains in the corona with a radius of gyration ( $R_g$ ), the form factor is defined as<sup>62</sup>

$$F_c(q, R_g) = 2(e^{-z} - 1 + z)/z^2 \quad (4)$$

where  $z = q^2 R_g^2$ .

The core–chain interference term  $S_{\text{sc}}$  is given by<sup>60</sup>

$$S_{\text{sc}} = [F_s(q)]^{1/2} \Psi(q, R_g) \sin(qR)/qR \quad (5)$$

The function  $\Psi(q, R_g)$  is the form factor amplitude of the chain

$$\Psi(q, R_g) = z^{-1}(1 - e^{-z}) \quad (6)$$

Finally, the chain–chain interference term  $S_{\text{cc}}$  is given by

$$S_{\text{cc}} = \Psi(q, R_g)^2 [\sin(qR)/qR]^2 \quad (7)$$

The interparticle interaction was captured from the analytical solution of the Ornstein–Zernike equation in the Percus–Yevick approximation, employing a hard-sphere potential.<sup>63</sup> Its analytical form is

$$S(q) = 1/[1 + 24\phi G(x, \phi)/x] \quad (8)$$

where  $x = 2qR_{\text{hs}}$ ,  $R_{\text{hs}}$  is the hard-sphere interaction radius,  $\phi$  is the volume fraction, and

$$G(x, \phi) = (\alpha/x^2)(\sin x - x \cos x) + (\beta/x^3)[2x \sin x + (2 - x^2) \cos x - 2] + (\gamma/x^5)\{-x^4 \cos x + 4[(3x^2 - 6) \cos x + (x^3 - 6x) \sin x + 6]\} \quad (9)$$

The functions  $\alpha$ ,  $\beta$ , and  $\gamma$  are

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

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

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

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

$$d\Sigma/d\Omega = \int d\Sigma/d\Omega(q, R) f(R) dR + B \quad (10)$$

The polydispersity in the micellar size ( $R = R_c$ ) has been taken into account by a Schultz distribution as given by the equation

$$f(R) = [(Z + 1)/R_{cm}]^{Z+1} R_c^Z \times \exp[-(Z + 1)/R_{cm})R_c][1/\Gamma(Z + 1)] \quad (11)$$

where  $R_{cm}$  is the mean value of the distribution,  $Z$  is the width parameter, and  $\Gamma$  is the mathematical gamma function. The polydispersity of this distribution is given by  $\Delta R_c/R_{cm} = 1/(Z + 1)^{1/2}$ .

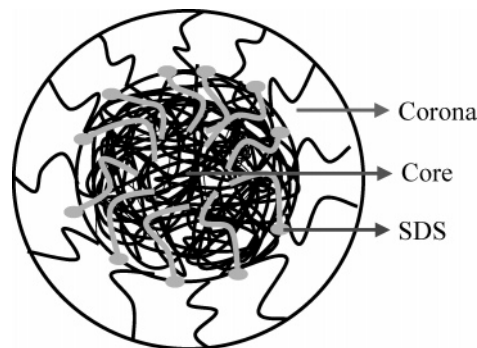
For analysis of the structure of the mixed micelles, it is assumed that the SDS molecules are dissolved in the micellar core. This assumption was made on the basis of a report that the interaction between the SDS and the PPO units is significantly stronger than that between the SDS and PEO units<sup>54</sup> and our contrast variation study, discussed in the following section. A schematic representation of the mixed micelles is shown in Figure 1. The values of  $R_c$ ,  $R_g$ ,  $R_{hs}$ ,  $\phi$ , and  $Z$  are used as variables in the fit. These parameters in the analysis were optimized by means of a nonlinear least-squares fitting program in Fortran.<sup>64</sup>

## Results and Discussion

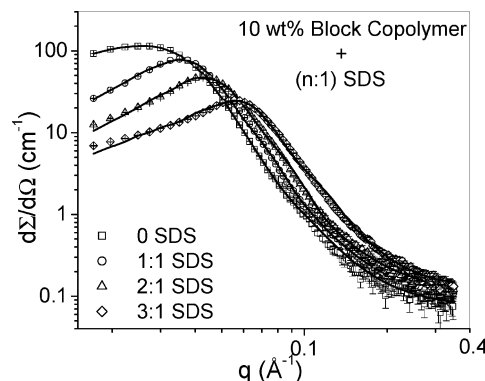
Figure 2 shows the SANS data obtained for 10% P123 solutions with varying SDS concentrations. All of the data were recorded at 30 °C, and the concentration of SDS is expressed as its molar ratio to that of the copolymer. It is observed that an increase in the SDS concentration results in a large decrease in the scattering cross section and a shifting of the peak position to higher  $q$  values. To understand the nature of the mixed surfactant system, contrast variation SANS patterns were recorded for the mixed solutions using deuterated SDS ( $d$ -SDS) as the surfactant. The SANS data of the block copolymer–surfactant mixtures with protonated SDS and  $d$ -SDS are shown in Figure 3. It shows that, at a fixed SDS concentration, the peak positions of the samples containing  $d$ -SDS and SDS are the same but the overall scattering intensities are significantly less in the case of the  $d$ -SDS-containing samples. The data for deuterated and protonated SDS can, in fact, be scaled to each other (inset of Figure 3; scaling factors of 1.32, 1.44, and 1.95 for the 1:1, 2:1, and 5:1, SDS concentrations, respectively), suggesting that the SDS–block copolymer interaction leads to the formation of mixed micelles. The compositions of the mixed micelles were calculated using the formula

$$\xi = [R(\rho_{dSDS} - \rho_{D_2O}) + (\rho_{D_2O} - \rho_{hSDS})]/[(\rho_{BC} - \rho_{hSDS}) - R(\rho_{BC} - \rho_{dSDS})]$$

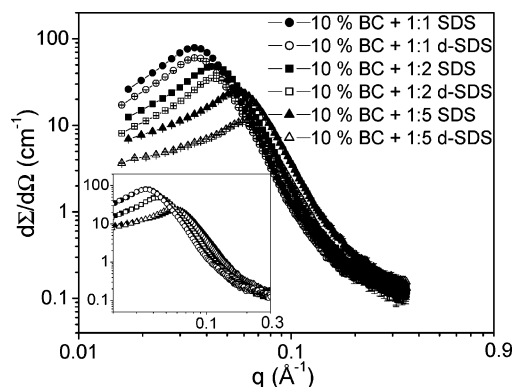
where  $\xi$  is the volume fraction of the block copolymer in the mixed micelles and  $R$  is  $(I_1/I_2)^{1/2}$ .  $I_1$  is the scattering intensity with hydrogenous SDS in the system, and  $I_2$  is the intensity with deuterated SDS for the same composition.<sup>47</sup>  $\rho_{dSDS}$ ,  $\rho_{hSDS}$ ,  $\rho_{D_2O}$ , and  $\rho_{BC}$  are the scattering length densities of the deuterated SDS, hydrogenous SDS, D<sub>2</sub>O, and block copolymer, respectively. The values of the volume fraction of the copolymer in the mixed micelles derived using this formula are 0.89, 0.86, and 0.77 for the 1:1, 2:1 and 5:1 SDS concentrations, respec-



**Figure 1.** Schematic representation of SDS–copolymer mixed micelle formation.



**Figure 2.** SANS data for 10% (EO)<sub>20</sub>(PO)<sub>70</sub>(EO)<sub>20</sub> solutions with different SDS concentrations recorded at 30 °C. The solid lines are fit to the data using a model for interacting hard-sphere colloids.



**Figure 3.** Contrast variation SANS data for 10% (EO)<sub>20</sub>(PO)<sub>70</sub>(EO)<sub>20</sub> solutions recorded at 30 °C. The inset shows the scaling of the data of the  $d$ -SDS-containing samples to those of SDS-containing samples. The scaling of the two data sets was used to calculate the composition of the block copolymer in the mixed micellar system.

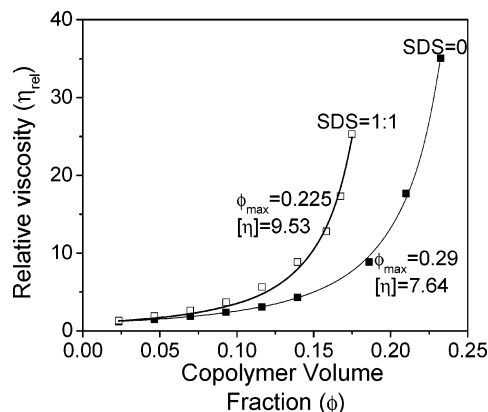
tively. On the other hand, the calculated values of the volume fractions of copolymer for mixed micellar solutions of these compositions are 0.95, 0.92, and 0.83, respectively. The volume fraction values obtained from the SANS data are thus smaller than the calculated values. These results are similar to those reported for F127<sup>47</sup> and could arise because of the presence of copolymer unimers in equilibrium with the mixed micelles.

The micellar parameters obtained from the fit to the data for 10% copolymer solutions with varying SDS concentrations (Figure 2) are summarized in Table 1. The core radius ( $R_c$ ) and the hard-sphere radius ( $R_{hs}$ ) decrease progressively with increasing SDS concentrations, and up to 1:1 SDS, the amount of decrease in  $R_c$  is significantly more than that in  $R_{hs}$ . Addition of SDS does not influence the value of  $R_g$  significantly, and it remains in the range  $1.2 \pm 0.2$  nm. It has been reported in the



**TABLE 1: Core Radius ( $R_c$ ), Hard-sphere Radius ( $R_{hs}$ ), Aggregation Number ( $N_{agg}$ ), Volume Fraction ( $\phi$ ), and Polydispersity ( $\Delta R_c/R_{cm}$ ) of the Micelles in 10% Block Copolymer (EO)<sub>20</sub>(PO)<sub>70</sub>(EO)<sub>20</sub> Solutions with Different SDS Concentrations**

SDS conc (mol/mol BC)	core radius ( $R_c$ ) (nm)	aggregation number ( $N_{agg}$ )	hard-sphere radius ( $R_{hs}$ ) (nm)	volume fraction ( $\phi$ )	polydispersity $\Delta R_c/R_{cm}$ (%)	shell thickness (nm)
0	4.79 $\pm$ 0.02	69 $\pm$ 1	9.41 $\pm$ 0.05	0.193 $\pm$ 0.003	27 $\pm$ 0.5	4.62
1:1	3.69 $\pm$ 0.03	30 $\pm$ 1	8.84 $\pm$ 0.03	0.312 $\pm$ 0.006	30 $\pm$ 1.1	5.15
2:1	3.21 $\pm$ 0.04	19 $\pm$ 1	7.17 $\pm$ 0.04	0.294 $\pm$ 0.008	25 $\pm$ 0.8	3.96
5:1	1.89 $\pm$ 0.03	4 $\pm$ 0.2	5.20 $\pm$ 0.10	0.272 $\pm$ 0.012	43 $\pm$ 1.2	3.31

**Figure 4.** Relative viscosity ( $\eta_r$ ) vs (EO)<sub>20</sub>(PO)<sub>70</sub>(EO)<sub>20</sub> volume fraction measured at room temperature (25 °C).

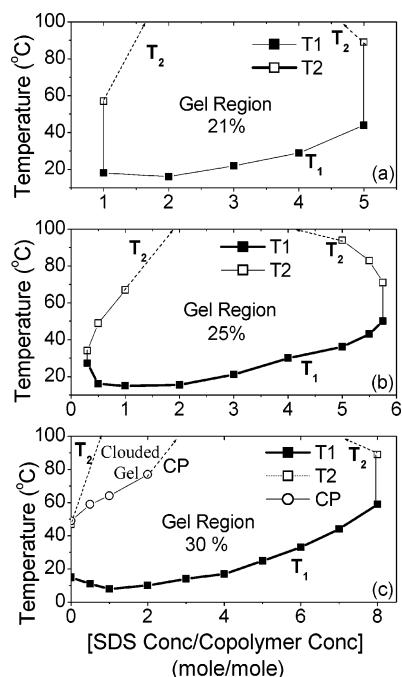
literature that, in the case of aqueous solutions of F88 [(EO)<sub>103</sub>-(PO)<sub>39</sub>(EO)<sub>103</sub>], the value of  $R_g$  remains similarly unaffected even when there is a large change in the values of  $R_c$  and  $R_{hs}$  with changing temperature.<sup>65</sup> The difference between the values of  $R_c$  and  $R_{hs}$ , which represents the shell thickness, increases upon addition of 1:1 SDS (Table 1). This suggests that the PEO chains are stretched in the corona region of the micelles in the presence anionic detergent molecules. As shown in Table 1, this increase in the shell thickness gives rise to a significant increase in the volume fraction of the micelles, even though the copolymer concentration remains fixed at 10%. The fact that the observed increase in the micellar volume fraction is much greater than the contribution coming from the added SDS suggests that the degree of hydration of the micelles increases quite significantly in the presence of 1:1 SDS. It is also evident from Table 1 that, although the micellar volume fraction first increases upon addition of SDS, it decreases with a subsequent increase in the SDS concentration because of a decrease in the shell thickness. A higher rate of decrease of  $R_{hs}$  as compared to that of  $R_c$  leads to the observed decrease in the shell thickness.

The changes in the volume fraction of the micelles upon addition of SDS are further evident from the changes in the relative viscosity ( $\eta_r$ ) of the copolymer solutions. The room-temperature (25 °C)  $\eta_r$  values of the solutions containing 1:1 and no SDS are shown in Figure 4 as a function of dry copolymer volume fraction. The dry copolymer volume fraction values were calculated using the specific volume of the copolymer as 0.93.<sup>66</sup> Both in the absence and in the presence of SDS, the viscosity increases first slowly at low polymer concentration and then in a more pronounced way at higher copolymer concentrations. The behavior is similar to those reported by Zhou et al. for aqueous solutions of the triblock copolymers L64 [(EO)<sub>13</sub>(PO)<sub>30</sub>(EO)<sub>13</sub>] and P105 [(EO)<sub>37</sub>(PO)<sub>58</sub>-(EO)<sub>37</sub>].<sup>67</sup> They showed that copolymer P105, with a larger PEO chain and a higher degree of micellar hydration, shows divergence in viscosity at a lower copolymer volume fraction than copolymer L64.<sup>67</sup>

The plots in Figure 4 show that the addition of SDS results in a significant increase in the relative viscosity and the effect

is 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  $\phi$  is the hard-sphere volume fraction,  $\phi_{max}$  is its limiting value at which the viscosity diverges, and  $[\eta]$  is the intrinsic viscosity.<sup>68,69</sup> The particles in the colloidal hard-sphere dispersions have an infinitely repulsive potential at distances up to a single-particle diameter from the center of the particles but zero potential at larger distances.<sup>70,71</sup> At sufficiently large volume fractions ( $\phi_{max}$ ), these dispersions lock into a rigid crystalline or noncrystalline structure and show a divergence in the viscosity.<sup>70,71</sup> In absence of any attractive potential, the formation of the gel state in these systems is considered as an disorder-to-order transition driven by entropy.<sup>70,71</sup> In the case of pluronic solutions, the limiting volume fraction of the hydrated polymers is  $\phi_{max} = 0.53$ , as, at this limiting volume fraction, they form isotropic gel phases.<sup>19–23,30–32</sup> Because of the high degree of hydration in the corona region of the micelles, these copolymer solutions form the gel phase at dry copolymer volume fractions much lower than 0.53. Figure 4 indicate that, in the presence of the 1:1 SDS-to-block copolymer ratio, the divergence in viscosity of the copolymer solution should occur at lower copolymer concentration than in the case of pure copolymer solutions. Fitting of the viscosity data shown in Figure 4 based on the above-mentioned equation shows that, upon addition of 1:1 SDS, the  $\phi_{max}$  value decreases significantly from 0.29 to 0.225. As discussed in the next section, the formation of a cubic gel is indeed extended to a lower copolymer concentration in the presence of SDS. The enhancement of micellar hydration in the presence of SDS is also reflected in an increase in the intrinsic viscosity  $[\eta]$  of the copolymer solutions from 7.74 to 9.53 upon addition of 1:1 SDS. Both of these values are much higher than the Einstein value of 2.5 for hard-sphere dispersions in solutions. 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 1:1 SDS.

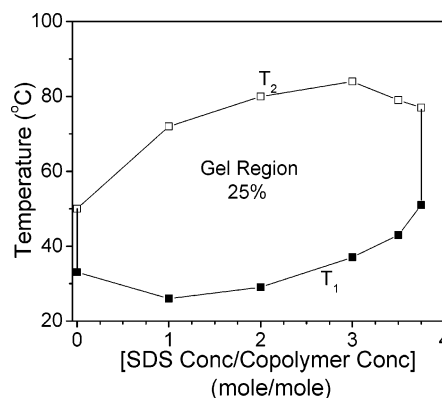
The changes in the degree of hydration of the micelles with the addition of SDS are also reflected in the gel formation characteristics of the copolymer solutions (Figure 5). The isotropic nature of the gel was confirmed by the absence of any birefringence when observed through crossed polarizers under an optical microscope. The isotropic gels formed by these copolymer solutions in aqueous media have two melting temperatures,  $T_1$  and  $T_2$ . At the critical micellar temperature (CMT), the volume fraction of the micelles remains small, as only a fraction of the unimers form micelles. As more and more unimers are converted into micelles with increasing temperature above the CMT, the volume fraction increases progressively and becomes sufficiently high for a gel to form at  $T_1$ .<sup>19–23</sup> The value of  $T_1$  decreases with increasing copolymer concentration.<sup>28</sup> The melting of the gel at  $T_2$  could arise either because of progressive dehydration of the copolymer micelles with increasing temperature or because of their sphere-to-rod shape transition.<sup>19,72,73</sup>



**Figure 5.** Lower ( $T_1$ ) and upper ( $T_2$ ) melting temperature of the gels formed by 21%, 25%, and 30% block (EO)<sub>20</sub>(PO)<sub>70</sub>(EO)<sub>20</sub> solutions as a function of SDS concentration. The dotted line with the arrow indicates that the corresponding temperature becomes greater than 100 °C.

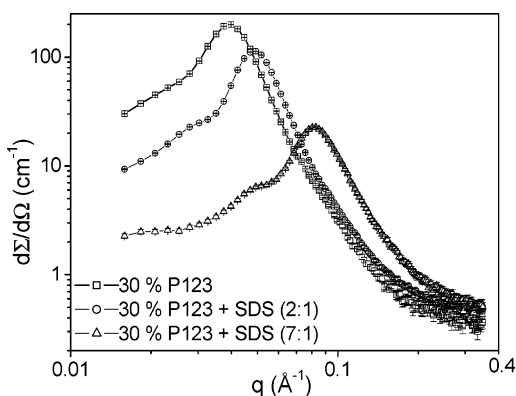
The effect of the addition of SDS on the isotropic gel phase formed by aqueous solutions of F127 [(EO)<sub>99</sub>(PO)<sub>70</sub>(EO)<sub>99</sub>] was studied systematically by Hetch et al.<sup>43</sup> and Ivanova et al.<sup>55</sup> It was observed that the temperature and concentration range of stability of the gel phase decrease with increasing SDS concentration, leading ultimately to its complete destruction at high SDS concentration.<sup>43,55</sup> It has been shown by SANS studies that the destruction of the gel phase occurs when the micellar volume fraction starts decreasing dramatically.<sup>43</sup> In view of this, attempts were made to understand whether the observed increase in the micellar volume fraction upon addition of SDS for P123 leads to any enhancement of the stability of the gel phase.

Figure 5a–c shows plots of the two melting temperatures (upper and lower) of the gel phase vs SDS concentrations, at 21%, 25% and 30% P123 concentrations, respectively. The 20% P123 solutions do not show any gelation in the presence of SDS. As shown in the figure, the stability of the gel is enhanced significantly upon addition of SDS. The 21% (Figure 5a) and 25% (Figure 5b) pure copolymer solutions do not show any gelation below their cloud points but form the gel phase in the presence of SDS at a wide range of temperature. The 30% copolymer solution is known to form the gel phase,<sup>3</sup> but in the presence of SDS, the temperature range of the stability of the gel increases quite markedly (Figure 5c). At a fixed copolymer concentration, the stability range first increases considerably with increasing SDS concentration but decreases at high SDS concentration, before the gel phase vanishes with further increases in the SDS concentration. The SDS concentration at which gel phase is destroyed increases with increasing copolymer concentration. Interestingly, for all three copolymer concentrations, the large enhancement in the temperature range of stability of the gel phase occurs because of a large increase in  $T_2$ . The decrease in  $T_1$  is much less prominent and occurs only at low SDS concentrations, after which there is systematic increase in  $T_1$  with increasing SDS concentration. The gelation temperature  $T_1$  is correlated with the CMT because an increase

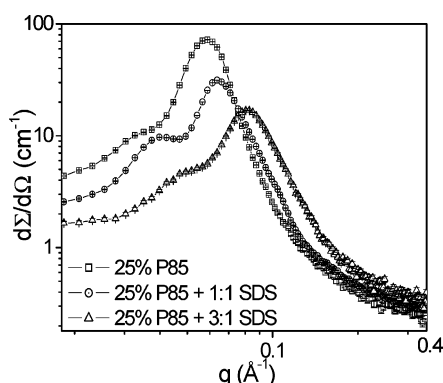


**Figure 6.** Lower ( $T_1$ ) and upper ( $T_2$ ) melting temperature of the gels formed by 25% (EO)<sub>26</sub>(PO)<sub>40</sub>(EO)<sub>26</sub> solutions as a function of SDS concentration.

in the micellar volume fraction with increasing temperature above the CMT leads to gelation. Any factor that modifies the CMT is thus likely to modify  $T_1$  in a similar fashion. At low concentration, SDS is known to reduce the CMT of aqueous solutions of F127, but at higher concentration, it leads to an increase in the CMT.<sup>46</sup> We suggest that an increase in the CMT with increasing SDS concentration at SDS concentrations above 1:1 leads to the observed increase in  $T_1$ . The difference in the observed effect of SDS on the gelation characteristics of P123 [(EO)<sub>20</sub>(PO)<sub>70</sub>(EO)<sub>20</sub>] compared to that reported for F127 [(EO)<sub>99</sub>(PO)<sub>70</sub>(EO)<sub>99</sub>] could arise from the difference in their ethylene oxide compositions. As is evident from the concentration dependence of the diffusion coefficients of the micelles measured by dynamic light scattering (DLS) studies, the value of the diffusion virial coefficient ( $k_0$ ) for F127 solutions ( $\sim 7.0$ ) is significantly higher than that for P123 solutions ( $\sim 3.0$ ).<sup>51,74</sup> This behavior arises because of a larger degree of hydration in the F127 micelles as compared to that in the P123 micelles. We suggest that, because the degree of micellar hydration is high in the pure F127 solutions, the addition of SDS does not lead to a further increase in it. Another factor that could contribute to the difference in behavior of the two copolymers is that copolymer P123 shows formation of micelles up to SDS/copolymer ratios as high as 30, whereas copolymer F127 shows suppression of the micellization process at SDS/copolymer ratios as low as 8.<sup>40</sup> The role of the block size ratio on the effect of SDS on the gelation characteristics of these copolymers is also evident from the behavior of P85 [(EO)<sub>26</sub>(PO)<sub>40</sub>(EO)<sub>26</sub>], which has a PO/EO block size ratio between those of P123 and F127. In aqueous media, P85 starts showing gelation at about 25% copolymer concentration, and as shown in the Figure 6, the influence of SDS on its gelation characteristics falls between those of P123 and F127. Unlike in the case of F127, there is an enhancement of the temperature range of stability of the gel phase for P85 upon addition of SDS, but the degree of enhancement and the maximum SDS concentration up to which the gel phase survives is significantly lower than that observed in the case of P123. Moreover, unlike in the case of P123, addition of SDS cannot induce gelation in P85 even at copolymer concentration of 23%, a concentration slightly lower than the 25% required for gelation in pure aqueous solutions. These results coupled with those reported for F127 suggest that the influence of SDS on the gelation characteristics of the aqueous copolymer is strongly dependent on the composition of the copolymer. Copolymers with low PO/EO ratios show a deterioration of the gelation characteristics, whereas those with high PO/EO ratios show an improvement in the gelation characteristics in the presence of SDS.



**Figure 7.** SANS data for 30% (EO)<sub>20</sub>(PO)<sub>70</sub>(EO)<sub>20</sub> solutions with different SDS concentrations recorded at 30 °C.



**Figure 8.** SANS data for 25% (EO)<sub>26</sub>(PO)<sub>40</sub>(EO)<sub>26</sub> solutions with different SDS concentrations recorded at 30 °C.

Results of SANS studies on aqueous solutions of P123 and P85 copolymers with varying SDS concentrations in the gel phase are shown in Figures 7 and 8, respectively. The data do not fit to the model employing spherical core-shell particles as was done in Figure 2 for the 10% concentration of P123 micelles. This observation is similar to that reported by Mortensen et al. on the gelation characteristics of F88 micelles<sup>20</sup> and suggests that a structural transition of the micelles is associated with the gelation process. Glatter et al.<sup>31</sup> reported that, in the case of aqueous solutions of P85, the spherical symmetric structure of the micelles becomes progressively distorted with increasing copolymer concentration on approaching gelation. The inability of the model to fit the data indicates that both the copolymer micelles lose spherical symmetry while forming the isotropic gel phase. In both cases, the addition of SDS leads to a shift in the position of the correlation peak to higher  $q$  values and a simultaneous decrease in the absolute scattered intensity. This suggests that, even though there is a distortion in the shape of the micellar aggregates in the gel phase, the effect of SDS on the gel phase is similar to that is observed at the 10% copolymer concentration (Figures 2 and 3). A decrease in micellar size and aggregation number, and correspondingly an increase number density of the micelles and a decrease in intermicellar distance, are thus expected to result in the gel phase upon addition of SDS. Table 2 shows that the intermicellar distances ( $d = 2\pi/q_{\text{max}}$ ) for both the P123 (Figure 6) and P85 (Figure 7) solutions decrease with increasing SDS concentrations.

## Conclusions

In conclusion, the effect of the addition of SDS to a triblock copolymer P123 aqueous solution has been studied by SANS

**TABLE 2: Interparticle Distances Calculated from Figures 6 and 7 for 30% P123 and 25% P85 Solutions with Varying SDS Concentrations**

sample composition	interparticle distance (nm)
30% P123, 0 SDS	15.8
30% P123, 2:1 SDS	12.76
30% P123, 7:1 SDS	7.73
25% P85, 0 SDS	10.69
25% P85, 1:1 SDS	9.99
25% P85, 3:1 SDS	7.76

and viscosity measurements. The triblock copolymer forms mixed micelles with SDS, and its aggregation number in the mixed micelles decreases with increasing SDS concentration. The volume fraction of the micelles, however, increases significantly in the presence of SDS because of an increase in the degree of hydration of the micelles in the corona region. It has been suggested that the increased hydration of the micelles is achieved by stretching of the EO blocks in the corona region in the presence of anionic SDS molecules. Quite interestingly, the enhancement in micellar volume fraction upon addition of SDS leads to a marked increase in the stability of the micellar gel phase. The gelation characteristics of P123 were compared with those of other two block copolymers P85 and F127. It was found that the effect of SDS on the micellar structure and on the formation characteristics of the micellar gel phase depends strongly on the composition of the copolymer.

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