Dominant Factors on the Micellization of $B_nE_mB_n$-Type Triblock Copolymers in Aqueous Solution

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The micellization parameters of a series of oxyethylene/oxybutylene ($B_nE_mB_n$) triblock copolymers ($B_4E_{40}B_4$, $B_5E_{39}B_5$, $B_5E_{91}B_5$, $B_6E_{46}B_6$, $B_7E_{22}B_7$, $B_7E_{40}B_7$, $B_{10}E_{271}B_{10}$, and $B_{12}E_{260}B_{12}$) were summarized to obtain collective conclusions on the dominant factors that affect the micellization of such sort of triblock copolymers in aqueous solution. The effects of the block lengths of both the hydrophobic end B blocks and the hydrophilic middle E block on the critical micellar concentrations, the association numbers, the second virial coefficients of micelles, the enthalpy of micellization, the hydrodynamic radius, and the intermicellar cross-linking are discussed. It was found that the micellization was mainly determined by the B block length while the micellar size and the intermicellar structure were influenced greatly by the E block length. The scaling theory that was derived from diblock copolymer micelle models can also be used in triblock copolymer miceller systems.

Introduction

The association behavior of oxyalkylene triblock copolymers in aqueous solution has been extensively reported during the past few years, especially for $E_nP_mE_n$, $P_nE_mP_n$ (Pluronic polymers), $E_nB_mE_n$, and $B_nE_mB_n$-type block copolymers, where E, P, and B represent, respectively, oxyethylene, oxypropylene, and oxybutylene units. An in-depth review of the physical chemistry of such block copolymers in aqueous solution, mainly focused on their micellization behavior, has appeared recently.[1] The closed association mechanism yields core−shell micelles for XYX-type triblock copolymers in solvents selective for the terminal X blocks. However, for YXY-type triblock copolymers in the same solvents selective for the middle X block, there are several possible self-assembly structures. First, flowerlike micelles can form if the central block takes on a loop conformation with the two end blocks becoming a part of the same micellar core.[2] Second, the assembly into a branched structure at low concentrations or a gellike network at high concentrations may occur because of the possible bridging function from the extended soluble middle block between the small clusters formed by the poorly solvated end blocks.[3] The intermediate situation will be that some of the coronal middle blocks show a looping geometry, while some other middle blocks may have one of the end blocks dangling in solution.[4,5]

In comparison with Pluronic block copolymers, the micellization of $B_nE_mB_n$-type block copolymers in aqueous solution is less reported, mainly owing to the limitation of available samples. Some of them were prepared by the University of Manchester[4] or the Dow Company.[6] Yang et al.[4] studied the association behavior of $B_4E_{40}B_4$, $B_5E_{39}B_5$, and $B_7E_{40}B_7$ in aqueous solution, while our group[7−9] reported the characterizations of $B_5E_{91}B_5$ and $B_{12}E_{260}B_{12}$. Because of the greater solubility difference between B and E blocks in water when compared with that of P and E blocks, $B_nE_mB_n$ triblock copolymers have a stronger ability to associate. Their association structures in dilute solution are basically close-associated flowerlike micelles, with some of the B blocks possibly dangling in the solution. The critical micelle concentration (cmc) decreased with increasing temperature. $B_{12}E_{260}B_{12}$ showed very strong intermicellar cross-linking even at only 2 wt % polymer concentration.[8] Other copolymers also suggested the existence of intermicellar linking. However, the cross-linking was not strong. Recently, we showed that for the triblock copolymer $B_6E_{46}B_6$ the intermicellar cross-linking, similar to that of $B_{12}E_{260}B_{12}$, began to form at very high (about 35 wt %) polymer concentration, but it was very weak.[10] Molecular associates, which were defined as small polymer aggregates containing only a few unimers, have been found to be present at high polymer concentration (e.g., 10 wt % for $B_5E_{91}B_5$ and $B_6E_{46}B_6$) in most of the above copolymer systems. Yang et al. indicated that there were several possible equilibria in polymer solution:[4] between unimers and molecular associates, between unimers and micelles, and between micelles and intermicellar open structures. The basic parameters of micellization, such as the cmc, the critical micelle temperature (cmt), the association number (n_w), the micellar sizes and the thermodynamic data were carefully measured and systematically reported by different authors.[4,7−10]

In this article, the dominant factors, mainly the block lengths and the length ratios, on the association behavior of close-associated $B_nE_mB_n$ triblock copolymers in aqueous solution are discussed. It has been a topic that has drawn the attention of many theoretical chemists.[11] Zhulina and Birshtein[12] used a scaling approach to show how the micellar characteristics depended on the diblock copolymer composition. By fixing the length of the solvent-phobic block and increasing the length

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of the solvent-philic block, the main micellar parameters (e.g., micellar size, association number, ...) would first be determined by the solvent-phobic block, then determined by the solvent-philic block, and at the end would be independent of the block length when the solvent-philic block was very long. Some quantitative expressions were also derived by other authors.[13−16] For triblock copolymers in a solvent selective for the middle block, the theoretical approach becomes more difficult and the experimental data are still comparatively fewer. The most noticeable work has been done by Alexandridis et al.,[17] who summarized micellar parameters of 12 $E_nP_mE_n$ triblock copolymer micelles. The effects of P and E block lengths on cmc, cmt, $\Delta G°$, $\Delta H°$, and $\Delta S°$ were extensively discussed. They also reported that there was no micelle formation in $P_nE_mP_n$/water systems even at high temperatures. Here we extend this study by using $B_nE_mB_n$ triblock copolymers that have hydrophobic end blocks and a hydrophilic middle block. Our discussions should be based mainly on the data ($B_5E_{91}B_5$, $B_6E_{46}B_6$, $B_7E_{22}B_7$, $B_{10}E_{271}B_{10}$, and $B_{12}E_{260}B_{12}$) from our research group because these data were obtained under similar experimental conditions so that they are more suitable for comparison. Other valuable works, especially those performed by Booth and co-workers, are also carefully considered. They extensively studied the effect of chain architecture on the formation and properties of E_nB_m, $E_nB_mE_n$, and $B_nE_mB_n$-type block copolymers[4] and presented the change of the cmc and the n_w as a function of the hydrophobic B block length. Although they performed a very insightful analysis, some objective factors prevented them from reaching conclusive results. First, for $B_nE_mB_n$ block copolymers, their samples had the B block lengths varying from only 4 to 7 segments, representing a factor of 1.75; for the E blocks, the lengths were about the same ($\approx$40), so the effect of the E block length could not be effectively discussed. Second, the linear regressions they have done were comparatively crude, so that they could only provide qualitative analysis rather than quantitative conclusions. In this paper we choose several $B_nE_mB_n$ block copolymers that have a large difference in the E block length (from 22 to 271). The difference in the B block length is also larger (from 4 to 12, representing a factor of 3), which gives us the advantage to summarize the micellar properties more effectively. Unlike those of Pluronics, for which different research groups often reported quite controversial experimental data, the studies on the $B_nE_mB_n$ triblock copolymers by several research groups showed enough universal behavior that makes it possible for us to organize the available data in order to test the model more quantitatively. A Communication has been published[18] that indicated that for the same systems, the micellar association number (n_w) and the hydrodynamic radius (R_h) are mainly determined by hydrophobic B block length and hydrophilic E block length, respectively. In this article, we complete our study to include other important micellar parameters such as the cmc, the second virial coefficient (A_2), and $\Delta H°$, resulting in a whole outline for the micellization behavior of such triblock copolymers in aqueous solution.

Experimental Section

Static light scattering (SLS) and dynamic light scattering (DLS) were used to characterize the formation and the structures of block copolymer micelles in aqueous solution. We used a standard laboratory-built light scattering spectrometer,[19] which was capable of both SLS and DLS measurements in an angular range of 15−140°. The spectrometer was equipped with a Spectra Physica model 165 argon ion laser operating at 488
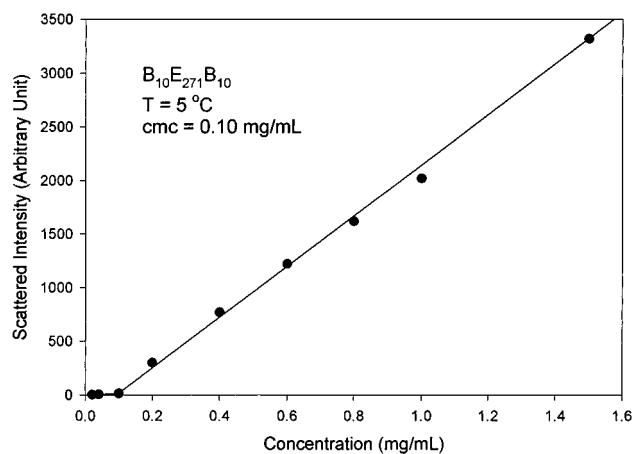

Figure 1. Critical micelle concentration (cmc) measurement of $B_{10}E_{271}B_{10}$ triblock copolymer in aqueous solution at 5 °C.

nm and a Brookhaven Instruments (BI 2030AT or BI 9000) correlator. The sample chamber was thermostated and could be controlled to with ±0.02 °C. The intensity−intensity time correlation functions were analyzed by the CONTIN method.[20] The basic principles of SLS and DLS techniques can be found in earlier publications of our research group.[21]

The procedures of synthesis, purification and preparation of polymer samples can be found in other recent publications.[4,7−10] It is noted that the Pluronic polyols both have chemical heterogeneity and are relatively polydispserse in the molecular weight distribution. However, the micelle formation due to free energy minimization is basically not affected by the polymer polydispersity. In the absence of mixed micelles as can be shown by dynamic light scattering (one narrow peak for the micelles), different size block copolymers are automatically incorporated into the micelles to yield only a very narrow micellar size distribution. On the other hand, as we have reported previously,[10] all the samples were purified by hexane to remove hydrophobic impurities (a chemical heterogeinity).

Results and Discussion

Critical Micelle Concentration (cmc). The cmc of block copolymer micelles is defined as the polymer concentration, above which the formation of micelles becomes increasingly important. One of the usual ways to measure the cmc value is by SLS. Figure 1 shows the cmc measurement of $B_{10}E_{271}B_{10}$ in aqueous solution at 5 °C. A sudden increase in the scattered light indicates the micellar formation. Furthermore, the sharp transition suggests that the polydispersity effect is negligible in our study. The cmc can be determined to be about 0.10 mg/mL. The $B_nE_mB_n$ triblock copolymer micelles we studied were all comparatively small (R_h < 13 nm), and the angular dependence of the scattered intensity was pretty weak. Therefore, only the scattered intensities of polymer solutions at a 90° scattering angle were measured. For $B_nE_mB_n$ block copolymers in aqueous solution, the cmc values became lower at higher temperatures.[4,7,9,10] At a specific temperature below the clouding temperature, the cmc values of different block copolymers varied with the block length. In Figure 2a,b, by combining the data reported by Yang et al.[4] and by our group, we plotted the logarithmic cmc values at 25 and 30 °C versus the total B monomer units in a polymer chain (the total length of two end B blocks). The longer the B block length, the smaller the cmc would be. We chose the block copolymers that had a large difference in the E block length (from 39 to 271 units); therefore, we can conclude that the cmc's of $B_nE_mB_n$ type triblock
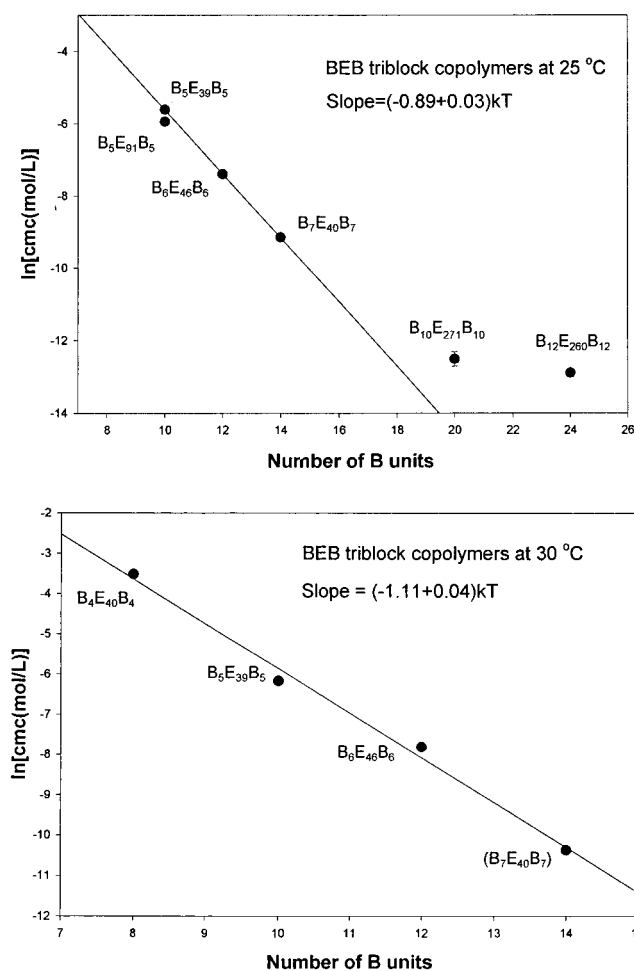
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Figure 2. (a, top) Plot of logarithmic cmc values of $B_nE_mB_n$ triblock copolymers in aqueous solution versus number of B units in a polymer chain at 25 °C. The value of $B_7E_{40}B_7$ was calculated by extrapolating the data at lower temperatures. (b, bottom) Plot of logarithmic cmc values of $B_nE_mB_n$ triblock copolymers in aqueous solution versus number of B units in a polymer chain at 30 °C.

copolymers are mainly determined by the length of the hydrophobic B block whereas the length of the E block has little effect. At 25 °C, the majority of the data points are basically on the straight line, except for those of $B_{10}E_{271}B_{10}$ and $B_{12}E_{260}B_{12}$, which have extraordinarily long E blocks. We ignored the data point of copolymer $B_4E_{40}B_4$ at 25 °C because it could not form micelles at any polymer concentration at this temperature. At 30 °C, the data of $B_{12}E_{260}B_{12}$ was not available owing to its low clouding temperature (25 °C for 1 wt % aqueous solution). Also, in both cases we could not include the data of $B_7E_{22}B_7$ because it phase separates at room temperature.

Some similar studies have been performed a long time ago and have been summarized by van Os[22] et al. on alkylpoly-(glycol ether) surfactants C_nE_m and by Wanka et al. on $E_nP_mE_n$ block copolymers and C_nE_m[23,24] surfactants in aqueous solution. Similar linear relations between the logarithmic values of the cmc and the block lengths of the block copolymers or surfactants have been reported.[23,24] Both blocks could influence the cmc value with the hydrophobic block having a strong negative effect and the hydrophilic block having only a minor positive effect. Owing to the limitation in available samples and the different methods used in determining the cmc (e.g., SLS, dye solubilization, or surface tension), the cmc values reported by different research groups also showed large discrepancies. We are not
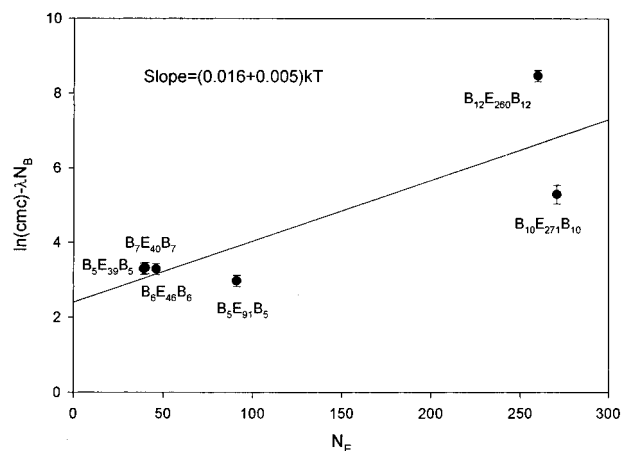

Figure 3. Estimation of the effect of E block on cmc values of $B_nE_mB_n$ triblock copolymers.

able to quantitatively deduce the effects of the E block on the cmc by using the current available samples. Mejiro et al.[25] reported that for the C_nE_m surfactants the effect of the E part was about 10−20 times smaller than that of the C part. The general expression was presented as

$$\ln(\text{cmc}) = \alpha{\cdot}N_C + \beta{\cdot}N_E \qquad (1)$$

where α and β were two constants depending on the external conditions, N_C and N_E are the numbers of C and E units in one part, respectively. Recently, Alexandridis et al.[17] indicated that for the $E_nP_mE_n$ triblock copolymers in aqueous solution, the cmc values could be expressed by similar mathematical relations like eq 1, both the P and the E blocks had effects on the cmc value, and the effects were comparable, although the effect due to the P block length was a little larger. In our case, this effect has been revealed by the data points of $B_{10}E_{271}B_{10}$ and $B_{12}E_{260}B_{12}$. Their deviation from the straight line shown in Figure 2a is likely due to the long E block length. It is noted that the experimental deviation from the straight line behavior for $B_{10}E_{271}B_{10}$ and $B_{12}E_{260}B_{12}$ is much larger than the experimental uncertainty as shown, for example, in Figure 2a, for $B_{10}E_{271}B_{10}$. However, the effect due to the E block seems to be quite small, since the B block is more hydrophobic than the P block. Although we do not have enough data to accurately calculate the effect of the E block on the cmc values, an estimation can be made by assuming that for the $B_nE_mB_n$ triblock copolymer micelles, eq 1 is still the proper formula:

$$\ln(\text{cmc}) = \alpha{\cdot}N_B + \beta{\cdot}N_E \qquad (2)$$

From Figure 2a, the constant α at 25 °C can be calculated from the slope λ to be $-0.89kT$. By subtracting $\alpha{\cdot}N_B$ from $\ln(\text{cmc})$, the effect of the E block can be estimated, as shown in Figure 3. The slope in Figure 3 is just the value of β in eq 2. However, the current data in Figure 3 are not good enough for a reliable linear regression. They can only qualitatively show that the E block does have a small positive effect on the cmc value, with the magnitude being about 40−50 times smaller than that of the B block.

From the slopes in Figure 2a,b, the transfer energy of a hydrophobic group from the aqueous medium into the micellar interior can be estimated[24]

$$\ln(\text{cmc}) = \gamma kT{\cdot}N_B \qquad (3)$$

where γ is a constant, k is the Boltzmann constant, T is the

absolute temperature (Kelvin), and N_B is the units of hydrophobic B blocks; γkT as a whole can be treated as the transfer energy needed for one hydrophobic (B or P) monomer unit. For $B_nE_mB_n$ block copolymers and by combining all the available data except those of $B_{10}E_{271}B_{10}$ and $B_{12}E_{260}B_{12}$, the transfer energy for one B unit is about $0.89kT$ at 25 °C. At the same temperature, the transfer energy of one P unit in the Pluronic polyoles ($E_nP_mE_n$) is about $0.2-0.3kT$,[24] while for the C_nE_m surfactants the value is around $1.2kT$.[24] Obviously, the transfer energy can be reduced when the less soluble block becomes less hydrophobic; e.g., the reduction can be attributed to the presence of polar oxygen atoms or (and) shorter carbon chains in the hydrophobic unit. It seems that the B block, which contains four carbon−hydrogen groups (two CH_2-, one CH_3-, and one $-CH-$) plus one oxygen atom, functions a little weaker than that of the C part, and that one B block might be equivalent to about three to four P blocks as revealed by the magnitude of the transfer energy. However, the transfer energy of the P block was calculated from the cmc values of $E_nP_mE_n$ block copolymers, in which the P block resided in the middle, the transfer energy of the C part in C_nE_m was calculated on the basis of surfactants, and finally, for $B_nE_mB_n$, the B blocks were the end blocks. It is known that the chain architecture has a great effect on the cmc values of block copolymers (e.g., the cmc of $P_nE_mP_n$ is much higher than that of $E_nP_mE_n$ under similar conditions).[1] It is reasonable to consider that the chain architecture may also affect the cmc increment owing to the hydrophobic block length. Our discussions have neglected this point. However, the results we have obtained here are consistent with former reports.[26−27] By comparing the effect per hydrophobic unit on the thermodynamic parameters (e.g., $\Delta H°$) of $E_nP_mE_n$ and $E_nB_mE_n$ triblock copolymer micelles, Yang et al.[26] showed that one B unit was equivalent to about four P units. We[27] reported that by studying the cloud-point temparetures of $B_nE_mB_n$ and $P_nE_mP_n$ triblock copolymers in aqueous solution, one B unit was equivalent to about 4.4 ($\approx$4) P units. Thus, this factor of 4 appears to be a good guideline to compare the physical properties of triblock copolymers containing P or B units.

The temperature dependence of the transfer energy can also be checked by comparing the slope in parts a and b of Figure 2. At 30 °C, the value of the transfer energy is about $1.1kT$, higher than the value at 25 °C. By assuming that the temperature changes have little effect on the middle E block, this increase can be taken as additional evidence of the increase in the hydrophobicity of B blocks with increasing temperature, besides the fact that the absolute cmc values at higher temperatures become smaller.

2. Association Number (n_w). The association number of micelles can be determined by measuring the molecular weight of the micelles by SLS and then using the modified Debye equation[4]

$$H(c - c_{cmc})/[R_{Bz}(I - I_{cmc})/I_{Bz}] = 1/M_w + 2A_2(c - c_{cmc})$$
$$(4)$$

where $H \equiv 4\pi^2n_{Bz}^2(dn/dc)^2/N_A\lambda^4$ is an optical parameter with n_{Bz} being the refractive index of a reference standard, benzene; dn/dc being the refractive index increment of the polymer sample; N_A being Avogadro's constant; λ being the laser wavelength in a vacuum (488 nm); in eq 4, c, c_{cmc} are the polymer concentration and the micellar concentration, respectively; R_{Bz} is the Raleigh ratio of benzene; M_w is the weight-average molecular weight of micelles; and I, I_{cmc}, and I_{Bz} are the total scattered intensity of the micellar solution, of the
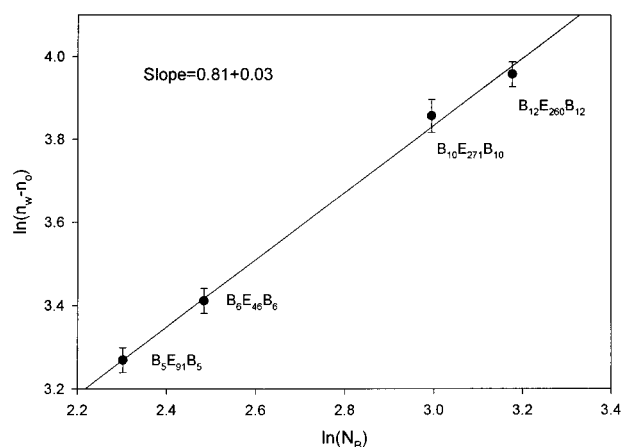

Figure 4. Plot of association number (n_w) of $B_nE_mB_n$ triblock copolymers versus the $^4/_5$ power of total number of B monomer units (N_B) in one copolymer chain.

polymer solution at cmc, and of benzene, respectively. The n_w of the micelles can be estimated from M_w. Usually, for closed associated micelles, the association number shows only a temperature dependence but little or no concentration dependence in the dilute solution regime. We have reported that the B block length also plays a dominant role in determining the n_w value, which increases about linearly with an increase in the number of B units.[18] So far there is insufficient evidence to show whether the E block has a noticeable effect. However, we can safely conclude that even if it has, the effect should be quite small.

The relevant theoretical support can be found in Halperin's work[13] on diblock copolymer micelles when the solvent-philic block is much longer than the solvent-phobic block. He derived the relation

$$n_w \sim N_b^{4/5} \qquad (5)$$

with N_b representing the number of monomeric units in one solvent-philic block. To test the above theory in the case of triblock copolymer micelles, Figure 4 shows a plot of n_w versus $(N_B)^{4/5}$. A linear relation can be obtained from the data points, and this result does not contradict to the theory provided by Halperin.[13] Therefore, basically our results show that for triblock copolymers, their micellization behavior can also be described by the scaling theory derived from a diblock copolymer model. Similar conclusion can also be drawn from the study on the micellar sizes, as to be shown later. It is known that in both kind of micelles, the micellar corona formed by solvent-philic blocks can exist as random coils in solution;[11] however, for triblock copolymers in a solvent selective for the middle block, the freedom of the micellar corona will be limited since the two ends have to go back to the same micellar core. This limitation will certainly affect the micellar formation (increase in entropy) and micellar size. But from our experiments, it seems to show that the micellization of these two kinds of micelles follows similar rules.

Also, by extrapolating to $n_w = 1$, it suggests that under certain fixed external conditions (e.g., temperature or pressure), there exists another critical condition due to the block lengths below which micellization cannot occur at any polymer concentrations except by changing the external conditions.[21] In Figure 4, by ignoring the minor effect due to the E block, we can conclude that for $B_nE_mB_n$ triblock copolymers in water, 8−9 B block units are needed for micellization at 25 °C. A higher value can be expected at a lower temperature and vice versa.
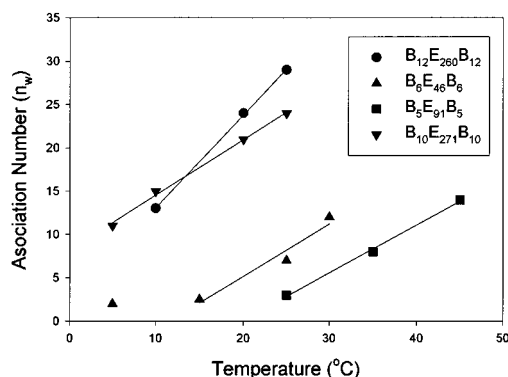
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Figure 5. Plot of association number (n_w) of $B_nE_mB_n$ triblock copolymers versus temperature.
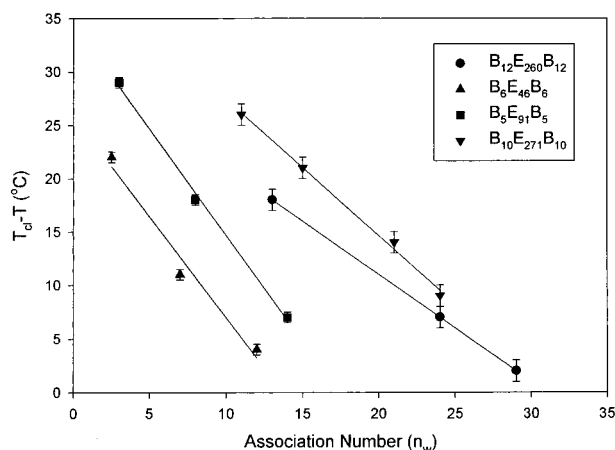

Figure 6. Plot of association number (n_w) of $B_nE_mB_n$ triblock copolymers versus temperature difference away from their respective cloud-point temperatures. The uncertainties in cloud-point temperatures are indicated.

Booth and co-workers presented similar relations between the B block length and the n_w for $E_nB_mE_n$, $B_nE_mB_n$, and E_nB_m-type block copolymers at 30 °C.[4,26] They reported that for diblock copolymers, both blocks have an effect on the n_w value with the effects by the two blocks being comparable to each other. With only a limited number of $B_nE_mB_n$ triblock copolymer samples, it was difficult for them to speculate on the effect of E block on such triblock copolymer micelles. Here we have sufficient data to show that for $B_nE_mB_n$ triblock copolymer micelles, the hydrophobic B block becomes more important while the effect of the hydrophilic E block can essentially be ignored.

For the polyalkylene block copolymer micelles in aqueous solution, the association number usually increases with increasing temperature.[1] The increase in hydrophobicity for hydrophobic blocks at higher temperatures is responsible for the increase in the n_w. Figure 5 shows that for the four triblock copolymers in the plot, the slopes of four lines formed by the data points from the different polymers are similar; i.e., the n_w increases at a similar rate with increasing temperature for the triblock copolymers with different B block and E block lengths. There is an exception: $B_6E_{46}B_6$ at 5 °C, which is obviously off from the other four lines. However, the n_w under that condition is only 2, and actually they are not real core−shell micelles, but molecular associates.

In Figure 6 the relation between the n_w and the relevant temperature labeled as the distance away from the clouding temperature is presented. The clouding temperatures of block copolymer/water systems are defined as the temperature at which

phase separation occurs. For each data the uncertainty denotes the range of clouding (or cloud-point) temperatures at different polymer concentrations for the corresponding block copolymer. If we extrapolate the lines to $n_w = 1$ (unimer), all the lines have offsets at around 25−35 °C on the y-axis; i.e., the micellization behavior of $B_nE_mB_n$ triblock copolymers begins to happen at about 25−35 °C lower than their clouding temperatures. It suggests that there exists a certain relationship between the micellization, a kind of microphase separation, and the macrophase separation of $B_nE_mB_n$ block copolymers in aqueous solution, and that there may be some form of similarities among the phase diagrams of $B_nE_mB_n$/water systems.

3. The Second Virial Coefficient (A_2). The A_2 of micelles is an indication of the nature of micellar interaction in solution. A negative value of A_2 indicates a strong interaction among solute particles and suggests that the solute is in a poor solvent. The magnitude of A_2 denotes the strength of the interactions. For triblock copolymer micelles in aqueous solution, the A_2 value often shows a temperature dependence. At higher temperatures, the solvent becomes worse for both kind of polymer blocks; therefore, the A_2 value becomes smaller or more negative. For both $B_5E_{91}B_5$ and $B_6E_{46}B_6$ micelles, a transition of the A_2 value from positive to negative with increasing temperature has been reported.[7,10] At a fixed temperature, the length of the B block seems to have major effect on the A_2 value. In Table 1, the longer hydrophobic B block length makes the A_2 value smaller from $B_5E_{91}B_5$ to $B_6E_{46}B_6$, and finally $B_{10}E_{271}B_{10}$ and $B_{12}E_{260}B_{12}$ have two large negative values for A_2. Strong micellar interactions exist among $B_{10}E_{271}B_{10}$ and $B_{12}E_{260}B_{12}$ micelles, possibly owing to the high hydrophobicity of the B end blocks, which are dangling in solution to form more open structures instead of only flowerlike micelles.

From above conclusions on the values of the cmc, the n_w, and the A_2 of block copolymer micelles, we can clearly see that a higher temperature or a longer hydrophobic block length can produce a similar effect on $B_nE_mB_n$-type triblock copolymers in aqueous solution. Under both of the conditions water becomes a poorer solvent so as to lower the cmc and to increase the n_w as a result of strong solute−solute interactions. Therefore, to achieve a certain desired micellization parameters, we can either change the temperature or change the length of the blocks.

4. Enthalpy of Micellization ($\Delta H°$). The thermodynamic parameters of micellization, such as the change of Gibbs free energy (ΔG), the change of enthalpy (ΔH), and the change of entropy (ΔS) can be calculated from the temperature dependence of cmc values obtained from SLS measurements[7,17] and by assuming that the value of $\Delta H°$ is temperature independent:

$$\Delta H° = R[d \ln(cmc)/d(1/T)] \qquad (6)$$

and

$$\Delta G° = RT \ln(cmc) \qquad (7)$$

Among the three parameters, the $\Delta H°$ value is the most proper one for comparison because of its weak temperature dependence. As shown in Figure 7, a plot of $\Delta H°$ versus the number of B units in the polymer chain obtained through eq 6 exhibits roughly a linear relationship. Again, by considering the randomly distributed E block lengths, one can conclude that the B block length has the dominant effect. The $\Delta H°$ values of micellization are positive, decreasing with increasing number of B units. Similar work had been done by Meguro et al.;[25] they studied monodisperse octaethylene glycol-n-alkyl ethers (C_nE_8) in aqueous solution by using the surface tension

TABLE 1: Comparison of Micellar Parameters between $B_5E_{91}B_5$, $B_6E_{46}B_6$, and $B_{12}E_{260}B_{12}$

property	temperature dependence	$B_5E_{91}B_5$	$B_6E_{46}B_6$	$B_{10}E_{271}B_{10}$	$B_{12}E_{260}B_{12}$	governing factor
cmc (mol/L, 25 °C)	strong	2.6×10^{-3}	6.2×10^{-4}	3.9×10^{-6}	2.5×10^{-6}	the length of B block, see Figure 1a
association number (n_w, 25 °C)	strong	3	8	25	29	the length of B block, see Figure 3
A_2 (cm^2 mol g^{-2}, 25 °C)	weak	3×10^{-5}	-3×10^{-5}	-8×10^{-5}	-1×10^{-4}	the length of B block
$\Delta H°$ (kJ/mol)	weak	81	72	33	24	the length of B block, see Figure 6
R_h (nm)	weak	7.1–7.9	5.7–6.3	12.5–13.0	12.0–12.7	the length of E block, see Figure 7
K_d (cm^3 g^{-1}, 25 °C)	yes	-2.6	-6.7	-124	-139	
bridging function to form interconnected micelles	yes	moderate	weak	strong	strong	the length of middle block and a certain hydrophobicity of the end blocks
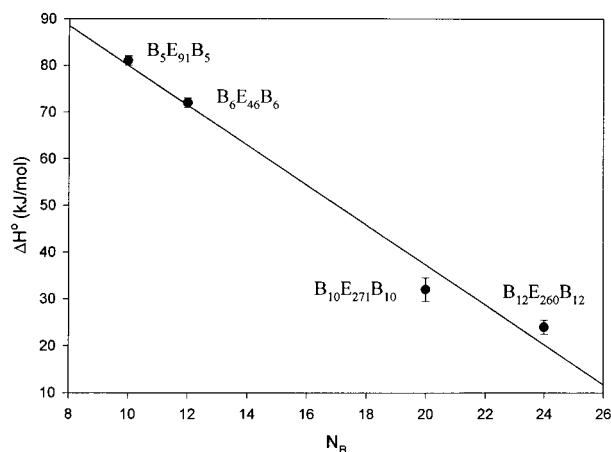
Figure 7. Plot of the enthalpy change ($\Delta H°$) of micellization versus total number of B monomer units in one copolymer chain.

Figure 8. Plot of the enthalpy change ($\Delta H°$) of micellization per average monomer unit versus the monomer unit ratio of B block over E block.

technique. They obtained the result that by fixing the E block length, the thermodynamic parameters changed linearly ($\Delta H°$ and $\Delta G°$ decreased while $\Delta S°$ increased) with increasing C units. In their system, they also reported that the positive $\Delta H°$ became smaller with higher C content. The $\Delta H°$ of micellization could be attributed from two sources: (1) a transfer energy of hydrophobic parts from the aqueous environment to the micellar core [$\Delta H°(h)$], which should have a negative value and should decrease with increasing hydrophobic block length; (2) another energy due to the interactions between the hydrophilic blocks and the water molecules [$\Delta H°(w)$], which should also have a negative value. The net enthalpy effect $\Delta H°$ ($=[\Delta H°(h)] - [\Delta H°(w)]$, as shown in Figure 7) is usually positive for surfactant/water systems. Therefore, to accomplish the micellization process, the entropy change must be positive to make the total $\Delta G°$ negative; i.e., the micellization process should be entropy-driven. From Figure 7 the conclusion can be drawn that the [$\Delta H°(h)$] due to the hydrophobic B block basically determines the value of the enthalpy change ($\Delta H°$). The difference in the E block length certainly will lead to different [$\Delta H°(w)$] values. However, this effect seems to be negligible within our experimental range. Again this observation differs from the results reported by Alexandridis et al.[17] on $E_nP_mE_n$ triblock copolymer micelles. They showed that both kinds of blocks had an effect on the thermodynamic parameters, and an empirical equation that contained the constants of block lengths, total molecular weight, and polymer concentration was presented to calculate the $\Delta G°$ of the micellization process. The more hydrophobic B block is responsible for the discrepancy in our observation, although one B unit is equivalent to about four P units.

Another approach can further elucidate the effects of the total polymer chain length and the block length ratio on $\Delta H°$. Figure 8 shows that the enthalpy change ($\Delta H°$) of micellization per average monomer unit increases with increasing B content. After
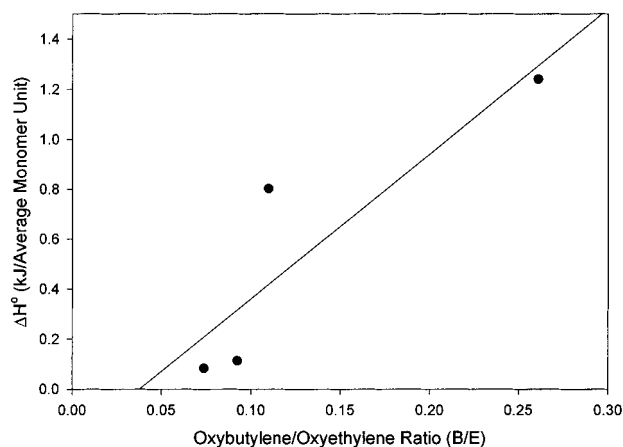
normalizing to the total number of nomomer units ($N_B + N_E$) in the copolymer molecule, $\Delta H°$ approaches zero when the ratio of N_B/N_E goes to zero. A similar conclusion was also drawn by Armstrong et al.[28] when studying $E_nP_mP_n$/water systems by using differential scanning densitometry. These observations prove that it is the hydrophobic part of the copolymer that is responsible for the micellization. Furthermore, by comparing the slopes of two linear regressions, it is interesting to notice that the slope from $B_nE_mB_n$ triblock copolymers (≈ 6) are about four times higher than that from $E_mP_nE_m$ triblock copolymers (≈ 1.5), again it suggests that one B monomer unit has the effect equivalent to about four P monomer units.

5. Micellar Size and Intermicellar Interactions. The dynamic light scattering (DLS) technique with CONTIN analysis can provide information on the apparent diffusion coefficient ($D_{app.}$) of moving particles in solution. By extrapolating the $D_{app.}$ values to zero scattering angle and zero micellar concentration ($c_{mic.}$), the D_0, and then the hydrodynamic radius ($R_{h,0}$), can be obtained from the relations

$$D_0 = D_{app.}/(1 + k_dc_{mic.}) \tag{8}$$

and

$$D_0 = kT/6\pi\eta R_h \tag{9}$$

with k being the Boltzmann constant, T being the absolute temperature (kelvin), and η being the solvent viscosity. In a previous publication,[18] we showed a linear relationship between the R_h of micelles and the E block length of the block copolymers. The $B_5E_{91}B_5$ has the shortest B blocks among these four polymers, but its micellar size is larger than that of $B_6E_{46}B_6$, suggesting that the effect of the B block on the micellar size is quite trivial. The E blocks form micellar shells in aqueous solution, with micellar shells having a much lower polymer

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density than the micellar cores. Therefore, for closed-associated micelles, the micellar size is mainly determined by the thickness of the micelle shell, and the dominant effect of E block on the micellar size is quite reasonable.

The above conclusion may not be valid for all the block copolymer micelles. For example, the R_h values of many $E_nP_mE_n$ micelles in water do not obey this rule. We notice that the above rule is applicable if, first, the hydrophobic block is comparatively small, i.e., the contribution to the total R_h due to the micellar core can be neglected; second, the difference in the hydrophobicity between the two kinds of blocks should be sufficiently large, i.e., the micelles have compact cores and fairly loose shells.

It is interesting to compare our conclusion with theoretical results. As early as 1983, Noolandi and Hong[14] developed a theory for diblock copolymer micellar parameters by minimizing the Gibbs energy of an isolated micelle. Bluhm and Whitmore[15] used the model for a specific diblock copolymer system, polystyrene−polybutadiene in hexane, and obtained

$$R^{(core)} \sim N_b^{0.67}N_a^{-0.01} \tag{10}$$

and

$$R^{(shell)} \sim N_b^{0.12}N_a^{0.54} \tag{11}$$

Halperin[13] also presented a model for diblock copolymer micelles in the case of $N_a \gg N_b$

$$R \sim N_b^{4/25}N_a^{3/5}\alpha \tag{12}$$

where α is the length of a monomeric unit. All of the above expressions indicate the dominant effect of solvent-philic blocks on the micellar size. In Figure 9a,b, the relations based on eqs 9 and 10 are presented. We can conclude that for triblock copolymers, the scaling approach remains applicable although the limitations in the number of available samples and in the experimental precision make it impossible to distinguish which one is better.

In eq 8, the parameter k_d is related to the second virial coefficient A_2 by the relation[4]

$$k_d = 2A_2M_w - k_f - 2\nu \tag{13}$$

with M_w being the particle mass, k_f being the frictional coefficient, and ν being the partial specific volume of micelles. If we accept the approximation that M_w, k_f, and ν are concentration-independent,[4] the value of k_d will be mainly affected by A_2 while changing copolymer concentration. For $B_nE_mB_n$ block copolymer micelles in aqueous solution, $D_{app.}$ generally decreased with increasing micellar concentration. From eq 8, we can see that the k_d values are negative under this condition, indicating a substantial attractive interaction among the micelles. The intermicellar interactions are recognized as the effect due to some of the hydrophobic B end blocks, which are not in the micellar cores but dangling in solution.[4,10] From this viewpoint it seems that the lengths of both the B block and the E block will affect the interaction. With longer B end blocks, the intermicellar interaction can become stronger, while longer E blocks can make the B blocks extend into the solution more easily. In Table 1, the k_d values of $B_{10}E_{271}B_{10}$ and $B_{12}E_{260}B_{12}$ have much larger negative values (-120 and -139 cm³/g at 25 °C, respectively) than that of $B_5E_{91}B_5$ and $B_6E_{46}B_6$ (-2.6 and -6.7 cm³/g at the same temperature, respectively), suggesting a collective effect of the long B and E blocks. The k_d
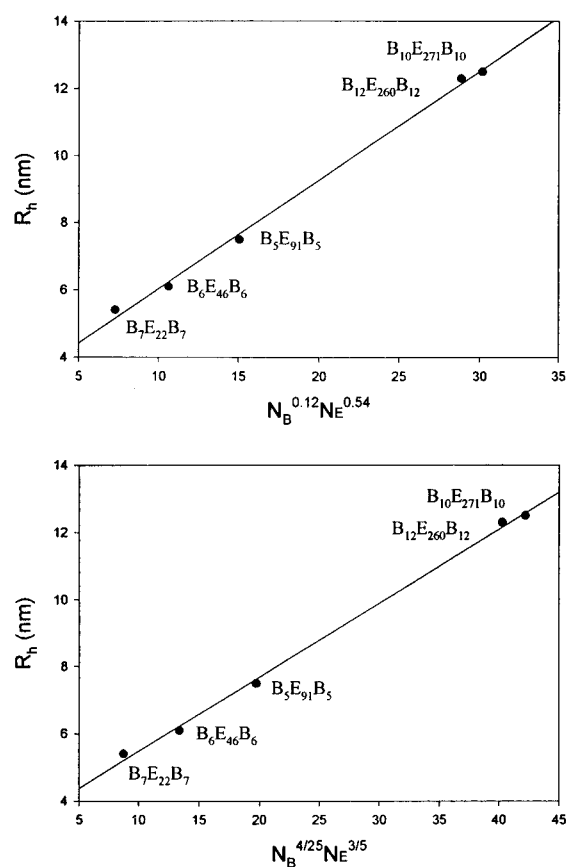

Figure 9. (a, top) Plot of hydrodynamic radius (R_h) of $B_nE_mB_n$ triblock copolymers versus $N_B^{0.12}N_E^{0.54}$. (b, bottom) Plot of hydrodynamic radius (R_h) of $B_nE_mB_n$ triblock copolymers versus $N_B^{4/25}N_E^{3/5}$.

of $B_6E_{46}B_6$ is a little lower than that of $B_5E_{91}B_5$, suggesting that the effect of the B block is more important.

6. Intermicellar Cross-Linking. Owing to the special chain architecture of $B_nE_mB_n$-type block copolymers, the formation of flowerlike micelles needs to bend the E blocks and keep the two end B block in the same micellar core. It is obviously an entropy-loss process. Therefore, another possibility is that the two B blocks in one polymer chain reside in two adjacent micelles and the E block is used as a bridge. This kind of cross-linking among the micelles can finally promote an open network structure. For $B_nE_mB_n$ block copolymers, a fraction of the B blocks can be dangling in solution and they have potential for cross-linking when the polymer concentration is sufficiently high. For $B_{12}E_{260}B_{12}$, strong micellar cross-linking was observed by DLS even at 2 wt % polymer concentration.[9] For $B_5E_{91}B_5$, we recently found that moderate supramolecular open structures were formed at much higher concentration (e.g., 25 wt %). Finally, for $B_6E_{46}B_6$, even at 35 wt % polymer concentration, the bridging function to form interconnected micelles remained quite weak.[5]

More experimental evidence can be found by measuring the viscosity of the polymer solutions. Recently we indicated that at the same polymer concentration (e.g., 15 wt %), the viscosities of $B_{12}E_{260}B_{12}$ and $B_{10}E_{271}B_{10}$ were much higher than those of the others, and $B_{10}E_{271}B_{10}$ had an even higher viscosity than $B_{12}E_{260}B_{10}$.[29]

Conclusions

The block length of $B_nE_mB_n$ type triblock copolymers plays an important role in determining the micellization behavior of such block copolymers in aqueous solution. As summarized

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in Table 1, the length of the hydrophobic end B blocks is the dominant factor on the cmc values, the association numbers, the second virial coefficient, and the thermodynamic parameters of the closed-associated flowerlike micelles. Increasing the B block length is similar to increasing the solution temperature; both of them enhance the hydrophobicity of polymer chains. The effect of the E block is quite small when compared with that in $P_n E_m P_n$ triblock copolymer micelles. However, the length of E blocks determines the micellar sizes when the B blocks are much shorter and highly hydrophobic. The intermicellar interaction and the formation of interconnected micelles are likely to depend on the lengths of both B and E blocks. Within our experimental range, the theoretical results from scaling theory by using diblock copolymer as the model are still valid for $B_n E_m B_n$ triblock copolymer micelles in aqueous solution.

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