Effects of Block Lengths on the Association Numbers and Micellar Sizes of $B_nE_mB_n$ Type Triblock Copolymer Micelles in Aqueous Solution

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Introduction. The association behaviors of block copolymers in selective solvents have been extensively reported during the last few years.[1,2] It has been noted that the core−shell micellar structure is fairly common for closed association mechanisms. In an open association mechanism, more open and extended structures are sometimes formed at low polymer concentrations and the polymer solution becomes a gel-like network at high concentrations. The bridging function is achieved from an extended soluble middle block between the small clusters formed by the poorly solvated end blocks.[3,4] Although the characterization of the micellar systems has become routine, the results from different research groups and through different physical techniques can sometimes be amazingly different.[1] This problem, combined with the limit in the number of available samples and the uncertainties among the samples (e.g., different polydispersities), makes it difficult for the readers to draw conclusive results, e.g., quantitative relations between micellization parameters and the block lengths of block copolymers. The most noticeable study in this area is on alkylpoly(oxyethylene) glycol ethers (C_nE_m) in aqueous solution where the quantitative effects of chain lengths on cmc and thermodynamic parameters were systematically reported.[5,6] However, even for the polymers C_nE_m, which show very good chemical homogeneity and can be used as a standard model, there is no report on the relations between chain length and association number or micellar size. Yang *et al.*[7,8] made some valuable attempts on studying block poly(oxyalkylene)s (B_nE_m, $B_nE_mB_n$, and $E_nB_mE_n$, where B and E were oxybutylene and oxyethylene, respectively) in aqueous solution. However, due to the limited numbers (three $B_nE_mB_n$ samples with one being in the unimer state) of samples studied, they were not able to make quantitative conclusions. In spite of the shortage of experimental data, theoretical approaches on the relation between the block length and the micellar properties for diblock copolymer micelles have been developed and reviewed.[2] Here we present the linear relations between the micellar lengths and two important micellar parameters: the association number (n_w) and the hydrodynamic radius (R_h) in $B_nE_mB_n$/water systems. (The data of $B_7E_{22}B_7$ and $B_{10}E_{271}B_{10}$ are reported for the first time, while the others are cited from the literature.[9−11]) All of the measurements were performed in the regions where only close-associated micelles were formed. We took advantage of the fact that our samples cover very large ranges on both the B block length (10−24 BO units) and the E block length (46−271 EO units). This makes it possible to yield convincing and accurate enough conclusions on the dominant factors behind the basic micellization parameters of these block copolymer micelles.

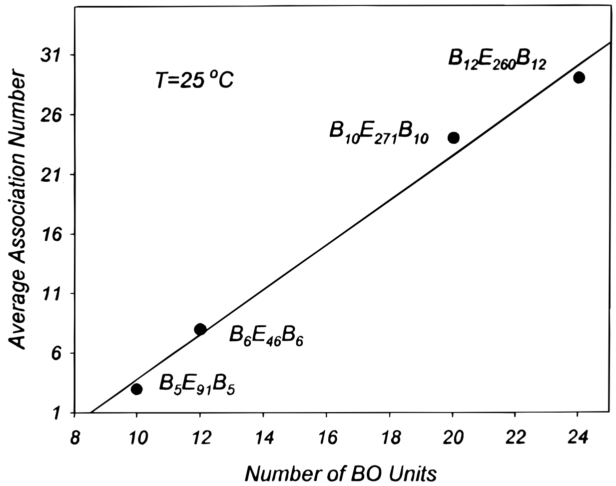

Figure 1. Plot of the average association number of $B_nE_mB_n$ triblock copolymer micelles in water at 25 °C versus the number of hydrophobic BO units in a polymer chain.

Experimental Procedures. Several triblock copolymers, including $B_5E_{91}B_5$, $B_6E_{46}B_6$, $B_7E_{22}B_7$, $B_{10}E_{271}B_{10}$, and $B_{12}E_{260}B_{12}$, were involved in our study. In order to avoid the anomalous micellization behavior before the onset of critical micellization formation,[12] the polymers were purified by hexane[13] or hot octane (only for $B_{10}E_{271}B_{10}$) extraction. The light scattering measurements and sample preparation have been described elsewhere.[12] The polymer solutions were prepared by first dissolving the $B_nE_mB_n$ copolymer in water at low temperatures (<5 °C) in order to ensure complete solute dissolution. The polymer solution was then filtered by a Millipore sterile filter (pore size 0.1 μm). The CONTIN[14] method was used to analyze the intensity−intensity time correlation function $G^{(2)}(\tau)$. All the light scattering experiments were performed at 25 °C except for $B_7E_{22}B_7$, for which the measurements were done at 15 °C because of its low clouding temperature (18 °C for a 1 wt % solution).

Results and Discussion. Figure 1 shows a plot of the average association number (n_w) of $B_nE_mB_n$ block copolymer micelles versus the total number of oxybutylene (BO) units in the polymer chain. For closed-associated micelles, there exists a critical micelle concentration (cmc), above which the formation of micelles becomes increasingly important. The cmc value can be measured by detecting the sharp increase in the scattered intensity with increasing polymer concentration at a certain fixed temperature.[9−11] The n_w of micelles can be measured by static light scattering (SLS) and then calculated by using the modified Debye equation:[7]

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

where $H \equiv 4\pi^2 n_{\mathrm{Bz}}^2 (\mathrm{d}n/\mathrm{d}c)^2/N_A\lambda^4$ is an optical parameter with n_{Bz} being the refractive index of a reference standard, benzene; dn/dc, the refractive index increment

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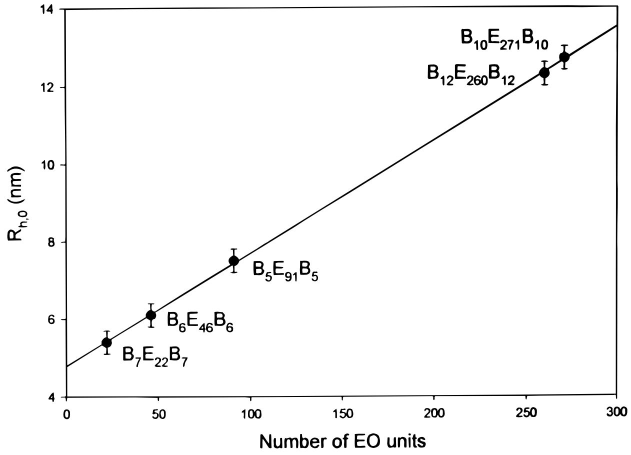

Figure 2. Plot of the average hydrodynamic radius of $B_nE_mB_n$ triblock copolymer micelles in water versus the number of hydrophilic EO units in a polymer chain.

of the polymer sample; N_A, Avogadro's constant; λ, the laser wavelength in vacuum (488 nm); c, the polymer concentration; R_{Bz}, the Raleigh ratio of benzene; M_w, the weight-average molecular weight of micelles; A_2, the second virial coefficient; and I, I_{cmc}, and I_{Bz}, the total scattered intensities of the micellar solution, of the polymer solution at cmc, and of benzene, respectively. The n_w can be estimated from M_w.

Figure 2 shows a plot of the hydrodynamic radii ($R_{h,0}$) of micelles versus the number of oxyethylene units (EO) in $B_nE_mB_n$ triblock copolymers. The CONTIN method was used to analyze the first-order field correlation function $g^{(1)}(\tau)$, as determined by dynamic light scattering (DLS) where $G^{(2)}(\tau) = A(1 + \beta|g^{(1)}(\tau)|^2)$, with A and β being the background and a coherence factor, respectively.

$$g^{(1)}(\tau) = \int_0^{\infty} G(\Gamma) e^{-\Gamma\tau}\, d\Gamma \tag{2}$$

where Γ is the characteristic line width and $G(\Gamma)$ is the normalized line width distribution. With $\Gamma = Dq^2$ for translational diffusive motions, $D = D_0(1 + k_Dc)$, where D_0 represents the diffusion coefficient extrapolated to infinite dilution. Then, with the Stokes–Einstein relation $D_0 = kT/6\pi\eta R_{h,0}$, the $R_{h,0}$ of the micelles can be calculated, with q, k_D, k, T, and η being the magnitude of the scattering wave vector, a constant, the Boltzmann constant, the absolute temperature and the solvent viscosity.

Two conclusions can be drawn from the above two plots.

1. From Figure 1, a linear relationship is presented by plotting the n_w versus the number of BO units. By considering the randomly distributed E block lengths along the straight line, we can figure out that, at a fixed temperature, the n_w of $B_nE_mB_n$ triblock copolymer micelles is determined mainly by the hydrophobic B block length; increasing one unit will enhance the n_w by about 1.9 at 25 °C. Obviously, the value should have a temperature dependence. More generally, an increase in the length of the hydrophobic block will increase the hydrophobicity of the polymer in the solvent. Therefore, a lower cmc value can be expected. Here we show that the hydrophobic block is responsible not only for the cmc but also for the n_w. Similar considerations on n_w were also presented by Yang *et al.*[7] in their studies on $E_nB_mE_n$, E_nB_m, and $B_nE_mB_n$ aqueous solutions. From Figure 1 we can also conclude that when the number of B units is equal to 8 or even lower, the association number will go down to 1 (unimers, we cannot expect $n_w < 1$). This conclusion is consistent with the fact that $B_4E_{40}B_4$ molecules do not form micelles at 25 °C.[7]

2. From Figure 2, we found another linear relationship, between the hydrodynamic radius of the micelles and the length of the E block. Except for $B_7E_{22}B_7$, which was measured at 15 °C because of its low clouding temperature in water, all the other samples were measured at 25 °C. Since the $R_{h,0}$ of micelles has little temperature dependence, we can put all the data in one plot and make comparisons. It is clear that the micellar size is mainly determined by the hydrophilic E block. In aqueous solution, the E blocks form micellar shells and it is common sense that the micellar shell has a much lower polymer density but occupies much more space when compared with the micellar core. Therefore, for closed-associated micelles, the dominant effect of the middle E block on the micellar size is quite reasonable. For the E block length over the range of our samples, the linear relationship holds quantitatively.

From the slope of the line in Figure 2, the R_h will increase to about 0.029 nm with an increase of one EO unit. If we use the widely accepted model that the E blocks have a loop conformation and assume that all the E blocks take on a circular structure, the corresponding effect of one EO unit in the $R_{h,0}$ increment is about 0.12 nm by using the zigzag length of each EO unit to be 0.36 nm.[15] Therefore, it is more likely that the micellar shell takes on a comparatively compact structure. It is also indirect evidence of the looping structure of micellar shells, because, for star-like micelles, the R_h for micelles with the same block lengths and R_h increment with increasing block length should be much larger.

From the preliminary results above on $B_nE_mB_n$/water systems, we can conclude that the two most important micellar parameters, the association number (n_w) and the hydrodynamic radius of micelles ($R_{h,0}$), are determined mainly by the length of hydrophobic B end blocks and the hydrophilic E middle block, respectively. Although we have drawn these conclusions only from $B_nE_mB_n$ triblock copolymers in water, it can be expected that, for other block copolymers, their micellization behavior should also follow similar rules. It has been noticed that the experimental data are in essential agreement with the theoretical predictions by Halperin[16] and others.[17–19] However, more data are needed to make a quantitative comparison. Further detailed studies on other micellar parameters, such as the cmc, thermodynamic properties, the micellar interactions, and the relation between micellization and microphase separations, are in progress.

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References and Notes

(1) Chu, B.; Zhou, Z. In *Nonionic Surfactants: Polyoxyalkylene Block Copolymers*; Nace, V. M., Ed., Marcel Dekker: New York, 1996; Chapter 3.

(2) Tuzar, Z.; Kratochvil, P. In *Surface and Colloid Science*; Matijevic, E., Ed.; 1993; Vol. 15.

(3) Raspaud, E.; Lairez, D.; Adam, M.; Carton, J.-P. *Macromolecules* **1994**, *27*, 2956.

(4) Mortensen, K.; Brown, W.; Jorgensen, E. *Macromolecules* **1994**, *27*, 5654.

(5) Rosen, M. J. *Surfactants and Interfacial Phenomena*; John Wiley: New York, 1978.

(6) Meguro, K.; Takasawa, Y.; Kawahashi, N.; Tabata, Y.; Uneo, M. *J. Colloid Interface Sci.* **1981**, *83*, 50.

(7) Yang, Y.-W.; Yang, Z.; Zhou, Z.; Attwood, D.; Booth, C. *Macromolecules* **1996**, *29*, 670.

(8) Yang, Y.-W.; Deng, N.-J.; Yu, G.-E.; Zhou, Z.-K.; Attwood, D.; Booth, C. *Langmuir* **1995**, *11*, 4703.

(9) Zhou, Z.; Chu, B.; Nace, V. M. *Langmuir* **1996**, *12*, No. 21, 5016.

(10) Zhou, Z.; Yang, Y.-W.; Booth, C.; Chu, B. *Macromolecules* **1996**, *29*, 8357.

(11) Liu, T.; Zhou, Z.; Wu, C.; Chu, B.; Schneider, D. K.; Nace, V. M. *J. Phys. Chem.* **1997**, *101*, 8074.

(12) Zhou, Z.; Chu, B. *Macromolecules* **1987**, *20*, 3089.

(13) Reddy, N. K.; Fordham, P. J.; Attwood, B.; Booth, C. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 1961.

(14) Provencher, S. W. *Makromol. Chem.* **1979**, 180, 210; *Comput. Phys. Commun.* **1982**, *27*, 213, 229.

(15) Wu, G.; Zhou, Z.; Chu, B. *Macromolecules* **1993**, *26*, 2117.

(16) Halperin, A. *Macromolecules* **1987**, *20*, 2943.

(17) Zhulina, E. B.; Birshtein, T. M. *Vysokomol. Soedin.* **1985**, *27*, 511.

(18) Bluhm, T. L.; Whitmore, M. D. *Can. J. Chem.* **1985**, *63*, 249.

(19) Whitmore, M. D.; Noolandi, J. *Macromolecules* **1985**, *18*, 657.

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