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Self-Assembly Characteristics of BEB-Type Triblock Copolymers

Zukang Zhou and Benjamin Chu*

Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11794-3400

V. Mark Nace

Dow Chemical Company, Texas Operations,
Freeport, Texas 77541-3257

Yung-Wei Yang and Colin Booth

Manchester Polymer Center, Departments of Chemistry and Pharmacy, University of Manchester,
Manchester M13 9PL, United Kingdom

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Introduction. Commercially available triblock copolymers of ethylene oxide (E) and propylene oxide (P), usually in the form of $E_mP_nE_m$, known as Pluronic polyols, have found diverse industrial applications.[1] In recent years, a great many fundamental studies have been devoted to the self-assembly and the structure characteristics of supramolecular particles, mostly in the form of polymeric micelles, for the EPE-type triblock copolymers in aqueous solution.[2] Of particular interest are the properties of such water-soluble triblock copolymers in a solvent which is selectively good for the *middle* block. If the selective solvent is water, the self-assembly behavior of $P_nE_mP_n$ triblock copolymers, known as reverse Pluronics or Pluronic R, has been reported.[3] Many PEP-type triblock copolymers will probably form flower-like micelles in water with an entropy-driven closed association mechanism. However, it is anticipated that when the middle E block becomes sufficiently long, the two end P blocks may not necessarily return to the *same* micellar core. Then, an extended network structure may result. The relationship between the self-assembly of block copolymers in solution and chain architecture can be extended to other types of longer-chain block copolymers, such as poly(*tert*-butylstyrene)-*block*-polystyrene-*block*-poly(*tert*-butylstyrene) (P(*t*-BS)−PS−P(*t*-BS)) in *N,N*-dimethylacetamide (DMA), which is a good solvent for the middle PS block[4] and poly(caprolactone)-*block*-poly(ethylene oxide)-*block*-poly(caprolactone).[5] Butylene oxide (B) is more hydrophobic than propylene oxide. Thus, a study of the micellization behavior of $B_nE_mB_n$ triblocks becomes of interest.

Experimental Procedures. $B_5E_{91}B_5$ and $B_6E_{46}B_6$ were received from Dow Chemical Co., while $B_{12}E_{260}B_{12}$ was prepared by the Manchester Polymer Center. In order to avoid the anomalous micellization behavior before the onset of critical micelle formation,[6] the $B_nE_mB_n$ triblocks were purified by hexane extraction.[7] The light scattering measurements and sample preparation were the same as described elsewhere.[6] The copolymer solutions at high concentrations (e.g., 10% (w/w)) were prepared by first dissolving the $B_nE_mB_n$ copolymer in water at low temperatures (e.g., 5 °C) in order to ensure complete solute dissolution. The copolymer solution was then filtered, since the presence of dust could interfere with light scattering experiments. The filtered solution was then brought to the desired temperature for a sufficiently long time to ensure that the association process has reached a dynamic equilibrium among the species (unimers, micelles, etc.) present. The CONTIN method was used to analyze the intensity−intensity time correlation function $G^{(2)}(\tau)$.[8] All the dynamic light scattering (DLS) experiments were performed at 25 °C.

Results and Discussion. Figure 1 shows plots of the intensity contribution function $\Gamma G(\Gamma)$ versus the apparent hydrodynamic radius for $B_5E_{91}B_5$ (hollow circles) and $B_6E_{46}B_6$ (filled circles) at three different concentrations: (a) 1% (w/w), (b) 5% (w/w), and (c) 10% (w/w), respectively. The fourth panel (d) in Figure 1 shows the association behavior of dilute $B_{12}E_{260}B_{12}$ solutions at 0.048% (w/w) (denoted by hollow circles) and 2% (w/w) (denoted by filled circles). The CONTIN method was used to analyze the first-order field correlation function $g^{(1)}(\tau)$ as determined by DLS where $G^{(2)}(\tau) = A(1 + \beta|g^{(1)}(\tau)|^2)$, with A and β being the background and a coherence factor, respectively.

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

where $G(\Gamma)$ is the normalized linewidth distribution and $\Gamma G(\Gamma)$ represents the intensity contribution of particles having a characteristic linewidth Γ with log Γ as the x-axis. By means of $\Gamma = Dq^2$ for translational diffusive motions and $D = kT/6\pi\eta R_h$ for Stokes−Einstein relation, the x-axis in Figure 1 has been transformed to an apparent hydrodynamic radius (R_h) whose interparticle interactions have been assumed to be negligible. In reality, such an assumption is invalid at high concentrations. It is used as an indicator for the apparent size, including interparticle interactions.

Several observations can be summarized as follows.

1. In dilute aqueous solutions with $C = 1\%$ (w/w) (see Figure 1a), $B_6E_{46}B_6$ forms micelles with an R_h value of about 6 nm in coexistence with single copolymer chains, while $B_5E_{91}B_5$ exists only as unimers; i.e., the micellization process is dominated by the hydrophobic B end blocks. Dynamic light scattering can also be used to characterize the size (R_h) distribution of $B_nE_mB_n$ triblocks, as shown typically for $B_5E_{91}B_5$ by hollow circles in Figure 1a.

2. In the intermediate concentration range (e.g., $C = 5\%$ (w/w); see Figure 1b), both $B_5E_{91}B_5$ and $B_6E_{46}B_6$ form a mixture of unimers and micelles. At the same solution concentration of 5% (w/w), the intensity contribution made by the unimers is greater for $B_5E_{91}B_5$, since $B_5E_{91}B_5$ has a larger critical micelle concentration (cmc) value. However, $B_5E_{91}B_5$ micelles show a broader size distribution as caused by the stronger tendency of forming branched associated structures. Similar conclusions can be drawn from Figure 1c with $C = 10\%$ (w/w), thus reinforcing our finding of the existence of some branched open structures, instead of well-defined flower-like micelles formed by the closed association process.

3. $B_{12}E_{246}B_{12}$ already forms micelles with $R_h = 12$ nm at concentrations as low as $C = 0.048\%$ (w/w). Interestingly, at $C = 2\%$ (w/w) secondary and tertiary associated structures, i.e., branched structures, are observed together with the primary micelles.

From the preliminary results above and the recent work[9,10] on $B_nE_mB_n$, we can conclude that the cmc depends mainly on the hydrophobic strength of the B end blocks. The cmc decreases strongly with increasing B end block length. However, in order to create polymer micelles with the two B end blocks of the same polymer chain not ending in the same micellar core, the middle E block should be sufficiently long. Appropriate open structures made up of $B_nE_mB_n$ triblock copolymers can

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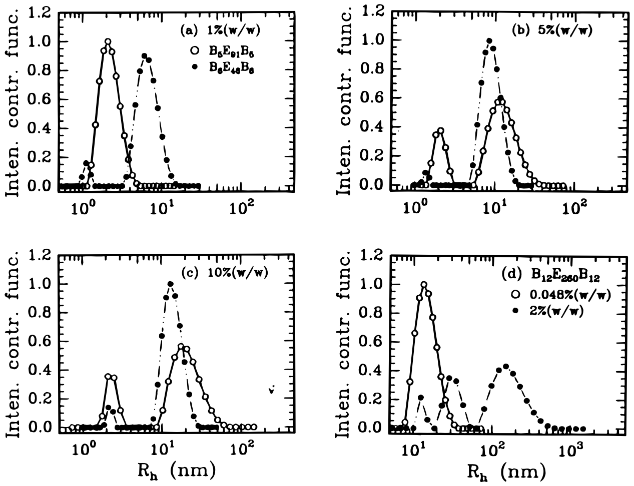

Figure 1. Plots of intensity contribution function ($\Gamma G(\Gamma)$) versus apparent hydrodynamic radius (R_h) of $B_nE_mB_n$ triblock copolymers in water at 25 °C.

indeed be designed. Further studies on the cmc, the critical micelle temperature, the clouding temperature, and the resultant phase diagram as well as the supramolecular structures produced by such self-assembled triblock copolymers are in progress.

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References and Notes

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