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Phase Behavior and Association Properties of Poly(oxypropylene)–Poly(oxyethylene)–Poly(oxypropylene) Triblock Copolymer in Aqueous Solution

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ABSTRACT: Static and dynamic light scattering and viscometry experiments were performed to study the phase behavior and association properties of a PEP-type (P and E represent poly(oxypropylene) and poly(oxyethylene), respectively) triblock copolymer, Pluronic R 17R4 [$(PO)_{14}(EO)_{24}(PO)_{14}$], in aqueous solution. While at room temperature, 17R4 exists in the form of single coils even at fairly high concentrations, this copolymer does form micelles in aqueous solution at elevated temperatures, thus exhibiting a temperature-induced micellization behavior similar to that of the EPE-type triblock copolymers. To study the effect of the chain architecture, 17R4 and L64 [$(EO)_{13}(PO)_{30}(EO)_{13}$] constitute a good pair of subjects for comparison, since they are very similar in chemical composition and are only slightly different in the total molecular weight. L64 forms micelles over large temperature and large concentration ranges, leaving a small corner for unimers at low temperatures and dilute concentrations. In strong contrast, 17R4 forms associated structures only at high copolymer concentrations within a narrow temperature region of a wedged shape. High critical micelle concentration but small aggregation number and small micellar radius are characteristics of 17R4 micelles formed in water. The entropy loss associated with the looping geometry of the middle poly(oxyethylene) block in micelle formation should be responsible for the largely reduced micellization ability of the 17R4 triblock copolymer in water. Interestingly, all the standard thermodynamic functions of micellization obtained for 17R4 are approximately only half as much as those for L64 in water.

Introduction

Block copolymers are of both academic and industrial importance. A large number of studies have been reported on the micelle formation and the structural characteristics of polymeric micelles for diblock and triblock copolymers in selective solvents. A solvent is considered as selective if it is a thermodynamically good solvent for one type of block but a nonsolvent for the other type of block. For triblock copolymers, the chain architecture is expected to have some noticeable influence on their association properties in solution. For example, when dissolved in the same selective solvent, triblock copolymers of the ABA and the BAB type may behave differently. On the one hand, it is now well recognized[1,2] that for symmetrical triblock copolymers in selective solvents that are good for the outer blocks, uniform spherical micelles are formed in dilute solution, with the insoluble block constituting a relatively compact core and the soluble blocks forming a swollen protective corona. In other words, the micellization process obeys the closed association mechanism. On the other hand, much less understanding has been achieved about the solution properties of triblock copolymers in solvents which are selectively good for the middle block. The answers, in either experimental or theoretical aspects, to the basic question whether or not associated structures are formed have been contradictory among the limited number of articles[3–9] available in the literature. For instance, some earlier work[4,5] reported no experimental evidence for the formation of polymolecular micelles, but several recent studies[6–8] argued that polymeric micelles were experimentally observed. In addition, some authors[7,9] proposed that branched or networklike structures due to the interchain association might exist in the semidilute region.

On the basis of their model calculation, ten Brinke and Hadziioannou[10] concluded that the entropy loss associated with the looping of the middle block would preclude the possibility of micelle formation. However, recently Balsara et al.[8] examined the calculation and claimed that the loss of entropy arising from the looped coronal blocks was overestimated and that with the necessary looping of the coronal blocks the micelle formation could still be expected under some conditions. Moreover, computer simulations on small symmetric triblock copolymers[11,12] in dilute solution showed that a variety of structures, including transitory aggregates, micelles with backfolding of the middle block, and branched assemblies, might occur, depending on the strength of net attractive interactions between the terminal blocks. Obviously, more experimental and theoretical work are needed to get a better understanding of the solution behavior of triblock copolymers in solvents selectively good for the middle block.

Among water-soluble block copolymers, Pluronic (poly(oxyethylene)–poly(oxypropylene)–poly(oxyethylene), abbreviated as EPE) and Pluronic R (poly(oxypropylene)–poly(oxyethylene)–poly(oxypropylene), abbreviated as PEP) series are of particular importance, because triblock copolymers of ethylene oxide and propylene oxide constitute a big family of important polymeric surfactants and have found widespread applications in different areas. A large number of fundamental and applied research have dealt with the micelle formation and the gelation behavior of the EPE-type triblock copolymers in aqueous media. However, to date, little is known about the solution properties of the PEP-type block copolymers.

In our laboratory in the past few years, we have performed a series of studies on the EPE-type triblock copolymers in solution, concentrating our attention mainly on (1) the temperature-induced micelle formation in aqueous medium,[13,15] (2) anomalous micellization and composition heterogeneity,[14,15,19] and (3) colloidal behavior of the ternary system xylene–$(EO)_{13}(PO)_{30}(EO)_{13}$–water,[16–18] including polymeric reverse micelles caused by

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the presence of water. The present work, as motivated by the largely unbalanced research efforts on these two classes of triblock copolymers, is aimed at studying the effect of chain architecture on association behavior, focusing on the colloidal properties of a PEP copolymer dissolved in water. In so doing, we need to compare the solution properties of the PEP- and EPE-type block copolymers of the same composition. Therefore, we have chosen Pluronic R 17R4 ($(PO)_{14}(EO)_{24}(PO)_{14}$) and Pluronic L64 ($(EO)_{13}(PO)_{30}(EO)_{13}$) as the subjects under comparison, because both of them have the same ethylene oxide content (40% by weight) and differ only slightly in the total chain length although the chemical nature of the middle block and the block length difference should be remembered. An additional reason is that in the literature some basic data have been reported on aqueous L64 solutions.[14,15,20-22] From the light scattering and viscosity results, we found that 17R4 does form micells at elevated temperatures in water, exhibiting a temperature-induced micellization behavior in the similar manner as L64 does. But the ability of 17R4 to form micelles in water is largely reduced, which can be attributed most likely to the entropic penalty associated with the looping geometry of the middle poly(oxyethylene) block.

Experimental Section

Materials and Solution Preparation. For our investigations, we used a Pluronic R 17R4 sample which was obtained as a gift from BASF Corp. This copolymer sample was used without further purification. 17R4 contains approximately 40% by weight oxyethylene units, having an average composition of $(PO)_{14}(EO)_{24}(PO)_{14}$ with a nominal molar mass of 2650 g/mol. The water used throughout was deionized and redistilled in an all-glass still. Like L64 solutions in water, aqueous solutions of 17R4 also show anomalous association behavior which manifests itself as a strong opalescent appearance before the onset of micellization. Correspondingly, on the scattered intensity–temperature curves of aqueous 17R4 solutions, in particular of higher concentrations, characteristic maxima were observed. The related peak region shifted to lower temperature with increasing copolymer concentration. As reported previously,[14,15] this kind of anomaly is due to the composition heterogeneity of the triblock copolymer used. A small portion of the copolymer specimen with a higher content of the insoluble block should be responsible for the anomalous behavior. As demonstrated in refs 14 and 15, such anomalous behavior disappeared if we had removed the minor "insoluble" portion by carrying out filtration in close vicinity to the maximum scattering temperature. Accordingly, the preparation of 17R4 solutions in water was made in the following way. 17R4 solutions at concentrations $C \geq 8.0 \times 10^{-2}$ g/mL that showed a profound anomalous scattering were prepared and filtered individually by using the Millipore VC membrane filter (0.1-μm pore size) at a selected temperature which led to a maximum scattered intensity for the unfiltered copolymer solution. For concentrations less than 8.0×10^{-2} g/mL, the 17R4 solutions were prepared by diluting a stock solution (C = 10% w/v) that had been filtered in advance at 41.5 °C to remove the minor "impurities". The weight loss due to filtration was usually about 1–2% of the copolymer and was taken into account in calculating the solution concentration. The light scattering cells (17-mm o.d.) with clarified solutions were flame-sealed under vacuum.

Viscosity Measurements. A modified Ubbelohde capillary viscometer was used to measure the solution viscosity. The temperature of the thermostat bath was controlled to within 0.02 °C. After the desired temperature was set, each solution was temperature-equilibrated for at least 20 min prior to viscosity measurements. An average flow time was taken for four to six consecutive measurements on the same copolymer solution to calculate the viscosity value. The solution density data which are necessary for determining solution viscosities were obtained by using a calibrated pycnometer.

Light Scattering Measurements. We used a standard, laboratory-built light scattering spectrometer[13] capable of both time-averaged scattered intensity and photon correlation spectroscopy measurements in an angular range of 15–140°. The scattering cell was held in a brass thermostat block filled with refractive index matching silicone oil, and the temperature was controlled to within ±0.02 °C. To obtain the absolute scattered light intensity, benzene was used as the reference standard. Intensity correlation function measurements were carried out in the self-beating mode by using a Brookhaven BI 2030AT 136-channel digital correlator. A Spectra-Physics Model 165 argon ion laser operating at 488 nm was employed as the light source. The detailed procedure of determining the translational diffusion coefficient (D) was the same as in ref 15. The cumulants[23] and CONTIN[24] methods were used for the data analysis of the dynamic light scattering results. Note that because of the ill-posed nature of the Laplace inversion involved, CONTIN gives the most probable solution among a number of fitted solutions.

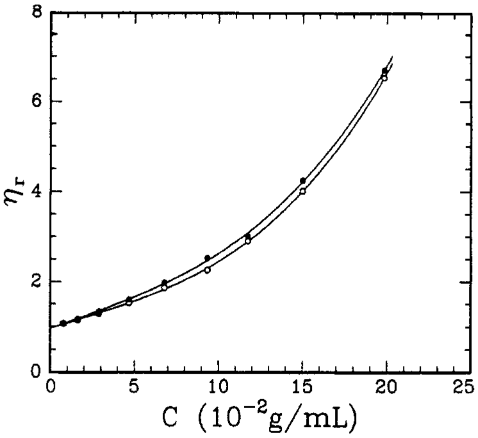

Figure 1. Plots of relative viscosity vs concentration for aqueous 17R4 solutions at 25.0 (filled circles) and 40.0 °C (open circles).

Since 17R4 and L64 are closely similar in their chemical composition except for the chain architecture, the dn/dC values for 17R4 solutions in water at 488 nm were assumed to be the same as those of L64 solutions,[15] namely, 0.140 and 0.136 cm^3/g at 25.0 and 40.0 °C, respectively.

Results and Discussion

In general, for block copolymers in selective solvents, the self-assembly process can be initiated either by an increase in concentration via the critical micelle concentration (cmc) or by changing the temeprature via the critical micelle temperature (cmt). In other words, by monitoring an appropriate property of the system of interest, an inflection point which corresponds to the cmc or cmt, can usually be found on the concentration curve or the temeprature curve. For convenience, here we first follow the concentration dependence approach at two different temperatures, i.e., 25.0 and 40.0 °C. Figure 1 shows the relative viscosities of 17R4 solutions at the two temperatures as a function of concentration. Two points are seen: (1) The slope, i.e., the viscosity increase rate, becomes increasingly larger with increasing concentration. However, the inflection point if any, in which we are interested, can hardly be determined even with large uncertainties. (2) The two viscosity curves have a common shape and differ only slightly in the magnitude. Accordingly, based on the viscosity behavior shown in Figure 1, it seems as if no significant structural change would occur in the copolymer solution by varying the temeprature from 25.0 to 40.0 °C. It is known that for the purpose of detecting occurrence of association or monitoring a variation in the aggregate size, light scattering possesses considerably higher sensitivity than viscometry. Figure 2 shows the concentration dependences of the scattered light intensity relative to that of benzene (25.0 °C) obtained at the two temperatures. By comparing part b of Figure 2 with part 1, a distinctive change in the scattering behavior

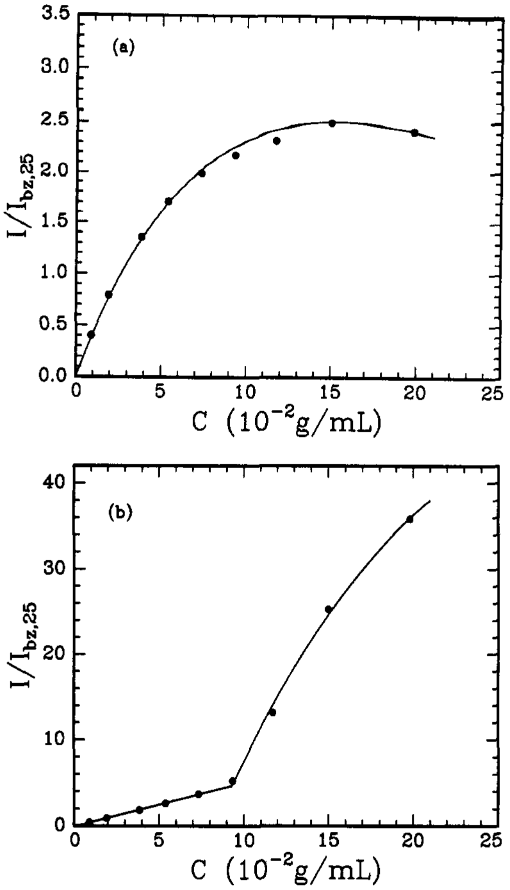

Figure 2. Plots of scattered light intensity relative to that of benzene at 25 °C vs concentration for 17R4 in water. (a) At 25.0 °C. The solid line represents the theoretical fit by using the hard-sphere model with R_{HS} = 1.0 nm. (b) At 40.0 °C. The inflection point yields a cmc value of 9.1 × 10^{-2} g/mL.

caused by an increase in temperature was observed, reflecting the formation of associated structures under certain temperature and concentration conditions. Again, two points are of interest: (1) At 25.0 °C, the scattering curve with a maximum is typical of a dispersion of hard-sphere particles with repulsive interactions between themselves, the size of which is independent of the solution concentration. Thus, the single coils of 17R4 can equivalently be viewed as hard spheres of constant size over the concentration range ($C \leq 0.2$ g/mL) studied. For 17R4 at 25.0 °C, as will be discussed later, its equivalent hard-sphere radius was estimated to be 1.0 nm. (2) At 40.0 °C, a sharp inflection (cmc) was found at $C \simeq 9.1 \times 10^{-2}$ g/mL, below which the scattered intensities observed were low and comparable to those obtained at 25.0 °C (note the difference in the intensity scale in parts a and b of Figure 2) and above which the scattering was markedly enhanced due to the formation of self-assembled structures, i.e., polymolecular micelles. In the following, we begin with the static and dynamic properties of 17R4 solutions in the unimer region. Such information is often necessary when we deal with the associated structures in the same system.

1. The Unimer Region. Static Light Scattering. Figure 3 shows the reduced scattered intensity results in the dilute solution region. For all the dilute solutions examined, the forward and backward scatterings were symmetrical, and thus, the excess scattered intensity at the 90° scattering angle was used. The weight-average molecular weight (M_w) and the second virial coefficient (A_2) were obtained by the relation

$$KC/R_{90} = 1/M_w + 2A_2C \qquad (1)$$

where K ($=4\pi n_0^2(\mathrm{d}n/\mathrm{d}C)^2/N_A\lambda_0^4$) is an optical constant with N_A, n_0, and λ_0 being Avogadro's number, the solvent refractive index, and the wavelength of light in vacuo, respectively. R_{90} is the excess Rayleigh ratio at a scattering angle 90° with vertically polarized incident and scattered light beams; C is the polymer concentration in grams per milliliter. The M_w and A_2 values obtained are summarized in Table 1. It is seen that the M_w values at 25.0 and 40.0 °C are identical as expected and that they are in good agreement with the nominal value of 2.65 × 10^3 g/mol, if we consider the influence of polydispersity which is often inevitable for commercially available copolymers. Note that for block copolymers which are heterogeneous in both molecular weight and composition, eq 1 yields an apparent molecular weight rather than a true weight-average molecular weight.[25] For the present system, however, the refractive indices of the two component blocks are close to each other, and therefore, eq 1 provides reliable information (to a few percent) on the weight-average molar mass concerned. Accordingly, when dissolved in water, the 17R4 diblock copolymer is molecularly dispersed in solution at both room temperature and the elevated temperature (40 °C).

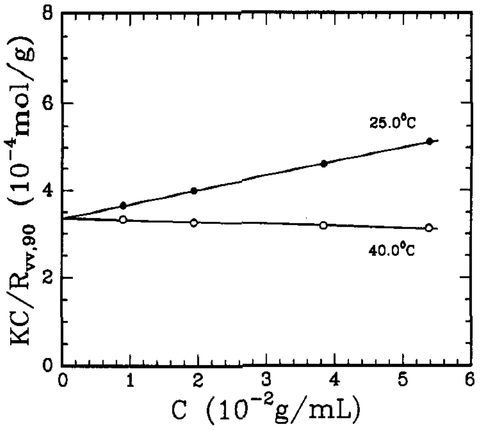

Figure 3. Plots of reduced scattered light intensity ($KC/R_{vv,90}$) vs concentration for 17R4 in water in the dilute region at 25.0 and 40.0 °C.

Table 1. Static and Dynamic Properties of the 17R4–Water System in Dilute Region

	25.0 °C	40.0 °C
molar mass, nominal, g/mol	2650	2650
M_w measd, g/mol	3.0×10^3	3.0×10^3
A_2, cm^3 mol g^{-2}	1.65×10^{-3}	-2.3×10^{-4}
R_{HS}, nm	1.0	
R'_{HS}, nm	1.1	
D_0, cm^2 s^{-1}	1.70×10^{-6}	2.53×10^{-6}
k_D, cm^3 g^{-1}	−3.1	−6.9
R_h, nm	1.5	1.4
[η], cm^3 g^{-1}	9.7	8.5
R_η, nm	1.6	1.5

For 17R4 in water, A_2, as a measure of polymer–solvent and segment–segment interactions, shows a strong temperature dependence as expected. As seen from Table 1, at 25.0 °C, A_2 has a large positive value of 1.65 × 10^{-3} cm^3 mol g^{-2}, meaning that remarkable solute–solvent interactions exist due to the hydrogen bond formation between ether oxygen atoms and water molecules. Alternatively, the strong repulsive interactions between the segments can explain why no micelles are formed at room temperature even for concentrated solutions of 17R4 in water. A small but negative A_2 value (= −2.3 × 10^{-4} cm^3 mol g^{-2}) was found at 40.0 °C, which suggests a profound enhancement of solute–solute interactions with increasing temperature. In the dilute region, such attractive interactions are, most likely, of *intrachain* nature, and consequently, unimers with a small contraction in the dimension were

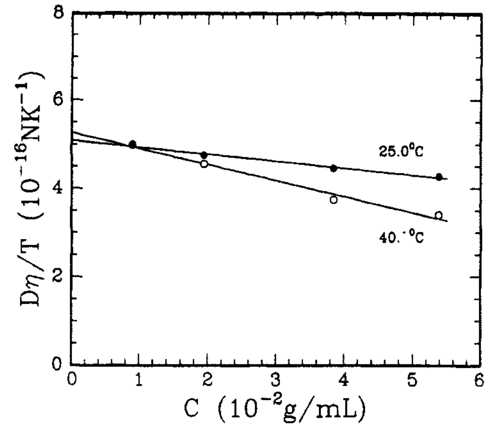

Figure 4. Plots of reduced diffusion coefficient ($=D\eta/T$) vs concentration for 17R4 in water in the dilute region at 25.0 and 40.0 °C.

experimentally observed at 40.0 °C, as will be described below. At high concentrations, the *interchain* attractive interactions become important, thus leading to the self-assembly phenomenon observed at 40.0 °C when a certain concentration threshold is exceeded.

Dynamic Light Scattering. Figure 4 shows the dynamic light scattering results at 25.0 and 40.0 °C in dilute solutions. The concentration dependence plots given in Figure 4 were obtained by using the cumulants analysis. In these plots, the reduced diffusion coefficient ($D_{\text{red}} = D\eta/T$, with η being the solvent viscosity) was used to take into account the viscosity variation with temperature when the Einstein–Stokes relation was employed for different temperatures

$$D = kT/6\pi\eta R_{\text{h}} \quad (2)$$

In so doing, the reciprocal intercept in Figure 4 is a direct measure of the particle size of interest. As shown in Table 1, the hydrodynamic radius (R_{h}) of 17R4 unimers at 40.0 °C has a value of 1.4 nm instead of the value 1.5 nm at 25.0 °C. This small but important difference confirms the above argument that the segment–segment interactions become increasingly important with increasing temperature and is also well consistent with the viscosity results, as will be discussed below. From the slope and intercept in Figure 4, the diffusion second virial coefficient (k_{D}) that accounts for the concentration dependence ($D = D_0(1 + k_{\text{D}}C)$) was found to be −3.1 and −6.9 cm^3/g at 25.0 and 40.0 °C, respectively. Qualitatively, these k_{D} values are in accordance with the relevant A_2 values of the unimers concerned.

Viscosity. Figure 5 shows the plots of reduced viscosity (η_{sp}/C) of dilute 17R4 solutions as a function of concentration. Another important parameter, i.e., intrinsic viscosity ([η]), serves as a measure of the hydrodynamic volume of a single particle in the solution under study. This characteristic physical quantity can be easily evaluated, for example, by extrapolating the reduced viscosity to infinite dilution based on the well-known Huggins equation

$$\eta_{\text{sp}}/C = [\eta] + k_{\text{H}}[\eta]^2C \quad (3a)$$

provided that the condition $[\eta]C < 1$ holds. Here k_{H} is the Huggins constant and its value depends, in most cases, on the solvent quality. The [η] values thus obtained were 9.7 and 8.6 cm^3/g at 25.0 and 40.0 °C, respectively. On the basis of the Kraemer equation

$$(\ln \eta_{\text{r}})/C = [\eta] - k_{\text{K}}[\eta]^2C \quad (3b)$$

plots of $(\ln \eta_{\text{r}})/C$ vs C are also given in Figure 5, yielding

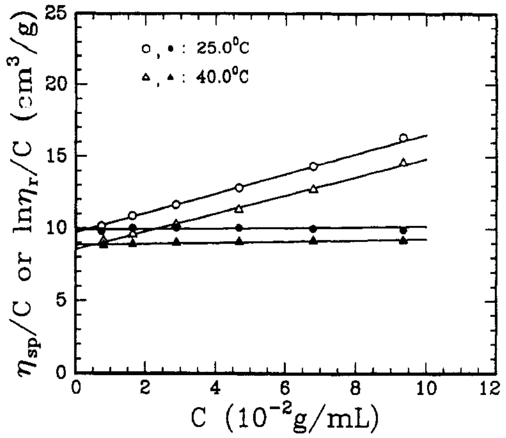

Figure 5. Plots of reduced viscosity or $(\ln \eta_{\text{r}})/C$ vs concentration for 17R4 in water in the dilute region at 25.0 and 40.0 °C.

[η] values of 9.9 and 8.8 cm^3/g at 25.0 and 40.0 °C, respectively. Assuming a sphere model, the viscometric hydrodynamic radius (R_η) can be estimated from the intrinsic viscosity data by using the expression

$$[\eta] = 10\pi R_\eta^{\,3}N_{\text{A}}/3M \quad (4)$$

Note that [η] belongs to the category of hydrodynamic properties, and therefore, R_η is the radius of spheres which are equivalent to the copolymer unimers with respect to their flow behavior. Here we also observed a small but noticeable contraction in R_η when the solution temperature was raised; namely, R_η was 1.6 and 1.5 nm at 25.0 and 40.0 °C, respectively.

Interestingly, for 17R4 in water, the Huggins slopes derived from Figure 5 have large values of 0.72 and 0.86 at 25.0 and 40.0 °C. In general, such influence of temperature on the k_{H} value is in line with the concept that the larger the Huggins slope, the more compact the coil structure is.[1,26] At the present moment, however, from these k_{H} values, it seems difficult to extract any kind of quantitative information concerning the 17R4–water system, since the theoretical interpretation of k_{H} is not yet available.

"Wet" Particle Size and "Dry" Particle Size. In dynamic light scattering measurements, the Brownian motion of the "wet" dispersed particles or "wet" macromolecules is monitored to provide the size information about the solvated colloidal particles or solvated polymer chains. The same wet nature also applies to the viscometric experiments, where the flow properties of solvated species are measured. In principle, the wet particle sizes obtained by different experimental techniques are expected to be close to each other, at least, for approximately symmetrical particles, although the location of the boundary that defines the motion of a particle relative to its surroundings may not be identical for different methods. An illustrative example is the above-mentioned R_{h} and R_η results, showing approximately the same values for 17R4 unimers, as listed in Table 1. On the other hand, in static light scattering measurements, the scattered light field monitored is a measure of the polarizability difference between the suspended particle or molecularly dispersed macromolecule and the surrounding medium. Thus, the information obtained concerns the "dry" dispersed particles. In brief, the "dynamic" approach yields the "wet" particle size and the "structural" approach gives the "dry" particle size. In some cases, knowing the ratio between them may provide information about the internal structure, e.g., the segment density distribution of the particles studied.

The scattering curve of the 17R4 solution at 25.0 °C, as shown in Figure 2a, can be used to deduce the dry particle size on the basis of the hard-sphere model. Assuming that the particles in the solutions at concentrations above the scattering maximum are the same as in the dilute solutions, the maximum and the consequent decrease of the scattered intensity can be attributed to the more rapid decrease of the structure factor as compared with the increase in concentration. By using the Percus and Yevick approximation,[27] the structure factor ($S(q)$) at zero scattering angle is related to the volume fraction of the hard spheres by the expression

$$S(q = 0) = (1 - \phi)^4/(1 + 2\phi)^2 \qquad (5)$$

where q $(=(4\pi n/\lambda_0)\sin(\theta/2))$ is the magnitude of the scattering vector. The volume fraction (ϕ) can be calculated from the solute concentration with the relation $\phi = 4\pi R_{HS}{}^3 N_A C/(3M)$. Thus, R_{HS} can be estimated through the theoretical fit to the experimental scattered intensity–concentration curve by using the hard-sphere approximation. In Figure 2a, the solid line is the theoretical fit, yielding a R_{HS} value of 1.0 nm. Consequently, at 25.0 °C, the single coils of 17R4 in water can be viewed as hard spheres of 2.0 nm in size with an equivalent scattering behavior. This dry particle size seems quite reasonable as compared to the wet size of about 3.0 nm.

The second virial coefficient obtained from the static light scattering experiments may provide another approach to estimate the dry particle size. For a dispersion of ideal hard spheres, A_2 is given by the expression

$$A_2 = 4N_A V/M^2 \qquad (6)$$

where V is the excluded volume of a spherical particle. For 17R4 in water, to a first approximation, an equivalent hard-sphere radius (R'_{HS}) can be used to calculate the excluded volume; i.e., $V = 4\pi R'_{HS}{}^3/3$. Thus, based on the A_2 value at 25.0 °C given in Table 1, we obtain $R'_{HS} = 1.1$ nm which is in good agreement with the R_{HS} value derived from the hard-sphere-model fitting over a broad concentration range.

Table 1 summarizes static and dynamic properties of the 17R4–water system in the unimer region.

2. Phase Behavior. Critical Micelle Temperature and Critical Micelle Concentration. For 17R4 in water, it is important to define experimentally the one-phase micelle region in the concentration–temperature diagram. By following the temperature dependence of the integrated scattered light intensity of a copolymer solution at a given concentration, one can determine the critical micelle temperature where a distinct change in scattered intensity takes place over a relatively narrow temperature interval. For a heat-induced micellization process, such as in the aqueous 17R4 solution, only unimers are practically present below the cmt. Above the cmt, micelle formation becomes increasingly important. Figure 6 shows a typical semilogarithmic plot of the excess scattered intensity extrapolated to zero scattering angle against temperature for a concentrated 17R4 solution with $C = 1.50 \times 10^{-1}$ g/mL. For block copolymers, as we discussed elsewhere,[13] a certain transition region rather than a sharp inflection on the temperature curve can often be expected. Nevertheless, the cmt value can be steadily estimated from the intersection of two straight-line portions, as shown in Figure 6. The cmt value thus obtained for the above solution was 37.0 °C. We also examined in a similar manner three other 17R4 solutions with $C = 9.93 \times 10^{-2}$, 1.17×10^{-1}, and 1.98×10^{-1} g/mL, and the cmt values were found to be 39.7, 38.4, and 34.6 °C, respectively. In the meantime, we may consider the solution concentration associated with each of these *cmts* as the critical micelle concentration at that temperature. Very importantly, like EPE block copolymers in water, for aqueous 17R4 solutions, the cmt shifts to a lower value with increasing concentration and the cmc shifts to a higher value with decreasing temperature.

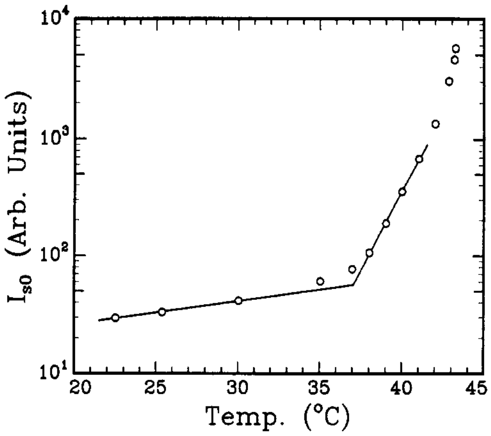

Figure 6. Semilogarithmic plot of the excess scattered intensity extrapolated to zero scattering angle (in arbitrary units) vs temperature for an aqueous 17R4 solution with $C = 1.50 \times 10^{-1}$ g/mL. The intersection of two straight lines defines the critical micelle temperature with a value of 37.0 °C.

Thermodynamic Functions of Micellization. For a closed association mechanism with relatively large aggregation number and a narrow distribution, the standard free energy and standard enthalpy of micelle formation ($\Delta G°$ and $\Delta H°$, per mole of the solute in the micelle) are related to the critical micelle concentration and its temperature dependence in the form[28]

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

$$\Delta H° = R[\text{d}\ln(\text{cmc})/\text{d}(1/T)] \qquad (8)$$

where the cmc is in molar concentration; the two standard states are the polymer molecules and micelles in ideally dilute solution at unity molarity. Equation 8 can be integrated to yield

$$\ln(\text{cmc}) \simeq \Delta H°/RT + \text{constant} \qquad (9)$$

provided that the $\Delta H°$ is approximately a constant in the temperature interval involved. For 17R4 in water, Figure 7a shows the linear plot obtained on the basis of eq 9. From the slope, the standard enthalpy of micellization between 35 and 40 °C was found to be 115 ± 6 kJ/mol. The other standard thermodynamic quantities at 40 °C were $\Delta G° = -9$ kJ/mol and $T\Delta S° = 124$ kJ/mol.

Figure 7b shows a similar reciprocal temperature dependence plot of cmc for L64 in water but displays a larger slope. To make this plot, the cmt values of 28, 30, and 33 °C for the concentrations of 20, 10, and 5 mg/mL (denoted by open symbols and obtained by scattered light intensity measurements) were taken from ref 22, and the cmc values of 7.1, 2.8, and 0.9 mg/mL at 27.0, 34.5, and 40.0 °C (filled symbols, from surface tension measurements) were quoted from ref 20. It appears that for aqueous L64 solutions, these two sets of micellization data from different sources with different experimental methods are basically consistent with each other except for the cmc data at 27 °C. Thus, the slope in Figure 7b yields $\Delta H° = 210 \pm 11$ kJ/mol. At 40 °C, $\Delta G°$ and $T\Delta S°$ were estimated to be −21 and 231 kJ/mol, respectively. By making a comparison of these thermodynamic quantities between 17R4 and L64, we can reach the following important conclusions:

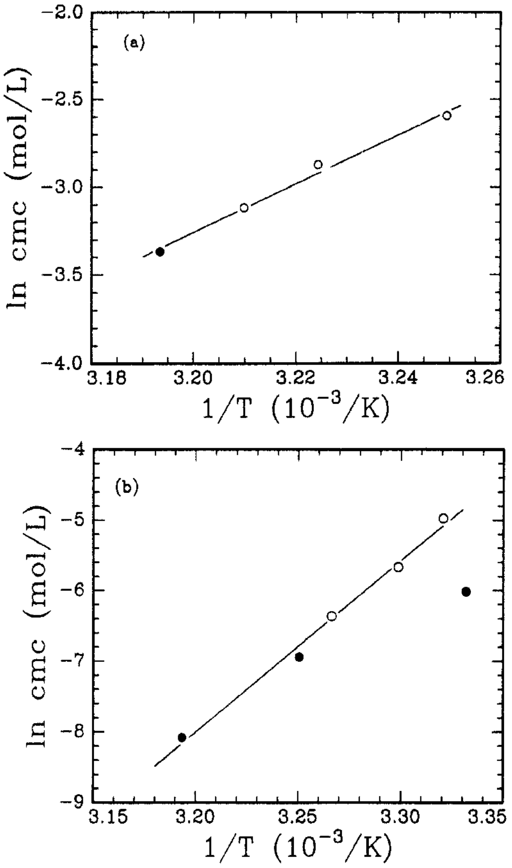

Figure 7. Plots of the logarithmic critical micelle concentration against the reciprocal of the absolute temperature. The least-squares fit yields $\Delta H°$. (a) 17R4 in water with $\Delta H° = 115 \pm 6$ kJ/mol. Open circles denote the cmt values, and the filled circle represents the cmc value. (b) L64 in water with $\Delta H° = 210 \pm 11$ kJ/mol. The cmc data (filled symbols) were taken from ref 20 and the cmt data (open symbols) from ref 22.

1. For both L64 and 17R4 in an aqueous medium, the micelle formation is an endothermic process as expected, which accounts for the fact that the cmc becomes smaller when the temperature is increased.

2. Hydrophobic interactions of entropy origin that are associated with the hydrophobic poly(oxypropylene) blocks in an aqueous environment are mainly responsible for the micelle formation, meaning that the micellization process is entropy driven.

3. For 17R4 in water, the entropy loss arising from the looping geometry of the middle poly(oxyethylene) block may largely reduce the above driving force for micellization. As a result, the free energy of micellization becomes much less negative, being about −9 kJ/mol at 40 °C as compared with $\Delta G° = -21$ kJ/mol for L64. Correspondingly, the critical micelle concentration of 17R4 at this temperature, the reciprocal of which may serve as a measure of micellization ability, is significantly greater than that of L64, namely, by a factor of about 100.

4. Interestingly, all the standard thermodynamic functions obtained for the micelle formation of 17R4 in water are approximately half as much as those for L64 in water. This seems likely not to be fortuitous, but some physical reasons stand behind. In this connection, pertinent theoretical work is needed to give quantitative or semi-quantitative evaluations on the effect of chain architecture on the association properties.

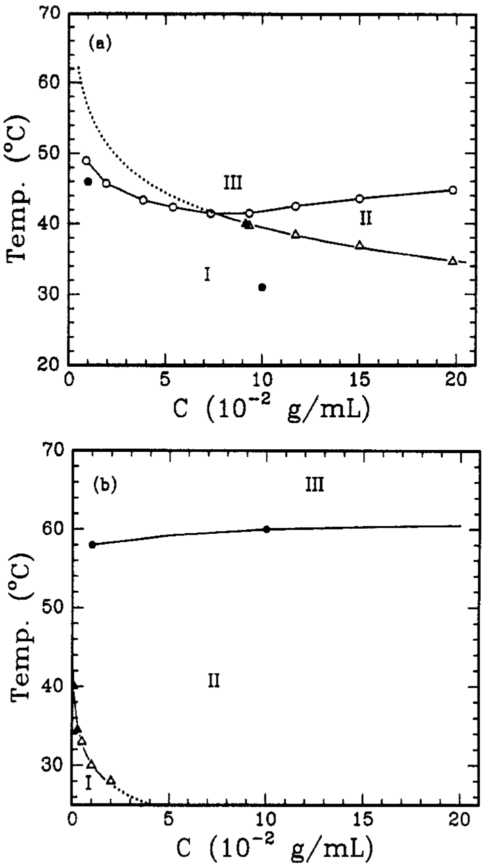

Figure 8. (a) Phase diagram of 17R4 in water. Regions I, II, and III are the one-phase unimer region, one-phase micelle region, and two-phase region of two immiscible isotropic solutions, respectively. (b) Phase diagram of L64 in water. Also, three phase regions are shown. See text for an explanation of the symbols and curves.

Phase Diagrams of 17R4 in Water and L64 in Water. The phase diagram of the 17R4–water system is shown in Figure 8a. In analogy to conventional nonionic surfactants, this binary system exhibits a coexistence curve with a lower consolution point at $T_c = 41.45$ °C and $C_c \approx 7.3 \times 10^{-2}$ g/mL. In the concentration–temperature plane, as will be discussed later, this consolute curve separates the one-phase molecular region or micellar region from the region where two immiscible (isotropic) solutions are present. It is known that for a critical binary mixture, direct measurements of the coexistence curve are not a simple task. For example, the accurate determination of the phase boundaries or the coexistence temperature is influenced by the kinetics of phase separation, which in turn depend on the rate of temperature change. Therefore, great caution should be exercised to avoid overshooting the two-phase boundary. In nonionic surfactant literature, one can often use the cloud-point curve to characterize the phase separation behavior in the C–T plane. In this work, for the purpose of determining the cloud point, the sudden variation of transmission or turbidity of the sample solution was monitored with a laser beam by slowly approaching the phase transition temperature. The temperature interval where an abrupt decrease in the transmission was observed was rather narrow and depended slightly on the rate of the temperature change. The midpoint or the end point of this transition was then defined as the cloud-point temperature. The uncertainty was estimated to be about 0.05 °C.

In Figure 8a, the cloud-point temperatures experimentally measured on 17R4 solutions are denoted by open circles. As reported in a BASF brochure,[29] the cloud points of 1% and 10% aqueous 17R4 solutions are 46 and 31 °C. They are shown in Figure 8a by filled circles. Figure 8a also shows the relevant cmt data (open triangles) and cmc data (filled triangle) to be connected by a solid line which represents the fitting results given in Figure 7a by the use of eq 9 with $\Delta H^\circ = 115$ kJ/mol. The dotted line represents an extension of the solid line to the dilute solution region where we have assumed that the two physical quantities in eq 9 (ΔH° and constant) have the same values as those determined in concentrated 17R4 solutions. Although such an assumption is somewhat oversimplified, it does not influence the conclusions to be drawn from the discussion presented below. As far as the phase behavior is concerned, it appears that, depending on the concentration and the temperature ranges involved, there exist three regions of interest, namely, the one-phase unimer region (region I), the one-phase micelle region (region II), and the two-phase region where two immiscible (isotropic) solutions are observed (region III).

17R4 and L64 are very similar in chemical composition and have only a small difference of about 9% in the total molar mass. Therefore, they constitute a good pair of subjects for comparison to study the effect of chain architecture on phase behavior and association properties. Figure 8b shows the phase diagram of L64 in water. The upper line is the cloud-point curve obtained on the basis of the manufacturer's technical data[29] and the knowledge that for concentrated L64 solutions in water the cloud-point temperature is weakly dependent on concentration. At the left-bottom corner of Figure 8b, there exists a small unimer region (region I) separated from the large micellar region (region II) by a solid curve that connects the experimental cmt and cmc values (denoted by open and filled triangles, respectively) as given in Figure 7b. A dotted line is drawn as an extension of the solid curve by using the same assumptions as described above.

On the basis of the comparisons made between parts a and b of Figure 8, several important points can be summarized as follows:

1. The phase behavior of L64 in water is relatively simple. Below the cloud-point curve, as illustrated by the extensive region II, L64 forms micelles over a large temperature range as well as a large concentration range. Unimers exist only in a small restricted area, mainly, at low temperatures and in dilute solutions. Note that the self-assembly of unimers into the micelle takes place at a lower concentration when the temperature is raised and at a lower temperature when the concentration is increased. This is typical of an entropy-driven micellization process. As reported elsewhere,[15,20-22] in region II, L64 micelles grow. The aggregation number and the micellar size increase with increasing temperature.

2. The phase behavior of 17R4 in water and its tendency toward self-assembly differ dramatically from those of L64, meaning that for triblock copolymers, the construction sequence of blocks has significant influence on their solution properties. In strong contrast to L64, the 17R4 unimer region extends over a broad concentration range and a large temperature range. But 17R4 forms micelles only at high concentrations ($C > 7.5 \times 10^{-2}$ g/mL) within a narrow, wedged-shape temperature range, the width of which expands moderately with increasing concentration. Moreover, the location of the cloud-point curve in the neighborhood of an intermediate temperature (~42 °C) largely restricts the effective temperature range of the micelle region. For instance, even at the highest concentration (C = 20% (w/v)) employed in this work, a temperature interval of only 10 °C is in effect. In the dilute region (e.g., $C < 7.5 \times 10^{-2}$ g/mL), when raising the temperature, we first meet the cloud-point curve rather than the cmt curve, and thereby, the formation of micelles becomes completely impossible, no matter whatever temperature has been selected.

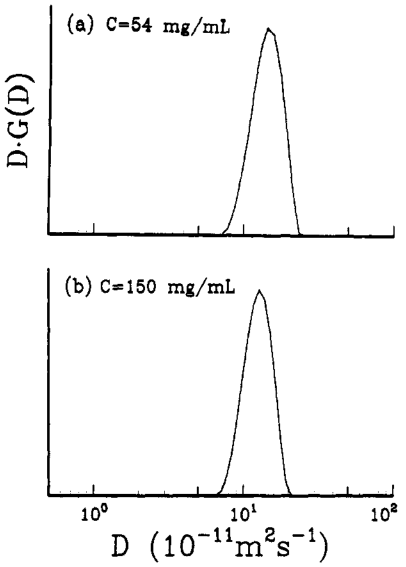

Figure 9. Relaxation rate distributions at 25.0 °C obtained by the CONTIN analysis of the intensity correlation function for aqueous 17R4 solutions of the indicated concentrations. In each case, only a narrow unimer peak was observed.

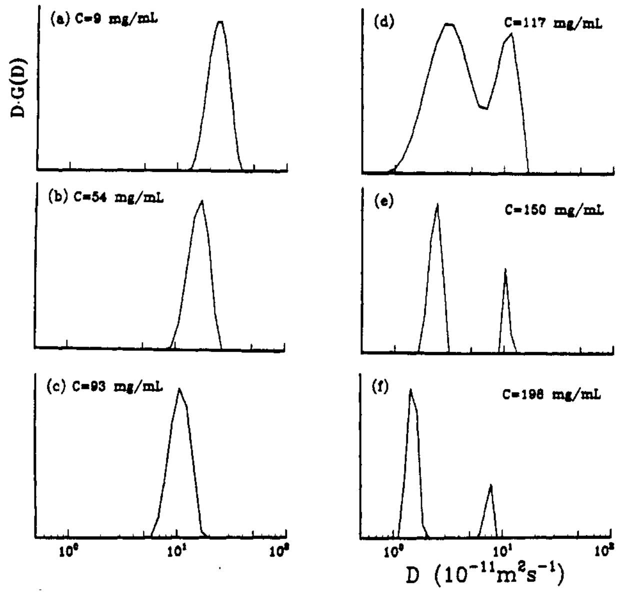

Figure 10. Relaxation rate distributions at 40.0 °C for 17R4 in water at different concentrations. Below or around the cmc, single unimer peaks were observed. Above the cmc, bimodal distributions were found. The peak area represents the scattered intensity contribution.

3. For 17R4 in water, region II consists of a mixture of unimers and micelles in equilibrium. This dynamic equilibrium shifts in favor of micelle formation when the concentration is increased. Figures 9 and 10 show the results of the CONTIN analysis obtained for 17R4 in water at a scattering angle of 35° at 25.0 and 40.0 °C, respectively. These relaxation rate distributions expressed in terms of D clearly demonstrate the features characteristic of the unimer region I and the micelle region II as shown in Figure 8a, respectively. Note that the distribution function $DG(D)$ is expressed in arbitrary units but normalized to the highest value at each concentration in order to facilitate a more meaningful comparison.[30] As shown in Figure 9, at 25.0 °C, the relaxation rate distributions at the two concentrations studied ($C = 5.4 \times 10^{-2}$ and 1.50×10^{-1} g/mL) reveal a narrow peak with a similar peak position in each case, which corresponds exactly to that of unimers, if the effect of interparticle interactions at a finite concentration has been taken into account. From Figure

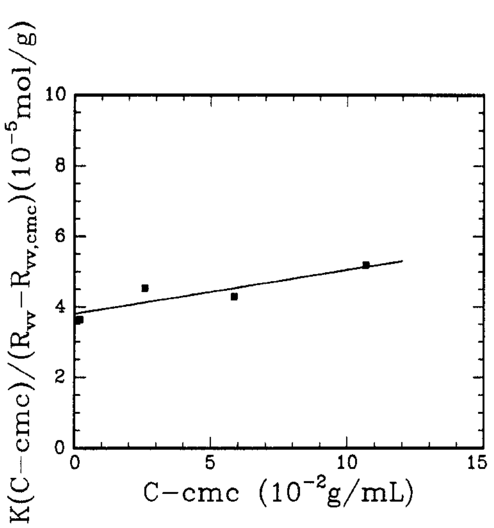

Figure 11. Plot of reduced scattered intensity at 40.0 °C with the cmc background scattering subtracted vs micelle concentration for 17R4 micelles in water.

10, two points are clearly seen: (1) At 40.0 °C and either below or around the cmc (~9.1 × 10^{-2} g/mL), for all three concentrations tested, a narrow unimer peak was observed, with the peak position shifting toward smaller mean diffusion coefficient with increasing concentration because of the negative k_D, as expected. (2) At the same temperature but above the cmc, a bimodal distribution was initiated at C = 1.17 × 10^{-1} g/mL. A further increase in concentration led to an increasing relative proportion of the slow micelle peak, because the peak area is a measure of the scattering intensity contribution. Thus, the results given in Figure 10 confirm the concept that for the 17R4–water system, a dynamic equilibrium exists in the micelle region II, meaning that due to the high cmc background, the amount of unimers in equilibrium with micelles cannot be neglected even at high copolymer concentrations.

4. The cloud points reported for 17R4 solutions in ref 29 are lower, especially at high concentrations, than those obtained in the present study. Most likely, this could be attributed to the influence of minor "impurities", which are often inevitable for commercial products. The difference also tells the importance of removal of minor "insoluble" components for proper research work on block copolymers.

3. The Micelle Region. As mentioned above, region II in Figure 8a consists of a mixture of unimers and micelles in equilibrium. To a first approximation, we may consider that as the total copolymer concentration increases above the cmc, the amount of unimers remains essentially constant. Accordingly, the micelle concentration is obtained by subtracting the cmc as background from the total concentration. In the case of small micelles, for which the intramolecular interference is absent, the Debye relation applies in the dilute region in the form

$$K(C - \mathrm{cmc})/(R_{vv} - R_{vv,\mathrm{cmc}}) = 1/M_w + 2A_2(C - \mathrm{cmc}) \quad (10)$$

where K is an optical constant as defined before. Here the dn/dC of micelles is considered to be the same as that of the molecularly dissolved solution. As shown in Figure 11, at 40 °C, by extrapolating the scattered intensity data to zero micelle concentration, we obtained a weight-average micellar molar mass of 2.65 × 10^4 g/mol. Thus, the aggregation number is about 10. From the slope, A_2 was determined to be ~6 × 10^{-5} cm^3 mol g^{-2}.

As described above, in Figure 10, the slow peaks observed at 40.0 °C above the cmc correspond to the micelle species. To eliminate the intermicellar interactions, the mean slow diffusion coefficient was plotted against the micelle concentration in order to obtain the micellar diffusion coefficient at infinite dilution, as shown in Figure 12. Furthermore, the hydrodynamic radius of 17R4 micelles at 40.0 °C was determined to be 4.0 nm by using the Einstein–Stokes relation (eq 2). Note that here the viscosity of the cmc solution at the given temperature should be used, because it serves as the background medium.

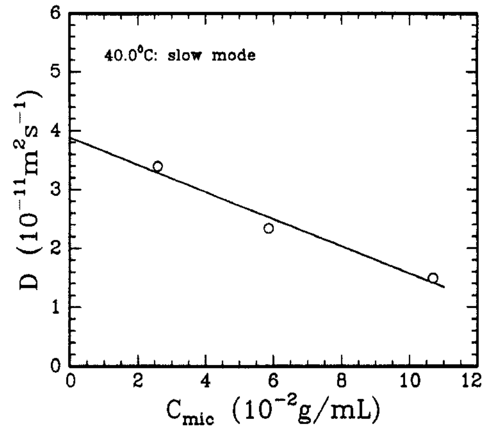

Figure 12. Plot of the mean diffusion coefficient associated with the slow micelle peak given in Figure 10 as a function of micelle concentration for 17R4 micelles in water.

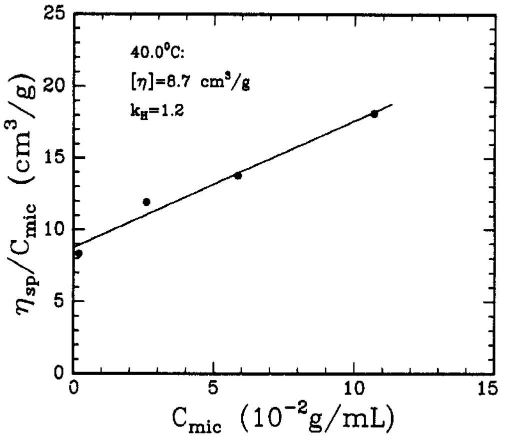

Figure 13. Plot of reduced viscosity of 17R4 micellar solutions vs micelle concentration at 40.0 °C.

Based on the same principle, the Huggins equation may also apply to 17R4 micellar solutions. To calculate correctly the reduced viscosity, the viscosity of the cmc solution was used instead of the solvent viscosity and the micelle concentration was taken to replace the total concentration. In this way, the intrinsic viscosity of 17R4 micelles at 40.0 °C was found to be 8.7 cm^3/g and the Huggins constant was 1.2, as shown in Figure 13. By use of eq 4, for 17R4 micelles at 40 °C, the viscometric hydrodynamic radius was calculated to be 3.3 nm, comparable to the above R_h value of 4.0 nm.

To summarize the effect of the chain architecture, Table 2 gives a detailed comparison of micellar parameters between 17R4 and L64 micelles, including the thermodynamic quantities of the micellization process.

Conclusions

It is known that in comparison with conventional surfactants, block copolymers are often less well-defined in composition homogeneity. This may cause complex states of aggregation in solution. In the present study, careful attention has been paid to this issue by taking

Table 2. Comparison in Micellar Parameters between 17R4 and L64 Micelles in Water

	Pluronic L64	Pluronic R 17R4
composition	$(EO)_{13}(PO)_{30}(EO)_{13}$	$(PO)_{14}(EO)_{24}(PO)_{14}$
HLB value	15	7–12
cmc at 40 °C, g/mL	9.0×10^{-4} [a]	9.1×10^{-2}
M_w, g/mol	2.8×10^{5} (42.5 °C)[b]	2.65×10^{4} (40.0 °C)
aggregation no.	88 (42.5 °C)[b]	10 (40.0 °C)
A_2, cm^3 mol g^{-2}	$\sim 6.0 \times 10^{-4}$ (42.5 °C)[b]	$\sim 6 \times 10^{-5}$ (40.0 °C)
R_h, nm	10.2 (42.5 °C)[b]	4.0 (40.0 °C)
ΔH^0, kJ/mol	210	115
ΔG^0 at 40 °C, kJ/mol	−21	−9
ΔS^0 at 40 °C, kJ/(mol K)	0.74	0.40

[a] Taken from ref 20. [b] Taken from ref 15.

advantage of our many years of experience in handling the anomalous association behavior originating from copolymer composition heterogeneity. When dissolved in water, both 17R4 (PEP sequence) and L64 (EPE sequence) reveal a one-phase unimer region, a one-phase micelle region, and a two-phase region of two immiscible solutions in the concentration–temperature plane. However, they behave quite differently concerning their association ability in solution. The main differences are as follows: (1) While L64 forms micelles over extended temperature and concentration ranges with only a small restricted *T–C* area for the unimers to exist, 17R4 undertakes an inverse "principle": a small *T–C* region of micelles but a large region for unimers. (2) The entropy penalty associated with the looping geometry of the solvent-affinitive middle block may largely reduce the tendency toward self-assembly, in particular, if the micellization process itself is entropy-driven but not enthalpy-driven. Even in this case, the possibility of micelle formation is not necessarily precluded, but the self-assembling tendency is, to a large extent, weakened. (3) As a result, L64 and 17R4 show remarkable differences in their micellar parameters. For instance, at 40 °C, 17R4 has a cmc value 100 times larger than L64, but the aggregation number is 9 times less.

Close to completion of this manuscript preparation, an interesting article[31] appeared in the current issue of this journal, using the mean-field lattice theory to treat theoretically the association behavior of Pluronic block copolymers in aqueous solution. By completing model calculations on the diblock (EP) and the two triblocks (EPE and PEP) with the same composition as that of Pluronic P105, i.e., $(EO)_{74}(PO)_{56}$, the author concluded that the PEP only forms micelles within a narrow temperature range and only at high concentrations and that EPE (Pluronic 105) and PEP differ in the cmc by a factor of 2. It was also predicted that PEP forms larger micelles than EPE, although among three of them the cmc of PEP is the largest. It seems that our experimental results on 17R4 partially support these predictions. A close collaboration between synthesis chemist (well-defined samples of designed composition and structure), experimentalist (high-quality conclusive data by different techniques), and theoretician (establishing a model capable of properly catching and predicting the key points of interest) will, no doubt, speed up our understanding of this interesting field.

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