Cloud-Point Temperatures of $B_nE_mB_n$ and $P_nE_mP_n$ Type Triblock Copolymers in Aqueous Solution

Tianbo Liu,[†] Vaughn M. Nace,[‡] and Benjamin Chu*,[†,§]

Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11794-3400; The Dow Chemical Company, Freeport, Texas 77541; and Department of Material Sciences and Engineering, State University of New York at Stony Brook, Stony Brook, New York 11794-2275

The cloud-point temperatures (T_{cl}) of 1 wt % poly(oxybutylene)−poly(oxyethylene)−poly(oxybutylene) ($B_nE_mB_n$) and of 1 wt % poly(oxypropylene)−poly(oxyethylene)−poly(oxypropylene) ($P_nE_mP_n$) were measured by detecting the sharp decrease in transmittance of the incident laser beam when phase separation occurs. The cloud-point temperatures were studied as a function of the length of both hydrophobic and hydrophilic blocks. A linear increase in the hydrophobic block length (B or P) leads to an exponential decrease in the cloud-point temperature. However, the middle hydrophilic block (E) shows only a weak positive effect; i.e., an exponential increase in the block length leads to a linear increase in the cloud-point temperature. On the basis of the available data, we can summarize our results in mathematical form and present a three-dimensional plot to predict the T_{cl} of $B_nE_mB_n$ (or $P_nE_mP_n$) triblock copolymers. The middle E block has a stronger effect on $P_nE_mP_n$ than $B_nE_mB_n$. It is also noted that one oxybutylene (B) unit has the effect equivalent to about 4.4 oxypropylene (P) units.

Introduction

The association and phase behavior of block copolymers have attracted a great deal of attention in recent years.[1,2] The study of polyoxyalkylene triblock copolymers in aqueous solution, including $E_nP_mE_n$, $P_nE_mP_n$, $E_nB_mE_n$, and $B_nE_mB_n$ type block copolymers, where E, P, and B represent oxyethylene, oxypropylene, and oxybutylene units, respectively, has led to the results that the triblock copolymers can form different micellar structures. Starlike micelles form the common association structure for block copolymers having a hydrophobic block (P or B block) in the middle, and flowerlike micelles can be expected with the hydrophilic E middle block forming a looping structure.

In comparison with the extensive systematic study on the micellization of triblock copolymers, studies of the phase behavior of these systems show more complexity, including several well-characterized phase diagrams.[3−7] However, the results have not yet reached the stage where general conclusions can be summarized.

The polyoxyalkylene surfactants have been used successfully in pharmaceutical and cosmetic industries. Their utilization can be correlated with the corresponding phase behavior in water. A brief and typical phase diagram for Pluronic F127 ($E_{99}P_{69}E_{99}$) in water was presented by Malmsten and Lindman.[3] Three major regions were found: a gel state, a solution state (including unimer solution and micellar solution), and a two-phase region at higher temperatures.

Low molecular weight polyoxyalkylene surfactants usually show a lower consolute temperature which can be identified as the cloud-point temperature, where the one-phase solution is separated into a dilute surfactant solution and some larger, insoluble polymer aggregates in suspension. The cloud-point temperature (T_{cl}) depends only weakly on polymer concentration, usually having the T_{cl} values equal to no more than a few °C higher at either lower (0.01 wt %) or higher (10 wt %) polymer concentrations. The lowest value of T_{cl} usually appears between one and several weight percent polymer concentration. The T_{cl} of 1 wt % polymer solution represents a typical value, and therefore such data have been widely reported in the literature as well as in industrial commercial reports.

The most widely known phase behavior of polyethylene-containing block copolymers are those of the polyethylene alkyl ether type C_nE_m,[8] where C represents the alkyl block. For such diblock copolymers, the values of n and m can be well-defined and altered during their synthesis. Therefore, a systematic change of the surfactant chemical structure can be made in order to assess the influence of some important factors, like the alkyl chain conformation and headgroup (E block) area, on the structure and stability of the mesophases formed.

Theoretical approaches on the effects of block lengths on the T_{cl} of block copolymers in solution have also drawn some attention. On the basis of the Flory−Huggins theory, Solc recently presented theoretical expressions for the phase separation of block copolymers in solution.[9] The author concluded that the effect of compositional heterogeneity in block copolymers is stronger than that of chain-length heterogeneity.

In this paper, we try to summarize the available experimental T_{cl} data for 1 wt % $B_nE_mB_n$ and $P_nE_mP_n$ type triblock copolymers in aqueous solution. Some of the data for $B_nE_mB_n$ block copolymers were reported by Yang et al.,[10] Zhou et al.,[11−13] and us.[14] Others came from our recent measurements. At this time, we present our discussions without considering the effects of polydispersity on the values of T_{cl}. By comparing the thermodynamic parameters of micellization, some discussions on the equivalent hydrophobicity between the end B block and the end P block are also presented.

Experimental Section

Preparation and Characterization of Samples. The synthesis procedure of $B_5E_{91}B_5$,[12] $B_6E_{46}B_6$,[14] and $B_{12}E_{260}B_{12}$[13] triblock copolymers has been reported in earlier publications.

---

* To whom the correspondence should be addressed.

† Department of Chemistry, State University of New York at Stoney Brook.

‡ The Dow Chemical Company, Texas Operations Research and Development.

§ Department of Materials Science and Engineering, State University of New York at Stony Brook.

⊗ Abstract published in *Advance ACS Abstracts,* September 1, 1997.

TABLE 1: Synthesis Conditions for Several $B_nE_mB_n$ Triblock Copolymers

	$B_7E_{22}B_7$	$B_6E_{10}B_6$	$B_{10}E_{15}B_{10}$	$B_{10}E_{271}B_{10}$	$B_{20}E_{29}B_{20}$	$B_{23}E_{68}B_{23}$
propylene glycol (g)	102	351	225	394	135	70
KOH (g)	5.9	21.0	13.2	23.3	8.1	4.3
EO (g)	1270	1760	1840	4390	2360	3260
amount of intermediate removed (g)	232	1014	244	198	1667	2252
intermediate remaining in reactor (g)	1146	1118	1834	4609	836	1082
intermediate molecular weight (g/mol)	971	444	659	1.19×10^4	1.26×10^3	2.98×10^3
BO (g)	1255	2465	4320	1015	2250	1495
product molecular weight (g/mol)	1.96×10^3	1.34×10^3	2.06×10^3	1.34×10^4	4.20×10^3	6.33×10^3
acetic acid used (g)	4.4	11.1	12.0	5.63	2.6	1.24
kinematic viscosity (cSt) (212 °F)	30	17	29		83	262

The synthesis procedure of $B_{20}E_{29}B_{20}$ is described here. Into a stirred, closed system steel reaction vessel was placed 135 g of 1,2-propylene glycol (The Dow Chemical Co.) and 8.1 g of KOH (Aldrich Chemical Co.). The reactor was purged with nitrogen, after which a vacuum was immediately applied. The purge/evacuation step was done three times in succession to rid adventitious oxygen. Reactor temperature was increased from ambient to 130 °C, and once stabilized, 2360 g of oxyethylene (E) (The Dow Chemical Co.) was fed at a rate sufficient to maintain an internal pressure of below 70 pounds per square inch absolute (psia). Following addition of E, the reactor temperature was maintained at 130 °C until the pressure drop over a 1 h period was less than 0.5 psia, after which the temperature was lowered to 80 °C. Phthalic anhydride analysis indicated that the polymer intermediate had a number-average molecular weight of 1.26×10^3 g/mol. A total of 1667 g of the material was removed from the reactor and set aside for analysis and also for allowing reactor space for the next oxide feed. At this time, 836 g of poly(ethylene glycol) diol remained in the reactor.

Reactor temperature was again raised to 130 °C, and 2250 g of 1,2-butylene oxide was added for formation of the hydrophobic end blocks. Final molecular weight of the block copolymer was determined to be 4.20×10^3 g/mol. The reactor contents were cooled to 60 °C, and 2.64 g of glacial acetic acid (Fisher Scientific Co.) was added to neutralize the basic catalyst. Potassium acetate from the neutralization was not removed from the product. Kinetic viscosity of the product was 83.0 cSt at 212 °F.

Four additional $B_nE_mB_n$ triblock copolymers ($B_7E_{22}B_7$, $B_6E_{10}B_6$, $B_{10}E_{15}B_{10}$, $B_{10}E_{271}B_{10}$, and $B_{23}E_{68}B_{23}$) were made using the same general procedure. Table 1 describes the synthesis conditions for several $B_nE_mB_n$ triblock copolymers.

Purification of Samples. The $P_nE_mP_n$ triblock copolymers (Pluronic), including 10 R-5 ($P_7E_{22}P_7$), 17 R-2 ($P_{14}E_{10}P_{14}$), 25 R-2 ($P_{18}E_{14}P_{18}$), 25 R-4 ($P_{18}E_{34}P_{18}$), and 25 R-8 ($P_{15}E_{155}P_{15}$), were obtained as gifts from the BASF Chemical Co. Hexane was used to remove some insoluble species, as well as a small fraction of block copolymer chains having higher hydrophobic components. The procedure has been described elsewhere.[14] The same method was also used for purifying the $B_7E_{22}B_7$ triblock copolymer, whose raw aqueous solution was quite turbid, similar to those of $B_5E_{91}B_5$[12] and $B_6E_{46}B_6$[14] before purification. Due to the low T_{cl} values of some samples, the procedure was carried out in an ice−water bath. We found that it was quite difficult to purify $B_6E_{10}B_6$ by hexane. Therefore, filtration of the opaque solution at very low temperatures (around 0 °C) was used to remove the chemical impurities. However, the temperature range of phase transition was a little broader than those of the samples purified by hexane. As reported earlier, $B_{10}E_{271}B_{10}$ was purified by hot octane.[15]

Cloud-Point Determination. The cloud-point temperatures of triblock copolymer/water systems were determined by monitoring the variation of the incident laser beam intensity
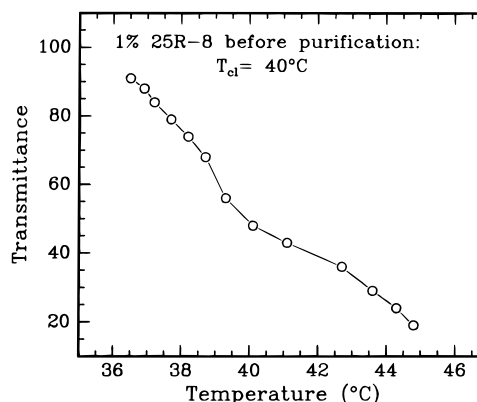

Figure 1. T_{cl} measurement of 1 wt % $P_{15}E_{155}P_{15}$ triblock copolymer in aqueous solution (before purification).

transmitted through the solution. We used a He−Ne laser operating at 632.8 nm as the incident light source. The measured polymer solution was kept in a water bath, and the temperature was controlled by a thermostat to ±0.1 °C. To ensure the system to reach equilibrium at different temperatures, the temperature was changed initially at a rate of only 1−2 °C/min. The onset of phase separation resulted in a sharp decrease in the transmitted laser beam intensity.

Results and Discussion

Cloud Points. Some of the cloud-point temperatures for the triblock copolymers in aqueous solution (usually 1 and 10 wt %) can be found in the bulletin of relevant chemical corporations (e.g., BASF Corp.). However, these data could not be used directly as the values could change drastically after sample purification.[11] Another example is given by Pluronic 25 R-8 ($P_{15}E_{155}P_{15}$), which has a T_{cl} value of about 40 °C for the 1 wt % solution, as reported in the commercial bulletin. Before purification, the T_{cl} measurement showed that the transmittance of the incident beam decreased slowly with increasing temperature, as shown in Figure 1. The midpoint transition could be located at about 40 °C. This intensity−temperature curve is quite typical of impure samples. After only one cycle of sample purification by hexane, the transition in the intensity transmittance became very sharp, as shown in Figure 2 with $T_{cl} = 77.5$ °C. This big temperature difference cannot be explained as only due to the change in sample polydispersity or even as only due to the existence of some copolymer chains that contain higher percentages of hydrophobic units. We believe that there were also amounts of insoluble impurities, which could be homopolymers (e.g., polyoxybutylene), in the sample when the block copolymers were synthesized. Table 2 lists the cloud-point temperatures of purified $B_nE_mB_n$ triblock copolymers (1 wt % aqueous solution) measured by us and reported by other research groups.

Effect of Chain Length on Cloud-Point Temperature. For $B_nE_mB_n$ and $P_nE_mP_n$ triblock copolymers, B and P blocks are
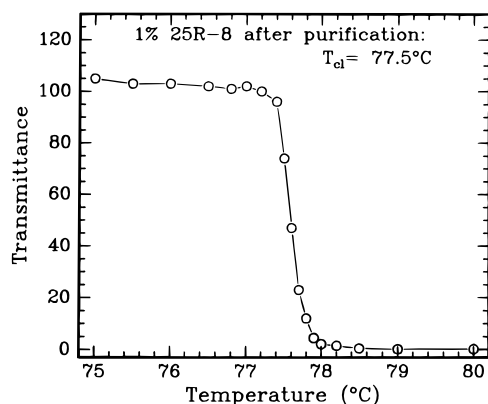
8076 *J. Phys. Chem. B, Vol. 101, No. 41, 1997*

Liu et al.

Figure 2. T_{cl} measurement of 1 wt % $P_{15}E_{155}P_{15}$ triblock copolymer in aqueous solution (after purification).

TABLE 2: Measured and Calculated T_{cl} of 1 wt % $B_nE_mB_n$ Triblock Copolymers in Aqueous Solution

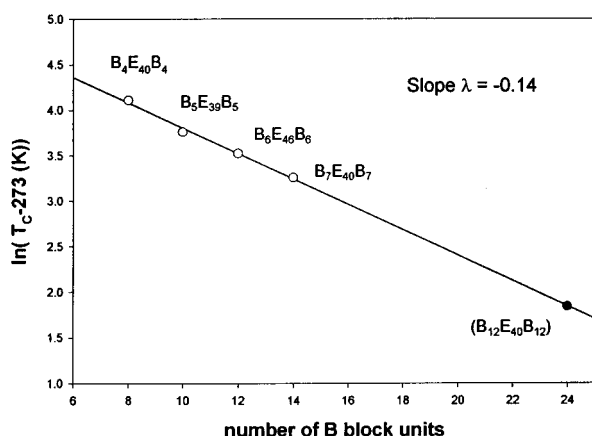|	T_{cl} (° C)			T_{cl} (° C)	
sample	measd	calcd	sample	measd	calcd
$B_4E_{40}B_4$	61	60	$B_{10}E_{15}B_{10}$	*a*	0
$B_5E_{39}B_5$	43	45	$B_{10}E_{271}B_{10}$	32	31
$B_5E_{91}B_5$	53	54	$B_{12}E_{76}B_{12}$	12	12
$B_6E_{10}B_6$	19	19	$B_{12}E_{114}B_{12}$	17	16
$B_6E_{46}B_6$	35	35	$B_{12}E_{260}B_{12}$	25	25
$B_7E_{22}B_7$	18	19	$B_{20}E_{29}B_{20}$	*a*	−4
$B_7E_{40}B_7$	26	25	$B_{23}E_{68}B_{23}$	*a*	4

a Insoluble.

Figure 3. Effect of B block length on the T_{cl} of 1 wt % $B_nE_mB_n$ triblock copolymers in aqueous solution. N_B denotes the number of B block units.

the hydrophobic blocks while the E block is the hydrophilic block. All of the blocks become more hydrophobic at higher temperatures, and then phase separation occurs. The hydrophobicity of the block copolymer increases with either a longer B (or P) block or a shorter E block. With the same E block length, a lower T_{cl} can be expected for block copolymers with longer B blocks. In Figure 3, we collected the available T_{cl} data of 1 wt % $B_nE_mB_n$ block copolymers that have similar E block length (around 40 oxyethylene units) but different total B block length (from 8 to 14). As the results were reported by different research groups, we estimated the error to be about 1 °C. Figure 3 was plotted by using the number of oxybutylene (B) units (N_B) in $B_nE_mB_n$ block copolymers as the *x*-axis and the logarithmic values of T_{cl}−273 K as the *y*-axis. It shows that the length of B blocks has a very strong negative effect on the T_{cl}, which decreases exponentially (from 26 °C for $B_7E_{40}B_7$ to 61 °C for $B_4E_{40}B_4$) with a linear increase in the B block length. The constant 273 K was introduced to ensure the linear
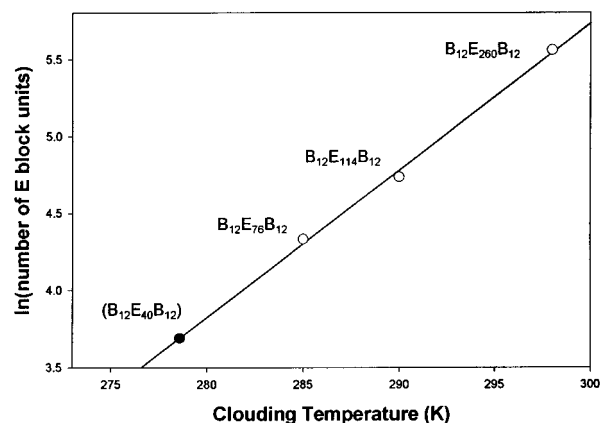

Figure 4. Effect of E block length on the T_{cl} of 1 wt % $B_nE_mB_n$ triblock copolymers in aqueous solution. N_E denotes the number of E block units.

relationship. Although we have no additional evidence to provide the physical meaning of this constant, the possibility suggests that this number may be related to the melting temperature of the solvent water, which happens to be 273 K. However, it is noted that the magnitude of this constant (273 K) also depends on how T_{cl} changes with N_B (see later discussion). The slope λ in Figure 3 is an indication of the relative effect of a single B unit on the T_{cl} and has the value of −0.14 for the 1 wt % $B_nE_mB_n$ triblock copolymers in water.

On the contrary, the longer the hydrophilic E block becomes, the better the copolymer can be dissolved in water. Thus, for the block copolymers with the same B block length, a higher T_{cl} value can be expected for the block copolymer with a longer E block. However, the E block length does not play as dominant a role in determining the T_{cl} as that of the B block. Figure 4 shows that, for the $B_nE_mB_n$ triblock copolymers with 24 BO units, an exponential increase in the E block units (N_E) only increases the T_{cl} values linearly (from 12 °C for $B_{12}E_{76}B_{12}$ to 25 °C for $B_{12}E_{260}B_{12}$); i.e., the E block has only a small positive effect on the T_{cl} value.

Figures 3 and 4 are actually interconnected. An important way to quantitatively prove this connection and then to confirm the interconnected formulations is to predict the T_{cl} of a 1 wt % polymer solution in water for an assumed new triblock copolymer $B_{12}E_{40}B_{12}$ by an appropriate extrapolation of experimental data. From Figure 3, where all the data come from the $B_nE_mB_n$ triblock copolymers with a similar E block length, we can calculate the estimated T_{cl} for $B_{12}E_{40}B_{12}$ to be about 5.3 °C. Separately, but independently, from Figure 4, the T_{cl} of $B_{12}E_{40}B_{12}$ can be estimated to be about 5.6 °C. Since all the experimental data points we were using had an error of about 1 °C, the two estimated T_{cl} values for $B_{12}E_{40}B_{12}$ coming from two independent plots coincide with each other quite well. Although this coincidence cannot guarantee that the real triblock copolymer $B_{12}E_{40}B_{12}$ has a T_{cl} value of about 5.5 °C for its 1 wt % aqueous solution, at least it shows that the relationships in Figures 3 and 4 are self-consistent.

A more quantitative relationship on T_{cl} (K) with B and E units can be formulated if we introduce a "parallel assumption"; that is, we assume that in a plot of T_{cl} versus $\ln(N_E)$, as shown in Figure 4, the lines are parallel at different fixed N_B values. Then,

$$T_{cl} = b_1(N_B) + b_2 \ln(N_E) \qquad (1)$$

where b_1 depends on N_B, but b_2 is independent of N_B. Similarly, for Figure 3 with $\ln(T_{cl} - 273)$ being proportional to N_B,

Cloud-Point Temperatures of $B_nE_mB_n$ and $P_nE_mP_n$

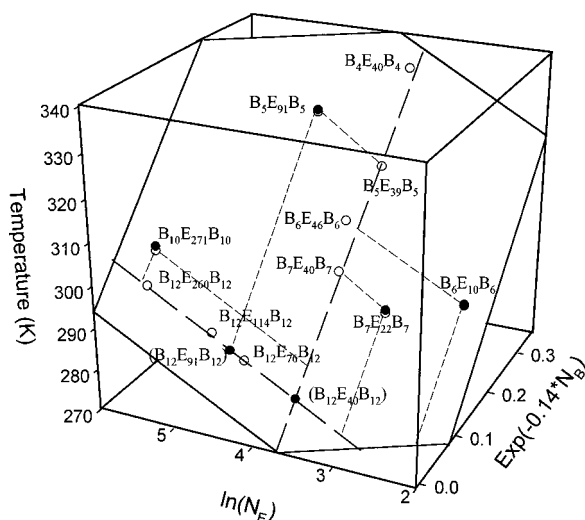*J. Phys. Chem. B, Vol. 101, No. 41, 1997* **8077**

Figure 5. Three-dimensional diagram of T_{cl} of 1 wt % $B_nE_mB_n$ triblock copolymers in aqueous solution. The open circles represent experimental data, and the filled circles represent calculated results.

$$T_{cl} - 273 \text{ K} = \exp[a_1(N_E) - a_2N_B] \qquad (2)$$

where a_1 depends on N_E and a_2 is independent of N_B. Thus, by combining eqs 1 and 2, we get

$$T_{cl} = \exp(-a_2N_B) + b_2 \ln(N_E) + \text{constant} \qquad (3)$$

Construction of a Three-Dimensional Diagram. The three variables in eq 3 can be used to construct a three-dimensional diagram for T_{cl} of $B_nE_mB_n$ triblock copolymers, as shown in Figure 5. The X and Y axes labeled in the bottom show the change of B and E block length, respectively. The two long dashed lines are the same as in Figures 3 and 4, their cross section is $B_{12}E_{40}B_{12}$, where we independently obtained the same value of T_{cl} for this assumed block copolymer from either data set. These two long dashed lines determine a plane that cuts the three XYZ coordinates, as shown in Figure 5.

Based on the data on the two long dashed lines in Figure 5, a general expression can be given for all of the 1 wt % $B_nE_mB_n$ triblock copolymers in aqueous solution:

$$T_{cl} \text{ (K)} = 188 \exp(-0.14N_B) + 10.6 \ln N_E + 233 \qquad (4)$$

The constants -0.14 (the slope λ in Figure 3) and 10.6 (the slope in Figure 4) above are characteristic for the B block and the E block, respectively. They quantitatively describe the length effects of different blocks on the T_{cl}.

Four additional examples, $B_7E_{22}B_7$, $B_6E_{10}B_6$, $B_5E_{91}B_5$, and $B_{10}E_{271}B_{10}$, are presented to further confirm the "parallel assumption". The calculated T_{cl} values for 1 wt % $B_7E_{22}B_7$ and $B_6E_{10}B_6$ in aqueous solution are both around 19 °C, and for $B_5E_{91}B_5$ and $B_{10}E_{271}B_{10}$, T_{cl} are about 53 and 31 °C, respectively. Again, the agreement with the experimental data is more than satisfactory, as listed in Table 2.

It is interesting to note that due to the "parallel assumption", all the experimental data points out of the two long dashed basic lines (including those of $B_5E_{91}B_5$, $B_7E_{22}B_7$, $B_6E_{10}B_6$, and $B_{10}E_{271}B_{10}$) should reside in this plane. This is a simple result of stereogeometry. In Figure 5, the filled circles represent calculated values while the open circles represent experimental data.

The boundary conditions for eq 3 are presented as follows. If we have very long B end blocks, the calculated T_{cl} may be lower than 0 °C, and if we have a very long E middle block, the calculated T_{cl} value may be much higher than 100 °C. That

TABLE 3: Measured and Calculated T_{cl} of 1 wt % $P_nE_mP_n$ Triblock Copolymers in Aqueous Solution

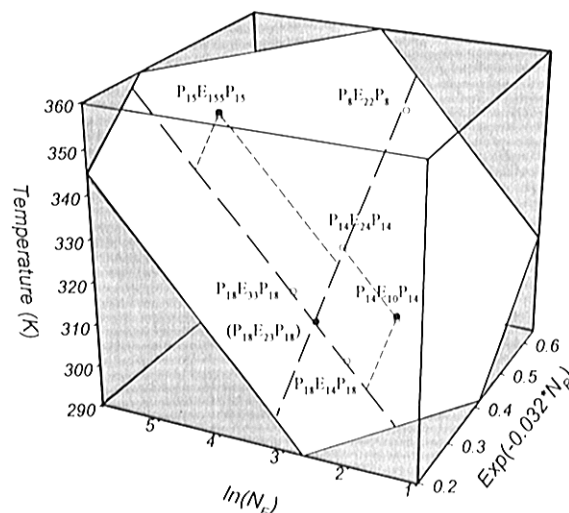| sample | T_{cl} (° C) | | sample | T_{cl} (° C) | |
	measd	calcd		measd	calcd
10 R-5 ($P_8E_{22}P_8$)	71	70	25 R-8 ($P_{15}E_{155}P_{15}$)	77.5[a]	77
17 R-2 ($P_{14}E_{10}P_{14}$)	34	35	25 R-2 ($P_{18}E_{14}P_{18}$)	30	30
17 R-4 ($P_{14}E_{24}P_{14}$)	49	50	25 R-4 ($P_{18}E_{33}P_{18}$)	44	44

[a] From Figure 2.

Figure 6. Three-dimensional diagram of T_{cl} of 1 wt % $P_nE_mP_n$ triblock copolymers in aqueous solution. The open circles represent experimental data, and the filled circles represent calculated results.

means for very long B blocks the 1 wt % triblock copolymers cannot be dissolved in water, even down to 0 °C, while for some others with very long E blocks, the triblock copolymers will be soluble at all temperatures until the boiling point of water. For 1 wt % $B_{23}E_{68}B_{23}$, $B_{10}E_{15}B_{10}$, and $B_{20}E_{29}B_{20}$ in aqueous solution, the calculated T_{cl} values are around or lower than 0 °C. The corresponding experiments have indeed shown that they are insoluble in water down to near 0 °C. As these samples are quite hydrophobic, we cannot effectively purify them. However, the preliminary studies clearly show these phase separation behaviors to be in agreement with the "parallel assumption". However, from eq 4, we note that if N_E is large enough, no matter how long the B block is, the polymer can always be dissolved in water over a certain temperature range ($T_{cl} > 273$ K). This is obviously incorrect when we intentionally choose extremely long B blocks. Therefore, there clearly exists an upper boundary for eq 3.

Diagram for $P_nE_mP_n$ Triblock Copolymers. We can extend our prediction to other similar triblock copolymers, such as $P_nE_mP_n$ triblock copolymers. However, there are two practical drawbacks for the $P_nE_mP_n$ series of block polymers. First, the available samples are quite limited. Second, the polydispersity of the commercial $P_nE_mP_n$ triblock copolymers appear to be larger than that of $B_nE_mB_n$ triblock copolymers.

Table 3 summarizes the T_{cl} of 1 wt % $P_nE_mP_n$ polymers after purification. A similar diagram (Figure 6) can be plotted like Figure 5. However, due to the limited number of available samples, we have to assume that the cross section of the two long dashed lines occurs at $P_{18}E_{23}P_{18}$, since each long dashed line has only two experimental data points. Nevertheless, we can write a general expression similar to eq 4:

$$T_{cl} \text{ (K)} = 116 \exp(-0.032N_B) + 16.5 \ln (N_E) + 223 \qquad (5)$$

when N_P is the number of P units. Equations 4 and 5 can also

be represented in 2-D parametric displays by holding either N_E or N_B/N_P constant. The 3-D plots are presented for readers to examine the cloud-point temperature behavior from a slightly different viewpoint. It is noted that the results are for a 1 wt % polymer solution.

Comparison of Equivalent Effect of B Unit and P Unit. It is an interesting question to find out how many P units are equivalent to one B unit since the B unit is more hydrophobic. One of the traditional ways is to calculate the transfer energy for one hydrophobic unit, i.e., the energy used to transfer one hydrophobic unit from bulk solution into the micellar core.[16,17] Another is to compare the effect of per hydrophobic unit on the thermodynamic parameters[18] (e.g., $\Delta H°$). By using the latter method, Bedells et al. indicated that one B unit was equivalent to 3−4 P units in $E_nB_mE_n$ and $E_nP_mE_n$ triblock copolymers in aqueous solution.[18] Now we try to answer this question by considering their effects on T_{cl}.

As mentioned above, the effects of different blocks can be represented by using eqs 4 and 5. The hydrophilic E block seems to play a much more important role in $P_nE_mP_n$ than in $B_nE_mB_n$ with the coefficients being 16.5 and 10.6, respectively. With the same E middle block, the effects of B end block and P end block on the T_{cl} values can be compared. From the coefficients (-0.14 for B unit and -0.032 for P unit) in the exponential parts of eqs 4 and 5, we can conclude that one B unit functions as about 4.4 P units, which is similar to the conclusion obtained by studying the micellization behavior.[18]

Conclusion

The effects of chain length on clouding temperature of 1 wt % purified $B_nE_mB_n$ and $P_nE_mP_n$ triblock copolymers in aqueous solution have been presented. Both hydrophobic and hydrophilic blocks have effects on the T_{cl} of block copolymers. T_{cl} becomes higher for shorter B (or P) end blocks or longer E middle blocks. The hydrophobic end blocks play a dominant role: their linear increase will lead to an exponential decrease in T_{cl}. The hydrophilic middle block has a minor contribution: its exponential increase only leads to a linear increase in T_{cl}.

By introducing a "parallel assumption", which has been proven to be acceptable for the above 1 wt % $B_nE_mB_n$ and $P_nE_mP_n$ triblock copolymers in aqueous solution, a general mathematical expression and a three-dimensional diagram have been presented for each type of the triblock copolymers. Thus, the clouding temperature for all $B_nE_mB_n$ and $P_nE_mP_n$ triblock copolymers (1 wt % polymer aqueous solution) can be predicted.

From the effects of chain length on the T_{cl} value, one can conclude that 1 B unit is equivalent to about 4.4 P units, in agreement with an earlier conclusion based on the micellization behavior.

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) Chu, B. *Langmuir* **1995**, *11*, 414.

(3) Malmsten, M.; Lindman, B. *Macromolecules* **1993**, *26*, 1282.

(4) Zhang, K. Ph.D. Thesis, University of Lund, 1994.

(5) Wanka, G.; Hoffmann, H.; Ulbricht, W. *Macromolecules* **1994**, *27*, 4145.

(6) Mortensen, K.; Pederson, J. K. *Macromolecules* **1993**, *26*, 805.

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

(8) van Os, N. M.; Haak, J. R.; Rupert, L. A. M. *Physicochemical Properties of Selected Anionic, Cationic and Nonionic Surfactants*; Elsevier: Amsterdam, 1993; pp 207−211.

(9) Solc, K. *Polym. Prepr.* **1994**, *31* (1), 584.

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

(11) Zhou, Z.; Chu, B. *Macromolecules* **1994**, *27*, 2025.

(12) Zhou, Z.; Chu, B.; Nace, V. M. *Langmuir* **1996**, *12*, 5016.

(13) Zhou, Z.; Chu, B.; Nace, V. M., Yang, Y.-W.; Booth, C. *Macromolecules* **1996**, *29*, 3663.

(14) Liu, T.; Zhou, Z.; Wu, C.; Chu, B.; Schneider, D. K., Nace, V. M. *J. Phys. Chem.*, in press.

(15) Liu, T.; Zhou, Z.; Wu, C.; Nace, V. M.; Chu, B. *Macromolecules*, submitted for publication.

(16) Wanka, G.; Hoffmann, H.; Ulbricht, W. *Macromolecules* **1994**, *27*, 4145.

(17) Liu, T.; Zhou, Z.; Wu, C.; Nace, V. M., Chu, B. Manuscript in preparation.

(18) Bedells, A. D.; Arafeh, R. M.; Yang, Z.; Attwood, D.; Heatley, F.; Padget, J. C.; Price, C.; Booth, C. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 1235.