

Thermodynamics of micellization of tapered statistical copolymers of ethylene oxide and propylene oxide in water

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Abstract

Two tapered statistical copolymers were prepared by the oxyanionic polymerization of ethylene oxide and propylene oxide and characterized by gel permeation chromatography and ¹³C NMR spectroscopy. We denote the copolymers t-E/P38 and t-E/P30, where E = oxyethylene, OCH₂CH₂, and P = oxypropylene, OCH₂CH(CH₃), and the number denotes the mole percentage P. In each case the copolymer chain length was ca. 100 oxyalkylene units. The association of the copolymers to form micelles in aqueous solution was checked by dynamic light scattering. The critical micelle temperatures (cmt) of the copolymers at several concentrations were determined by static light scattering and dye solubilization, and values of the apparent standard enthalpy of micellization ($\Delta_{\text{mic}}H_{\text{app}}^0$) were obtained. For both copolymers, a low value of $\Delta_{\text{mic}}H_{\text{app}}^0$ was found when the copolymer concentration exceeded ca. 150 g dm⁻³.

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1. Introduction

The hydrophobic nature of the oxypropylene unit has attracted considerable attention in recent years. With respect to oxyethylene/oxypropylene copolymers (E/P copolymers) most work centers around the commercially available EPE triblock copolymers [1], and a number of studies of diblock EP and reverse triblock PEP copolymers have been reported [2]. We use the notation E = oxyethylene, OCH₂CH₂, and P = oxypropylene, OCH₂CH(CH₃). By comparison, little is known about the self-association properties of tapered statistical copolymers of ethylene oxide and propylene oxide (t-E/P) in aqueous solution. By tapered we mean a copolymer that is prepared at high conversion in a batch reaction by a living polymerization method (in the present context by oxyanionic polymerization) whereby a difference in reactivity of two monomers changes the composition of the residual monomer mixture as the polymerization proceeds (composition drift), and in this way tapers the composition of the copolymer along each chain. In the oxyanionic polymeriza-

tion of a mixture of ethylene oxide (EO) and propylene oxide (PO), EO oxide reacts faster than PO, and, as a consequence, copolymer chains prepared using a monofunctional initiator can be hydrophilic at one end and hydrophobic at the other. Because a tapered statistical copolymer of this type has the character of a diblock EP copolymer, one of suitable composition may associate to form micelles. In the schematic diagram shown in Fig. 1, a tapered statistical copolymer is pictured with a true block copolymer and a true statistical copolymer, all with the same overall composition. In reality, the block copolymer would be prepared by sequential copolymerization of the two monomers (Fig. 1 indicates EO followed by PO), while the statistical copolymer would be prepared by copolymerization of a mixture of two monomers terminated at low conversion (e.g., 5%) to minimize composition drift, the initial feed composition and initiator concentration being adjusted to obtain the required composition and chain length.

This approach to the preparation of micellizable copolymers has been applied previously in the case of ethylene oxide and 1,2-butylene oxide. The reactivity ratios for the E/B system, $r_E = 4.1$ and $r_B = 0.17$ [3], induce more composition drift than those for the E/P system ($r_E = 3.1$ and

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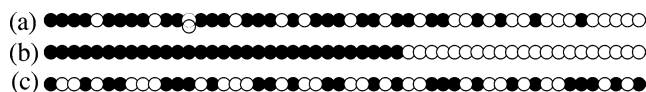


Fig. 1. Schematic diagram showing (a) a tapered, (b) a block, and (c) a statistical copolymer. The circles represent either P units (unfilled, 40 mol%) or E units (filled, 60 mol%).

$r_P = 0.30$) [4]. Tapered E/B copolymers (B = oxybutylene, $\text{OCH}_2\text{CH}(\text{C}_2\text{H}_5)$) have been prepared starting from monofunctional and difunctional initiators to form t-E/B [5] and t-B/E/B [6,7] copolymers, respectively. For example, Yu et al. [5] showed that a high-conversion t-E/B copolymer containing 20 mol% B overall, when dissolved in water at 30 °C, had a low critical micelle concentration ($\text{cmc} = 0.14 \text{ g dm}^{-3}$), and, above this concentration well developed micelles were found (hydrodynamic radius $r_h \approx 9 \text{ nm}$, association number $N \approx 30$).

Micellization in aqueous solutions of copolymers with statistical oxyethylene/oxypropylene components has been studied by Deng et al. [8,9], the copolymers having either one poly(oxyethylene) block and one statistical E/P block or two statistical E/P blocks of different composition. In that work the statistical blocks were formed at low conversion to minimize composition drift. In the copolymers a hydrophobic block of given composition (83 mol% P) was combined with hydrophilic blocks of various compositions in the range 23–10 mol% P, giving overall compositions in the range 63–49 mol% P and chain lengths in the range 135–158 oxyalkylene units (E and P). All were found to micellize, with values of the critical micellization temperature (cmt) for dilute solutions in the range 21–25 °C, but with rather low clouding temperatures, ca. 50 °C.

The tapered copolymers prepared in the present work were targeted on lower overall P content (30 and 40 mol% P) and shorter chain length (ca. 100 oxyalkylene units) than the copolymers prepared by Deng et al., the intention being to prepare copolymers that micellize but do not cloud. As discussed in previous reports [5–7], given accurate reactivity ratios for a living polymerization it is a simple matter to calculate the instantaneous composition of the copolymer formed at any conversion from

$$u = f_P / (f_P + r_E f_E) \quad \text{and} \quad w = f_E / (f_E + r_P f_P), \quad (1)$$

where quantities f_P and f_E are monomer mole fractions in the feed, u is the probability of adding P to an E chain end, and w is the probability of adding E to a P chain end. Accordingly, the reactivity ratios noted above were used to calculate instantaneous copolymer compositions at intervals of 0.1% conversion with the feed composition adjusted at each step. As the chains grow in direct proportion to conversion, the plot of copolymer composition against conversion (see Fig. 2a) directly reflects the composition profile along the copolymer chains. In the present case, as the copolymer chain length is ca. 100 oxyalkylene units, the abscissa (conversion) scale relates almost directly to the contour length of the copolymer chains in oxyalkylene units. As seen Fig. 1a,

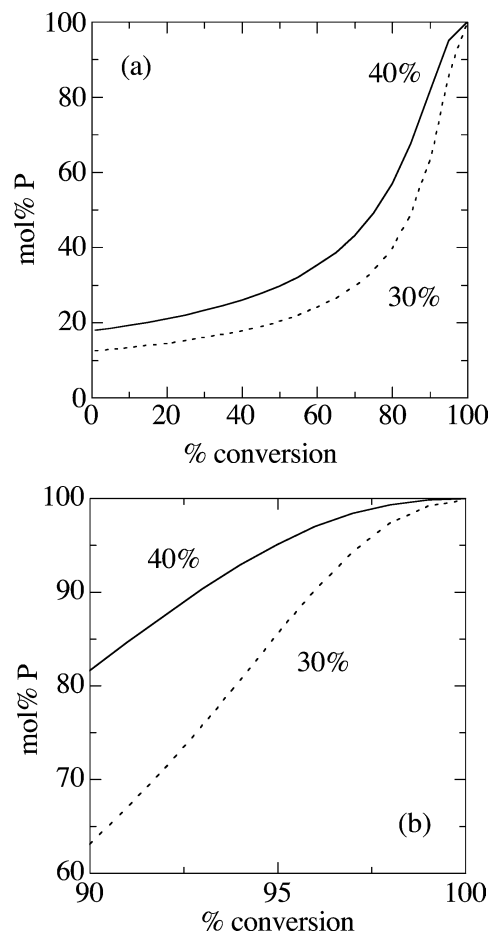


Fig. 2. Instantaneous copolymer composition (mol% P units) as conversion proceeds in the oxyanionic copolymerization of EO and PO. The initial feeds were 30 and 40 mol% PO, as indicated. Plot (a) shows the full conversion range and plot (b) shows the same data in the conversion range 90–100%. The curves are based on Eq. (1).

the composition along a chain with an overall composition of 40 mol% P varies from 18 mol% P at one end to 100 mol% P at the other, with an end sequence of 10 units with composition exceeding 82 mol% P (see Fig. 2b). The corresponding end sequence for a copolymer with 30 mol% P overall is considerably shorter, some 5 units long.

2. Experimental

2.1. Preparation and characterization

The copolymers were prepared by oxyanionic polymerization of ethylene oxide and propylene oxide. All reagents were distilled and dried before use, and vacuum line and ampoule techniques were used to minimize initiation by moisture at any stage. Initiator solution was prepared by reacting freshly cut potassium with diethylene glycol monomethyl ether [α -methyl, ω -hydroxydi(oxyethylene)], to give a product with mole ratio $[\text{OH}]/[\text{OK}] = 9$, which ensured a controlled rate of copolymerization. An aliquot of this initia-

tor solution was transferred by syringe into a weighed ampoule under dry nitrogen, and appropriate amounts of the dry monomers were transferred to the ampoule under vacuum. The ampoule, sealed under vacuum by a PTFE tap, was allowed to warm up to room temperature, shaken to mix the contents, and placed in a water bath at 45 °C for 2 weeks then the temperature was raised to 65 °C until conversion to copolymer was complete (a week or longer).

Characterization of the two copolymers by gel permeation chromatography (GPC), calibrated with poly(oxyethylene) standards, indicated narrow chain length distributions for the copolymers, i.e., $M_w/M_n < 1.05$, where M_w and M_n are the mass-average and number-average molar masses, respectively. Absolute M_n values of the copolymers were obtained by ^{13}C NMR spectroscopy by comparison of the integrals of resonances from the carbons of end groups and backbone groups, based on the assignments of Heatley et al. [10]. Denoting the two copolymers prepared as t-E/P38 and t-E/P30 (t meaning tapered statistical and the number being the overall mol% P), values of M_n were 5180 and 4920 g mol^{-1} , respectively, and their P contents were 0.45 and 36 wt%, respectively.

2.2. Light scattering

Static and dynamic light scattering measurements were carried out on well-filtered solutions, as described previously [11]. Static light scattering (SLS) intensities were measured by means of a Brookhaven BI 200S instrument using vertically polarized incident light of wavelength $\lambda = 488$ nm supplied by an argon-ion laser (Coherent Innova 90) usually operated at 500 mW. This method was used to detect the onset of micellization in solutions of known copolymer concentration. Scattering intensities relative to benzene were measured at intervals of 1–5 °C as the temperature was raised slowly, 0.1–1.0 °C min^{-1} . The cmt was defined as the temperature at which the scattering curve left the baseline established at low temperatures. SLS could not be used to determine micelle molar mass, and thereby micelle association number, because the concentrations needed to ensure a high extent of micellization were outside the dilute range (see Section 3).

Dynamic light scattering (DLS) measurements were made under similar conditions, using a Brookhaven BI 9000 AT digital correlator to acquire data. Experiment duration was in the range 10–20 min, and each experiment was repeated two or more times. In both methods, scattered light intensity was measured at angle $\theta = 90^\circ$ to the incident beam. The correlation functions from DLS were analyzed by the constrained regularized CONTIN method [12] to obtain distributions of decay rates (Γ), hence distributions of apparent mutual diffusion coefficient $D_{\text{app}} = \Gamma/q^2$ ($q = (4\pi n/\lambda) \sin(\theta/2)$, where n is the refractive index of the solvent), and ultimately of apparent hydrodynamic radius ($r_{\text{h,app}}$, radius of the hydrodynamically equivalent hard sphere corresponding to D_{app}) via the Stokes–Einstein equa-

tion

$$r_{\text{h,app}} = kT / (6\pi\eta D_{\text{app}}), \quad (2)$$

where k is the Boltzmann constant and η is the viscosity of the solvent at temperature T .

2.3. Dye solubilization

The general method was that described by Alexandridis et al. [13], but with the particular procedures used recently in our laboratory [14]. A Cary 1E UV–vis spectrometer with temperature controller was used to obtain UV spectra of copolymer solutions containing the hydrophobic dye (1,6-diphenyl-1,3,5-hexatriene) (DPH) at a concentration of 0.008 mmol dm^{-3} . The cmt was defined as the temperature at which the absorption (measured at 356 nm) left the baseline established at low temperatures.

3. Results and discussion

3.1. Micellization

DLS is a convenient method for confirming association in block copolymer solutions. The method is particularly sensitive to the formation of associates since, through the Rayleigh–Gans–Debye equation, the intensity of scattering from a particular species is proportional to the product of mass concentration and molar mass. Plots of fractional intensity from species with a given value of $\log(r_{\text{h,app}})$ against $\log(r_{\text{h,app}})$ are shown in Fig. 3 for a 10 wt% solution of copolymer t-E/P38 at $T = 20, 40,$ and 60°C . Similar plots were obtained for copolymer t-E/P30. At 20 and 40 °C the peaks at $\log(r_{\text{h,app}}) \approx 0.4\text{--}0.5$ ($r_{\text{h,app}} \approx 3$ nm) are assigned to unassociated molecules. At 60 °C the peak at $\log(r_{\text{h,app}}) \approx 1.0$ ($r_{\text{h,app}} \approx 10$ nm) is assigned to micelles.

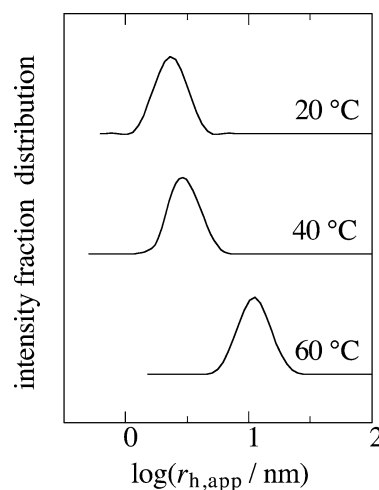


Fig. 3. Dynamic light scattering from 10 wt% aqueous solutions of copolymer t-E/P38 at the temperatures indicated. The plots show intensity fraction distributions of the logarithm of the apparent hydrodynamic radius.

Thus the DLS results confirm the presence of micelles in 10 wt% aqueous solutions of copolymer t-E/P38 at temperatures above 40 °C, with just unassociated molecules at lower temperatures.

3.2. Critical micelle temperature and thermodynamics of micellization

Fig. 4 shows examples of the experimental results obtained by the two methods (static light scattering and dye solubilization) employed to investigate the onset of micellization. The critical micelle temperatures obtained are collected in Table 1. Both static light scattering and dye solubilization measurements were possible at moderate copolymer concentrations (5–16 wt%), whereas interparticle interference so reduced the intensity of scattered light at higher con-

centrations as to make measurements impractical at higher copolymer concentrations (20–40 wt%).

For closed association to a narrow size distribution of micelles of average association number (N), the equilibrium between copolymer unimers (A) and micelles (A_N), written per unimer as



is described by the relation (concentration in mol dm⁻³)

$$K_c = [A_N]_{\text{eq}}^{1/N} / [A]_{\text{eq}}. \quad (4)$$

If the association number is large, then the equilibrium constant K_c is well approximated by

$$K_c = 1/[A]_{\text{eq}}, \quad (5)$$

where $[A]_{\text{eq}}$ can be considered to be the cmc, and the standard Gibbs energy and enthalpy of micellization are given by the relations

$$\Delta_{\text{mic}}G^0 = -RT \ln K_c = RT \ln(\text{cmc}) \quad (6)$$

and

$$\begin{aligned} \Delta_{\text{mic}}H^0 &= -RT d \ln(K_c) / d(1/T) \\ &= RT d \ln(\text{cmc}) / d(1/T). \end{aligned} \quad (7)$$

The process referred to is copolymer chains in their standard state of an ideally dilute solution at unit concentration (1 mol dm⁻³) going to copolymer chains in the micellar state. For Eq. (7) to apply to equilibrium (3) it is necessary that Eq. (5) is a good approximation of Eq. (4) at all temperatures, i.e., that N is large. If that were the case, the inverse of the cmt could be plotted against $\log(c)$ to obtain the standard enthalpy of micellization. Although values of N are not available in the present case, the plot will nevertheless yield

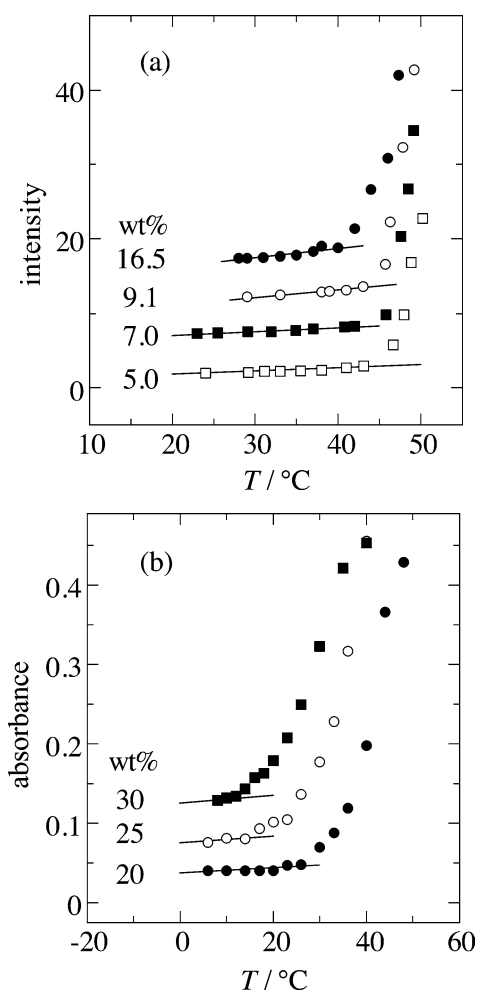


Fig. 4. Determination of critical micelle temperature for aqueous solutions of copolymer t-E/P38. (a) Temperature dependence of static light scattering intensity relative to that from benzene. (b) Temperature dependence of the absorbance at 356 nm of DPH. Copolymer concentrations are indicated. For clarity, the plots are displaced on the ordinate: in (a) by adding 5, 10, and 15 units for 7.0, 9.1, and 16.5 wt%, respectively; and in (b) by adding 0.05 and 0.1 unit for 25 and 30 wt%, respectively.

Table 1
Critical micelle temperatures of the tapered statistical copolymers^a

Copolymer	Method	c (wt%)	cmt (°C)
t-EP38	DLS	5.01	45
		7.00	44
		9.05	43
	Dye	16.5	40
		20.0	26
		25.0	17
		30.5	14
		35.0	16
		40.0	12
t-EP30	DLS	6.90	46
		9.56	41
		11.6	38
	Dye	7.00	49
		10.0	40
		12.0	42
		20.3	26
		25.0	23
		30.0	22
		35.0	15

^a Estimated uncertainty in cmt: $\pm 1^\circ\text{C}$.

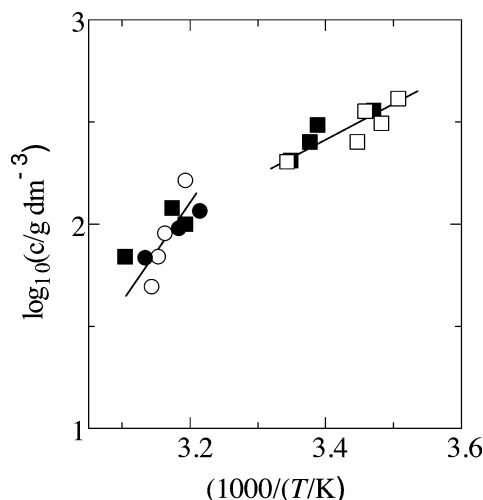


Fig. 5. Log(concentration) versus reciprocal critical micelle temperature (cmt) for aqueous solutions of copolymers t-E/P30 (filled symbols) and t-E/P38 (unfilled symbol). The data points are from static light scattering (circles) and dye solubilization (squares). Best straight lines through the two sets of points are shown.

apparent values of the standard enthalpy of micellization that have only semiquantitative significance with respect to K_c , but that correctly describe the concentration dependence of the cmc. In the plot shown in Fig. 5, the concentrations have been converted from weight percentages to grams per cubic decimeter, assuming additivity by mass fraction and using reported values of specific volumes of poly(oxyethylene) and poly(oxypropylene) [15] and of water. Concentrations in grams per cubic decimeter were also calculated using reported values of the partial specific volumes of the two components, the unimeric state in water [16].

The concentration dependences of the cmt found for the two copolymers do not differ significantly. Considered together, as in Fig. 5, the data points fall into two sets. At moderate concentrations (50–160 g dm⁻³) the data scatter about a line with slope corresponding to $\Delta_{\text{mic}}H_{\text{app}}^0 = 90 \pm 30 \text{ kJ mol}^{-1}$, whereas at higher concentrations (200–400 g dm⁻³) the data scatter about a line with slope corresponding to $\Delta_{\text{mic}}H_{\text{app}}^0 = 30 \pm 5 \text{ kJ mol}^{-1}$. Within the uncertainties assigned, these values were not significantly changed when concentrations were calculated using partial specific volumes.

The positive values of $\Delta_{\text{mic}}H_{\text{app}}^0$ point to the well-known fact that micellization is driven by the positive entropy change associated with the hydrophobic effect [17]. Marked reductions in $\Delta_{\text{mic}}H_{\text{app}}^0$ at copolymer concentrations exceeding 150 g dm⁻³ have been described for other systems, e.g., aqueous solutions of triblock copolymers E₉₃P₄₃E₉₃ (a fraction of commercial copolymer F127) and E₂₁P₄₇E₂₁ (commercial polymer P94) [18,19]. The role of water is ignored in the micellization equilibrium as conventionally written (see equilibrium (3)). This is a sufficient approximation for dilute solutions. However, as in [19], it is suggested that bulk water, both hydrogen-bonded and free, which dominates in di-

lute solutions, will be partly (even largely) replaced in more concentrated solutions by water that is hydrogen bonded to poly(oxyethylene), with a weakening of the hydrophobic effect and a consequent reduction in the standard enthalpy of micellization.

The value of $\Delta_{\text{mic}}H_{\text{app}}^0 \approx 90 \text{ kJ mol}^{-1}$ found for the present tapered copolymers in dilute solution can be compared with values exceeding 200 kJ mol⁻¹ reported for true EP diblock copolymers of similar chain length and composition [2,20]. In the corresponding comparison of values of $\Delta_{\text{mic}}H_{\text{app}}^0$ for tapered and diblock copolymers in the oxyethylene/oxybutylene system, a higher value was found for the tapered copolymer [5]. However, for EB block copolymers, the values of $\Delta_{\text{mic}}H_{\text{app}}^0$ are anomalously low, an effect that is attributable to collapse of B blocks in the molecular state, so that transfer of B units to the molecular core is a weakly endothermic process [2]. For example, $\Delta_{\text{mic}}H_{\text{app}}^0 \approx 130 \text{ kJ mol}^{-1}$ for tapered copolymer t-E/B20 (present notation) [5] but in the range 0–80 kJ mol⁻¹ for related EB diblocks, depending on block length [2]. The effect of incorporating E units into the hydrophobic block is to stop its collapse and gain a large endothermic effect per B unit. P blocks are much less hydrophobic than B blocks [2], and there is no evidence of their collapse in water [13,20], so that transfer of P units to the micelle core is strongly endothermic. In the E/P system, the incorporation of E units into the hydrophobic P block simply serves to dilute the overall endothermic effect.

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