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SELF-ASSOCIATION PROPERTIES OF OXYETHYLENE/OXYPROPYLENE/OXYETHYLENE TRIBLOCK COPOLYMER F88

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Abstract—Critical micelle temperatures (cmT) of triblock copolymer F88 (nominally $E_{102}P_{39}E_{102}$), where E = oxyethylene and P = oxypropylene in aqueous solution were determined by light scattering and eluent GPC (aqueous solvent). Two samples originating from different suppliers (BASF Inc. and ICI plc) were investigated. The overall formulae of the two samples (checked by NMR) were essentially identical, but their GPC curves (THF solvent) differed significantly. Comparison of the cmTs obtained, including published values from a dye solubilization method, showed good agreement between techniques but poor agreement between samples, i.e. differences of 10–15°C across a range of concentrations. © 1997 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Oxyethylene/oxypropylene/oxyethylene triblock copolymers ($E_mP_nE_m$) are of commercial importance and also excite academic interest on account of their association properties in aqueous solution. The current state of this work can be judged from recent publications [1–10] and the references therein. Variation in the association properties of different samples of nominally the same copolymer is remarked upon in many of these papers. Indeed, recognition of the problem as it affects the end-use properties of $E_mP_nE_m$ copolymers goes back many years: see e.g. Ref. [11]. Examination of commercial samples by analytical gel permeation chromatography (GPC) has often shown two peaks (or a peak and a shoulder) in their GPC curves [9, 10, 12, 13]. A thorough molecular characterization of Synperonic-PE F127 (ICI plc, nominally [14] $E_{106}P_{69}E_{106}$) involved fractionation into its two components followed by analysis by ^{13}C NMR [10]. That work showed that the two components were both triblock copolymers but of widely different composition. However, there is no evidence that this is the normal pattern, as the complexity of the chemistry of anionic polymerization of propylene oxide [15] as well as the need to exclude moisture in the second stage of sequential copolymerization gives ample scope for variation.

We have recently encountered an extreme example of variation in the critical micellization behaviour of two samples of $E_mP_nE_m$ copolymer F88, also known as Poloxamer 238. The samples were Synperonic-PE F88 and Pluronic F88. In order to remove uncertainty introduced by use of different methods in different laboratories, aqueous solutions of both copolymers were examined by two techniques (static light scattering and eluent GPC) across a range of temperature in order to detect their critical micelle temperatures. In addition, one of the samples had previously been examined by a dye solubilization method.

EXPERIMENTAL

Copolymers

Samples of copolymer F88 were provided by ICI plc, Wilton, U.K. (Synperonic-PE F88, Reference No. 830), and by BASF Corp., Parsippany, U.S.A. (Pluronic F88, Batch No. WPDN-616B), and were used as received. In the following they are denoted S-F88 and P-F88, respectively.

NMR spectra were obtained by means of a Varian Unity 500 spectrometer operating at 125 MHz. Samples were dissolved in $CDCl_3$ at a concentration of 5–10 g L^{-1}. Assignments of resonances have been reported previously [16]. Comparison of integrals for carbons from P units in the backbone and those from E units gave the overall composition. Comparison of integrals for carbons in block junction groups (P̄E) and in chain groups (P and E) gave the overall chain length and hence the number-average molar mass (M_n). Comparison of integrals for carbons in end groups (E*) and junction groups showed slight excesses of E* in both samples, which is attributable to small fractions of poly(oxyethylene), probably initiated by moisture introduced at the second stage of copolymerization. The molecular characteristics obtained in this way are listed in Table 1. Within the estimated error of determination, the two samples were identical in overall composition, with characteristics which met the grid specification [14].

The GPC system used to characterize the copolymers comprised four μ-Styragel columns (porosity range 10^3–10^6) with *N,N*-dimethylacetamide eluent at 70°C and a flow rate

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Table 1. Molecular characteristics of $E_mP_nE_m$ block copolymers

	S-F88	P-F88	Specification (F88)
NMR			
M_n	11,700	12,700	11,250
Composition (mol% E)	85	85	84
Composition (wt% E)	82	81	80
Poly(oxyethylene) impurity (wt%)	<2	<2	—
Formula	$E_{108}P_{37}E_{108}$	$E_{117}P_{41}E_{117}$	$E_{102}P_{39}E_{102}$
GPC			
M_{pk} (as if POE)	10,500/5200	9000/4500	—
wt%	75/25	91/9	—

The estimated uncertainties in values of molar mass and block length obtained from NMR are ±5%. Specified values are based on the Pluronic Grid [14]. Values of M_{pk} are as if poly(oxyethylene).

of 1 cm^3 min^{-1}. Samples were injected at a concentration of 2 g dm^{-3}. Calibration with poly(oxyethylene) standards of molar mass 10^2–10^6 g mol^{-1} indicated good resolution for the system across the elution-volume range 12 to 35 cm^3. GPC curves obtained for the two copolymers are illustrated in Fig. 1. Both GPC curves show two peaks but they differ in detail. Values of the molar mass at the peak [M_{pk}, poly(oxyethylene) calibration] and the area % under a peak (i.e. wt % of polymer) are listed in Table 1. It is seen that the satisfactory average characteristics obtained from NMR convey no information about the considerable differences in the molecular size distributions of the two samples.

Static light scattering

Solutions for light scattering measurements were clarified by filtering through 0.22 μm filters (Millipore Millex, Triton free). Water was similarly treated, except that 0.1 μm filters were used. The intensity of light scattered at 90°C from a solution of given concentration was measured over a range of temperatures by means of a Sofica PGD 40B photogoniometer modified for use with a Helium-Neon laser (632.8 nm). Measurements were made at intervals of approximately 0.5 or 1°C as the temperature was raised from 15 to 45°C at a heating rate ≤0.5°C min^{-1}. Allowance was made for thermal lag by calibrating the cell temperature against the bath temperature in a preliminary experiment. Typical intensity–temperature plots are shown in Fig. 2. The critical micelle temperature (cmT) of a given solution was obtained as that at which the scattering curve left the baseline established at low temperatures for the molecular solution.

Elution gel permeation chromatography

This is a relatively new method which has been described in detail elsewhere [9, 13, 17]. The present aqueous GPC system comprised two columns, each 30 cm long packed with TSKgel-PW (G4000 and G3000). Detection was by differential refractometry (GBC, Model LC1240). Eluent was prepared by dissolving a copolymer in distilled water followed by filtration and was pumped at 0.5 cm^3 min^{-1}. Probe solutions, prepared by dissolving the same copolymer in the eluent, were injected via a 0.1 mm^3 loop. The column temperature was controlled (to ±0.5°C) by means of an oven (ICI Instruments, Model TC1900), whilst stepping through the temperature range 25–45°C, allowing several hours at each temperature for thermal equilibration. The system was calibrated at appropriate temperatures with poly(oxyethylene) standards covering the molar mass range from 10^3 to 10^6 g mol^{-1} and was found to have satisfactory resolution across the elution volume range 10–20 cm^3.

In the EGPC method the micelle–molecule equilibrium in the eluent is probed by injecting a solution of the surfactant of different concentration. It is necessary that the probe does not significantly disturb the equilibrium. Given the dilution during the EGPC experiment this condition is not difficult to achieve. In the present work the effect of probe concentration was checked using copolymer S-F88 at a concentration in the eluent of 2.5 g L^{-1} and an eluent temperature at 41°C. Selected results are shown in Fig. 3, where it can be seen that at 41°C the copolymer was only partly micellized. Variation of the probe concentration over the wide concentration range had no detectable effect on the shape of the EGPC curve.

In experiments to measure the critical micelle temperature the temperature of a given eluent was varied and the lowest temperature at which a micelle peak could be detected was accepted as the cmT. Typical results are shown in Fig. 4. For that solution of copolymer S-F88 (2.5 g L^{-1}) the micelle peak was clearly visible at 32°C and above, and was just detectable at 30°C, which was assigned as the cmT. In the best solvents (i.e. at low temperatures) the molecule peak showed two components, but the resolution in the EGPC system was less than in the analytical system with DMA solvent (cf. Figs 1 and 4). Note that the molecule peak moved to higher elution volumes as temperature was increased (which is an adsorption effect), whilst the micelle peak moved to lower elution volumes (which is an effect of increasing hydrodynamic volume): see Ref. [9] for a detailed discussion.

RESULTS AND DISCUSSION

The values of the cmT obtained for the two copolymers over a range of concentration are listed in Table 2. A convenient representation of such data

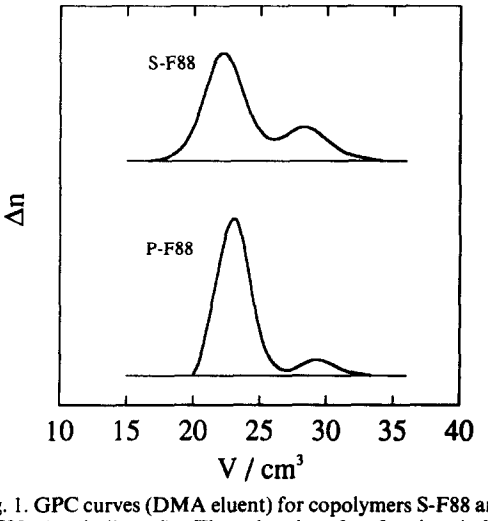

Fig. 1. GPC curves (DMA eluent) for copolymers S-F88 and P-F88 (as indicated). The plot is of refractive index difference (Δn) vs elution volume. The ordinate scales and zeros are arbitrary.

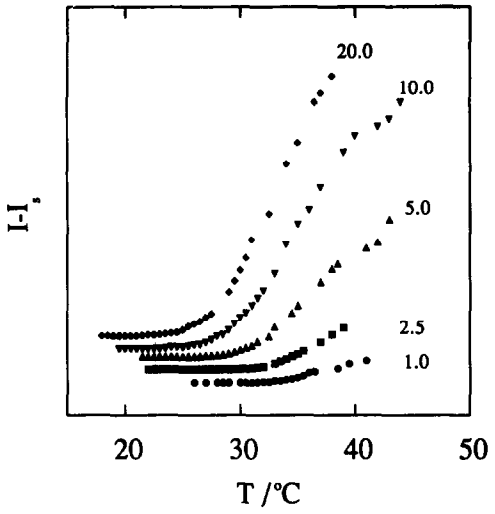

Fig. 2. Excess scattering intensity ($I - I_s$, I_s = scattering from pure solvent) vs temperature for solutions of copolymer S-F88 at the concentrations (g L^{-1}) indicated. The intensity scale is arbitrary. For clarity, the zeros of the curves have been displaced with respect to the ordinate.

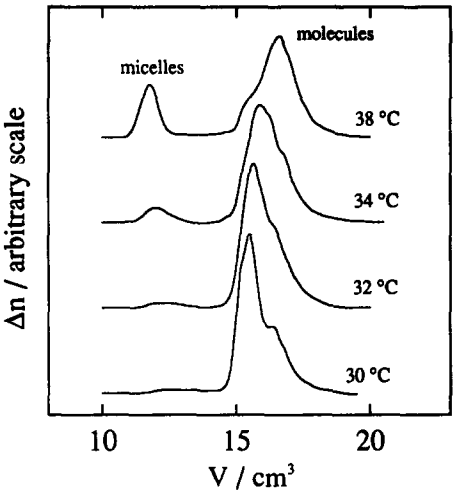

Fig. 4. EGPC curves for a 2.5 g L^{-1} solution of copolymer S-F88. The probe concentration was 0.5 g L^{-1} excess over eluent. Eluent temperatures are indicated. For clarity, the EGPC curves are displaced on the ordinate scale (Δn, refractive index difference).

is through a plot of log c against reciprocal cmT, as shown in Fig. 5.

The additional values are derived from measurements reported previously [4] and obtained by a dye solubilization technique. The solubilization of a dye was amongst the first methods used to detect the onset of micellization in $E_mP_nE_m$ block copolymers [18]. As described more recently [4, 19] the use of 1,6-diphenyl-1,3,5-heaxtriene (DPH) allows the experiment to be conducted at very low probe concentrations, i.e. without affecting the association properties of the surfactant. Examples of results obtained for copolymer P-F88 are shown in Fig. 6. In previous work [4] the cmT was obtained from these data by locating the first inflection in the curve. Values more closely related to those from the light scattering and EGPC methods were obtained in the present work as the temperature at which the intensity curve left the baseline. The difference is approximately 3°C. As seen in Fig. 5, this parallel method of data treatment meant that values of the cmT from the three methods were in excellent correspondence.

The agreement between the three methods is particularly pleasing since each has a particular strength. The EGPC method is well suited to very dilute solutions and benefits from the high sensitivity and stability of modern differential refractometers. The signal depends essentially on mass concentration (through the refractive index increment) and (because it is a separation method) yields mass fractions of micelles and molecules in a solution at equilibrium. Viscosity effects preclude its use at high concentrations. The light scattering method is less useful at very low concentrations, but can be extended to relatively high concentrations (see e.g. Ref. [10]). Since the intensity of scattered light depends on the product of mass concentration and molar mass

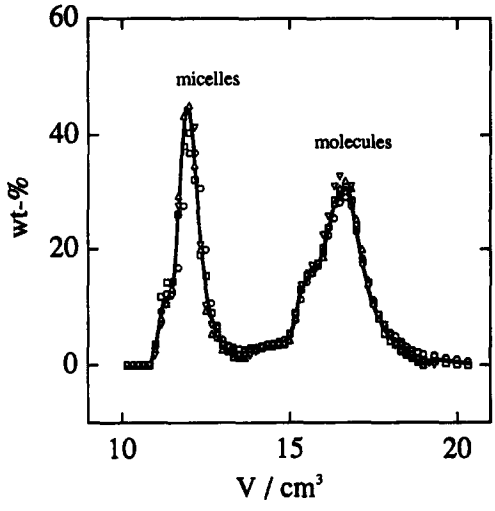

Fig. 3. Normalized EGPC curves for a 2.5 g L^{-1} solution of copolymer S-F88 at 41°C. The individual points represent probe concentrations in the range 2 to 20 g L^{-1} excess over eluent. Data points obtained for probe concentrations as low as 0.5 g L^{-1} excess (not shown) followed the same pattern but with increased scatter.

Table 2. Critical micelle temperatures for F88 copolymers[a]

	S-F88		P-F88		
c (g dm^{-3})	SLS	EGPC	SLS	EGPC	DS[a]
0.1	—	38	—	—	—
0.3	—	35	—	—	—
0.5	—	34	48	45	49
1.0	31.5	31	—	—	45
2.5	30	30	38	39	42
5	27	29	37	—	38
10	23	—	35	34	34
20	21.5	—	—	—	—
25	—	—	30	—	28
50	—	—	27	—	27
100	—	—	23	—	23
150	—	—	—	—	18

[a]SLS = static light scattering; EGPC = elution gel permeation chromatography; DS = dye solubilization.

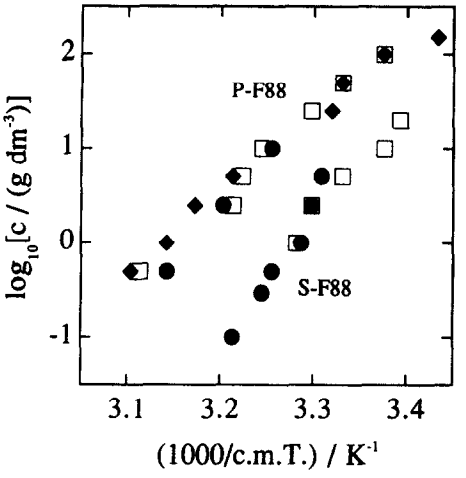

Fig. 5. Critical micelle temperatures for $E_mP_nE_m$ copolymers in aqueous solution. Logarithm of concentration vs reciprocal critical micelle temperature determined by (□) light scattering; (●) EGPC and (◆) dye solubilization for copolymers S-F88 and P-F88 (as indicated).

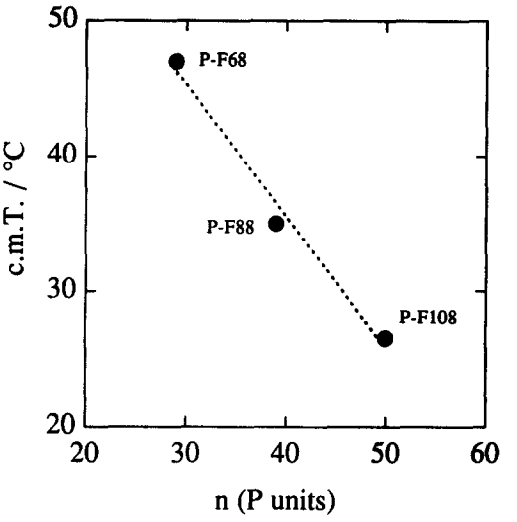

Fig. 7. Critical micelle temperature vs number of P units (n) for $E_mP_nE_m$ copolymers in aqueous solution. The data points are from Ref. [4] and are for Pluronic copolymers P-F68, P-F88 and P-F108 in present notation. The average slope (indicated by the dotted line) is -1°C per P unit.

through the Rayleigh–Gans–Debye equation, the method is sensitive to low concentrations of micelles of high molar mass. However, because of this physics of scattering, the signal relates to the intensity fractions of micelles and molecules in solution (i.e. the z-fraction, $z = wM$, where w is the mass fraction). The dye solubilization method is sensitive across a wide range of concentration, but depends on the equilibrium concentration of dye in the micellar phase. This property means that it relates in a direct way to the solubilization of organic molecules in micelles.

The most striking feature of Fig. 5 and Table 2, reflecting the main purpose of this paper, is the large difference in association behaviour of the two samples. Considered at equivalent concentration, the cmTs of solutions of S-F88 are some 10–15°C lower than those of solutions of P-F88. Considered at equivalent temperature, the solutions of the two copolymers differ in critical micelle concentrations by a decade or more. Yet the two copolymers have essentially the same average molar mass and composition (see Table 1) and both meet commercial specification. Indeed, such differences in overall molecular characteristics as do exist point to the opposite effect, since the values of average molar mass and average P content listed in Table 1 are both slightly higher for copolymer P-F88 than for copolymer S-F88.

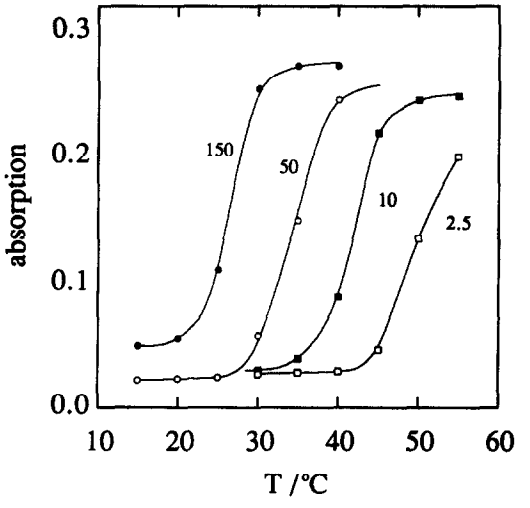

Fig. 6. Absorption intensity of DPH at 356 nm in aqueous solutions of copolymer P-F88 as a function of temperature. The concentrations of the solutions (g L^{-1}) are indicated.

Presumably the difference in association behaviour is related to the difference in molecular size distribution revealed by GPC (see Fig. 2). Since the two copolymers have the same overall molar mass and composition, then the evidence of the GPC curves is that copolymer S-F88 contains a wider spread of chain lengths (and so P-block lengths) than does copolymer P-F88. The relative values of M_{pk} listed in Table 1 are consistent with an average P-block length in the high-M fraction of copolymer S-F88 some 15–20% longer than that in the high-M fraction of copolymer P-F88. This is equivalent to a difference of 6–8 P units. The evidence from previous work [10] on copolymer F127 is that the association behaviour of a copolymer of this type is essentially that of its high-M fraction. Previously published results [4] show that the cmTs of the Pluronic $E_mP_nE_m$ copolymers F68 ($E_{76}P_{29}E_{76}$), F88 ($E_{103}P_{39}E_{103}$) and F108 ($E_{133}P_{50}E_{133}$), all of similar overall composition (80 wt % E), vary by approximately -1°C for each additional P unit: see Fig. 7. Assuming that this behaviour holds for both of the present samples of copolymer F88, the observed difference in association behaviour can be ascribed, at least in part, to a longer average P-block length in the high-M fraction of copolymer S-F88.

In academic studies it is common to work on samples as received from the manufacturer and to accept overall values of molar mass and composition

without further characterization. The present work makes particularly clear the scale of the differences which might be expected when comparing results obtained for different samples of nominally the same copolymer and also, by inference, the possibility of error when correlating properties within a series of copolymer samples.

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