Preparation and properties of stat-copoly-(oxyethylene–oxypropylene)-block-poly(oxyethylene): 2. Micellization and gelation properties in aqueous solution

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Aqueous solutions of a range of diblock copolymers with one stat-copoly(oxyethylene–oxypropylene) block and one poly(oxyethylene) block were investigated by a variety of techniques, including light scattering, photon correlation spectroscopy, surface tension and electron microscopy. Critical micelle concentrations and temperatures were determined and estimates made of micellar size and shape. The thermodynamic micellization functions were derived, and comparison made with those of a diblock-copoly(oxyethylene–oxypropylene). Thermally reversible gelation was noted, as were solubilization effects. The composition of the statistical block was of major importance in determining the hydrophobicity of a copolymer, and thereby its micellization and gelation properties.

(Keywords: diblock copolymer; micellization; gelation properties; light scattering)

INTRODUCTION

When a block copolymer is dissolved in a liquid which is a poor solvent for one of its components but a good solvent for the other, the copolymer may aggregate reversibly to form micelles. The phenomenon is well documented for both organic[1] and aqueous[2] solvents. In either case, the micelles consist of a core of the poorly soluble blocks surrounded by a fringe of the soluble blocks. At a given temperature micellization takes place above a certain concentration (critical micelle concentration, *cmc*) and is preceded at lower concentrations by positive adsorption at the air/water interface.

Block copolymers of propylene oxide and ethylene oxide are well known examples of aqueous surfactants. A number of triblock copolymers, both $E_xP_yE_x$ and $P_yE_xP_y$, are available commercially (e.g. Pluronics from BASF, Synperonics from ICI). (Here E represents an oxyethylene chain unit and P an oxypropylene chain unit.) The aggregation properties of these copolymers have been studied, although the reported results are often disparate: recent papers[3–5] cite some of the relevant literature. Diblock copolymers of propylene oxide and ethylene oxide are not readily available and their properties in aqueous solution have been little studied. It is known that P/E block copolymers with lengthy oxypropylene blocks are very hydrophobic and have very low *cmc*s[6].

A statistical E/P block can be substituted for the oxypropylene block. Variation of the composition of the statistical block gives control over the hydrophobicity of the copolymer and so over its properties in aqueous solution. In the previous paper[7] we have reported the preparation of well-defined diblock copolymers with statistical E/P and oxyethylene blocks. In this paper we describe an investigation of the micellization and gelation properties in aqueous solution of those copolymers.

Notation. A diblock copolymer with a statistical block of composition 30 mol% oxyethylene and 70 mol% oxypropylene and block length 75 chain units (counting both E and P) plus an oxyethylene block of 60 chain units is denoted $(E/P\text{-}30/70)_{75}E_{60}$.

EXPERIMENTAL

Materials

The preparation and characterization of the diblock copolymers has already been described[7]: their statistical blocks had sequence distributions in close correspondence with Bernoullian statistics, and their block length distributions were narrow. Water was distilled and filtered as described below.

Light scattering

Measurements were made using a Sofica PGD 40B photogoniometer. The solvent (water) and the solutions of the copolymer in water were clarified by filtration (Millipore, 0.22 μm). Measurements were made with light of wavelength 546 nm at a scattering angle of 90°.

Two types of light scattering measurements were made.

1. Solutions at a given concentration. Light scattering intensities were measured at intervals of 1–3°C as the temperature was raised from 18°C to above the critical micelle temperature (*cmT*). Additionally, for several

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solutions the temperature was raised above the cloud point.

2. Solutions at a given temperature. Light scattering intensities were measured for a range of concentrations above and below the *cmc*. The results were used to determine values of the *cmc* and also the weight-average micellar weight of the micelles. For the latter purpose, the refractive index increment was measured by use of a Bellingham and Stanley Abbé 60/ED refractometer.

Photon correlation spectroscopy (p.c.s.)

The p.c.s. measurements were made on clarified solutions at 25°C by means of a Malvern PCS100 spectrometer with incident light of wavelength 488 nm supplied by an argon-ion laser. The intensity of light scattered at 90° was detected, and the autocorrelation function of the photocurrent was determined with a Malvern K7027 correlator. Hydrodynamic radii were determined from the measured diffusion coefficients in the usual way, using the Einstein–Stokes equation.

Surface tension

Surface tensions (γ) of dilute aqueous solutions were measured by the detachment of a Wilhelmy plate. The glass plate was fashioned from a cover slip with the surface roughened by mild etching. Precautions were taken to ensure cleanliness: the water was distilled and filtered (Millipore, 0.22 μm). The plate was suspended from a Beckman LM-600 microbalance which was calibrated with standard weights. The accuracy of measurement was checked by frequent determination of γ of water. In an experiment, solutions were held at a given temperature (± 1°C) for as long as 48 h before γ was determined. It was found that equilibration was slow, but that changes after a period of 1 h were slight: in practice an equilibration period of 3 h was used for each measurement.

Electron microscopy

Drops of a micellar solution were allowed to spread on a carbon substrate supported by a copper grid before the water was quickly evaporated in an oven at a temperature a few degrees higher than the *cmT*. The specimen so prepared was examined under a Jeol 100CX electron microscope operated at 80 kV.

RESULTS AND DISCUSSION

Micellization

Critical micelle temperature by light scattering. At a given concentration of block copolymer micellization takes place at a certain critical temperature, i.e. the *cmT*. Because of the negative temperature coefficient of solubility of poly(oxyethylene) and poly(oxypropylene), the *cmT* is reached by increasing the temperature. Further increase in temperature leads eventually to phase separation, causing clouding of the solution. In our work, light scattering was used to determine the *cmT*, as illustrated in *Figure 1* for sample $(E/P\text{-}30/70)_{73}E_{60}$ dissolved in water at a concentration of 6 g dm^{-3}.

Three temperature regions can be defined in the scattering curve.

1. $T < 38$°C: unimer region. In this region the low intensity of scattered light is characteristic of unassociated chains.
2. 38°C $< T <$ 94°C: micellar region. In this region the intensity of scattered light increases sharply to a plateau above 60°C and, to the eye, the solution takes on a bluish cast. This behaviour is characteristic of the formation of micelles, with the micellar solution fully established above 60°C.
3. $T > 94$°C: cloudy region. In this region the intensity of scattered light increases very sharply and, to the eye, the solution becomes cloudy. This behaviour is characteristic of phase separation.

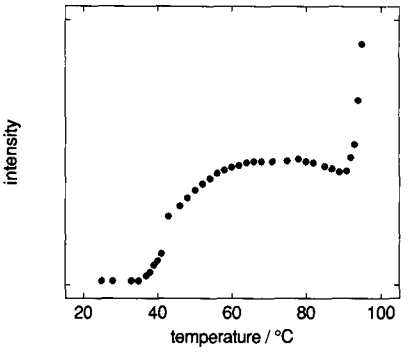

Figure 1 Light scattering intensity (arbitrary scale) *versus* temperature for a 6 g dm^{-3} solution of block copolymer $(E/P\text{-}30/70)_{73}E_{60}$

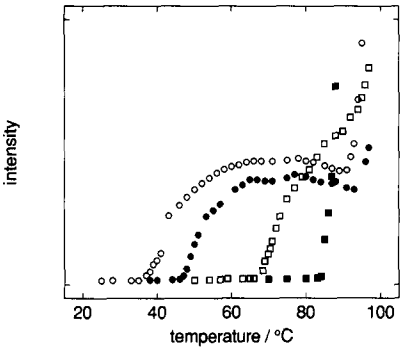

Figure 2 Light scattering intensity (arbitrary scale) *versus* temperature for a solution of block copolymers: (○) $(E/P\text{-}30/70)_{73}E_{60}$, $c = 6.0$ g dm^{-3}; (●) $(E/P\text{-}49/51)_{119}E_{79}$, $c = 4.4$ g dm^{-3}; (□) $(E/P\text{-}66/34)_{115}E_{120}$, $c = 3.3$ g dm^{-3}; (■) $(E/P\text{-}79/21)_{220}E_{271}$, $c = 10.2$ g dm^{-3}

For the system illustrated in *Figure 1*, these observations define the *cmT* at 38°C and the cloud temperature at 94°C. Light scattering curves for samples with different hydrophobic blocks are illustrated in *Figure 2*. Some samples, e.g. $(E/P\text{-}79/21)_{220}E_{271}$, showed no *cmT*, only a cloud point.

Values of the *cmT* and the cloud point (if determined) are listed in *Table 1*. The values of *cmT* obtained were affected by concentration (*Table 1* and *Figure 3*): this effect is discussed in detail later. Within the ranges investigated the effect of concentration on *cmT* was smaller than the effect of changing the composition of the hydrophobic block.

Critical micelle concentration by light scattering and surface tension. At a given temperature, micellization of a block copolymer in solution takes place at a certain critical concentration, i.e. the *cmc*. Plots of light scattering

Table 1 Critical micelle temperatures (*cmT*) of the block copolymers from light scattering

Sample	Concentration range (g dm^{-3})	*cmT* range (°C)	Cloud point (°C)
$(E/P\text{-}30/70)_{73}E_{36}$	0.7–5.1	36.0–29.5	–
$(E/P\text{-}30/70)_{73}E_{60}$	0.9–6.5	39.0–35.0	94
$(E/P\text{-}49/51)_{119}E_{21}$	3.4	–	59
$(E/P\text{-}49/51)_{119}E_{79}$	2.0–39.8	47.5–39.0	–
$(E/P\text{-}49/51)_{119}E_{119}$	1.4–12.7	51.0–45.0	–
$(E/P\text{-}66/34)_{115}E_{67}$	4.7	–	47
$(E/P\text{-}66/34)_{115}E_{120}$	2.2–14.4	66.0–63.0	–
$(E/P\text{-}66/34)_{115}E_{268}$	2.4–40.9	68.5–63.0	–
$(E/P\text{-}79/21)_{220}E_{78}$	5.7	–	80
$(E/P\text{-}79/21)_{220}E_{200}$	8.3	–	83
$(E/P\text{-}79/21)_{220}E_{271}$	10.2	–	84

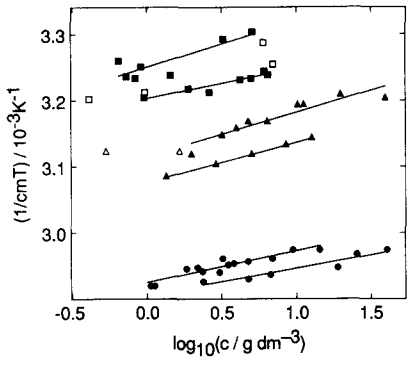

Figure 3 Reciprocal critical micelle temperature *versus* logarithm of concentration: (■) $(E/P\text{-}30/70)_{73}E_{36}$ (top) and $(E/P\text{-}30/70)_{73}E_{60}$ (bottom); (▲) $(E/P\text{-}49/51)_{119}E_{79}$ (top) and $(E/P\text{-}49/51)_{119}E_{119}$ (bottom); (●) $(E/P\text{-}66/34)_{115}E_{120}$ (top) and $(E/P\text{-}66/34)_{115}E_{268}$ (bottom). The open symbols are *cmc* measurements by surface tension and light scattering

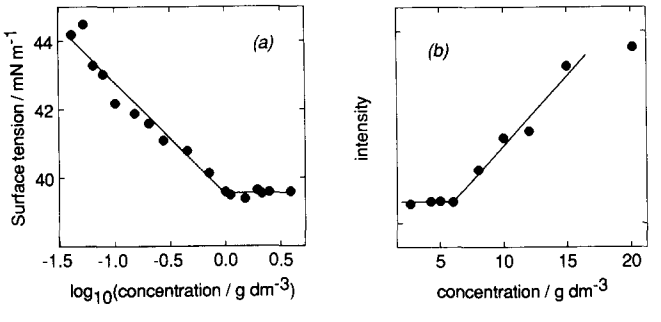

Figure 4 (a) Surface tension *versus* logarithm of concentration for aqueous solutions of block copolymer $(E/P\text{-}30/70)_{73}E_{60}$ at 38°C. (b) Light scattering intensity (arbitrary scale) *versus* concentration for aqueous solutions of block copolymer $(E/P\text{-}30/70)_{73}E_{36}$ at 31°C

intensity or γ against log(concentration, c) (*Figure 4*) showed discontinuities at concentrations identified as the *cmc*. The surface tension was constant above the *cmc*, as expected for a saturated surface monolayer (Gibbs monolayer). These measurements were made for a few samples only, in order to check the determinations of the *cmT*. The results (*Table 2*) are in broad agreement with the light scattering determinations of the *cmT* (*Figure 3*).

Micellar size and shape by electron microscopy. The electron micrographs were consistent with micelles of spherical shape and a narrow distribution of size. For sample $(E/P\text{-}66/34)_{115}E_{268}$ the number-average radius of the collapsed micelles isolated at 75°C was $R_n \sim 20$ nm and the ratio of average radii was $R_w/R_n \sim 1.05$. Other samples investigated in this way gave similar results: R_n in the range of 15–25 nm and $R_w/R_n \sim 1.1$.

Micellar size by p.c.s. Samples $(E/P\text{-}30/70)_{73}E_{36}$, $(E/P\text{-}30/70)_{73}E_{60}$ and $(E/P\text{-}49/51)_{119}E_{119}$ were investigated by p.c.s. The hydrodynamic radius of sample $(E/P\text{-}30/70)_{73}E_{60}$ in solution (0.96 g dm^{-3}) was $R_h \sim 16$ nm over the temperature range 39–50°C, and that of sample $(E/P\text{-}49/51)_{119}E_{119}$ in solution at 49°C was $R_h \sim 15$ nm over the concentration range 0.5–1.2 g dm^{-3}. Values found for sample $(E/P\text{-}30/70)_{73}E_{36}$ over similar ranges of concentration and temperature were larger ($\sim$50–80 nm), consistent with the presence of agglomerates of micelles.

Micellar weight by light scattering. Weight-average micellar weights of samples $(E/P\text{-}30/70)_{73}E_{36}$ and $(E/P\text{-}30/70)_{73}E_{60}$ were measured (solution temperature = 37°C). Refractive index increments were 0.135 and 0.142 cm^3 g^{-1}, respectively. As might be expected from the discussion above (p.c.s.), the micellar weight obtained for sample $(E/P\text{-}30/70)_{73}E_{36}$ was high ($M_w > 10^6$), consistent with agglomeration of micelles. That obtained for sample $(E/P\text{-}30/70)_{73}E_{60}$ was $M_w \sim 2 \times 10^5$, indicative of an aggregation number for the micelles at 37°C of $\sim$50.

General conclusions. The following general conclusions can be drawn from the results.

Micelles were not formed from samples having a low P content (20 mol%) in their statistical blocks. At a somewhat higher level of P (34–51 mol%), only samples with long E blocks formed micelles. All samples with a high P content (70 mol%) in their statistical blocks formed micelles.

The *cmT* increased markedly as the P content was decreased. The *cmT*s of samples with the same statistical block depended on their *E* block length, i.e. *cmT* increased as the E block length increased, though this effect was smaller.

For all solutions in which the copolymer formed micelles, the intensity of scattered light increased sharply at the *cmT*, which indicated closed association to large micelles. This conclusion was supported by the results of electron microscopy, p.c.s. and light scattering intensity.

For the few systems studied up to high temperatures, it was noted that the micellar region decreased in width as the P content of the statistical block was decreased

Table 2 Critical micelle concentration (*cmc*) from surface tension and light scattering

Sample	*T* (°C)	*cmc* (g dm^{-3}) Light scattering	*cmc* (g dm^{-3}) Surface tension
$(E/P\text{-}30/70)_{73}E_{36}$	39	–	0.41
	31	6.0	–
$(E/P\text{-}30/70)_{73}E_{60}$	38	–	0.97
	34	7.0	–
$(E/P\text{-}49/51)_{119}E_{79}$	47	–	0.53
$(E/P\text{-}49/51)_{119}E_{119}$	47	–	1.66

Table 3 Free energy of micellization[a]

Sample	(i)		(ii)		
	cmT (°C)	ΔG° at 5×10^{-4} mol dm^{-3} (kJ mol^{-1})	*T* (°C)	*cmc* (mol dm^{-3})	ΔG° (kJ mol^{-1})
$(E/P\text{-}30/70)_{73}E_{36}$	31.6	−19.3	35.4	1.27	−23.0
$(E/P\text{-}30/70)_{73}E_{60}$	36.7	−19.6	35.4	9.58	−17.8
$(E/P\text{-}49/51)_{119}E_{79}$	43.2	−20.0	45.3	2.39	−22.1
$(E/P\text{-}49/51)_{119}E_{119}$	47.1	−20.2	45.3	10.28	−18.2
$(E/P\text{-}66/34)_{115}E_{120}$	65.0	−21.4	65.8	3.52	−22.4
$(E/P\text{-}66/34)_{115}E_{268}$	66.8	−21.5	65.8	8.25	−20.0

[a]Estimated error in $\Delta G^\circ = \pm 0.1$ kJ mol^{-1}

and, other things being equal, as the length of the E block was increased. A manifestation of this was that the micellar plateau was not observed in the light scattering of samples based on $(E/P\text{-}66/34)_{115}$ (*Figure 2*).

Thermodynamics of micellization

The standard free energy of micellization per mole of chain may be calculated, assuming closed association into large micelles (as indicated above), from the relationship:

$$\Delta G^\circ_{mic} \approx RT \ln(cmc)$$

Further if the association number is independent of temperature the standard enthalpy of micellization can be obtained from the Gibbs–Helmholtz relationship:

$$\Delta H^\circ_{mic} \sim R[\mathrm{d} \ln(cmc)/\mathrm{d}(1/T)]$$

and the standard entropy of micellization (ΔS°_{mic}) obtained in the usual way from ΔG°_{mic} and ΔH°_{mic}. The standard states are the unassociated copolymer chains and micelles in ideally dilute solutions of unit molarity.

Our results take the form of *cmT versus c*, and more convenient expressions for calculation of ΔG°_{mic} and ΔH°_{mic} are:

$$\Delta G^\circ_{mic} = R(cmT) \ln(c)$$

$$\Delta H^\circ_{mic} = R[\mathrm{d} \ln(c)/\mathrm{d}(1/cmT)]$$

Plots of $(cmT)^{-1}$ against $\log_{10}(c)$ are illustrated in *Figure 3*. The lines shown were obtained by the least squares method (ignoring the *cmc* results), and their inverse slopes gave values of ΔH°_{mic}.

Free energy of micellization. The results (*cmT versus c*) overlapped considerably in the concentration range of 0.7–40.9 g dm^{-3} but only slightly in the temperature range of 29.5–68.5°C (*Table 1* and *Figure 3*). Accordingly values of ΔG°_{mic} were calculated in two ways: (i) from *cmT*s interpolated to a constant molar concentration of 5×10^{-4} mol dm^{-3}; (ii) from concentrations within the overlapping temperature range for samples taken in pairs (*Figure 3*) interpolated to three chosen values of *cmT* (*Table 3*).

The values of ΔG°_{mic} listed under (i) relate directly to the *cmT*s of the samples in solution at the chosen concentration. The systematic effects are a decrease in ΔG°_{mic} as the length of the E block is increased and as the P content of the statistical block is decreased. Both these effects are a consequence of the variation of the temperature at which ΔG°_{mic} is determined, coupled with the fact that poly(oxyethylene) has a negative temperature coefficient of solubility.

Table 4 Free energy of micellization (semiquantitative)

Sample	(iii)		(iv)	
	T (°C)	ΔG° (kJ mol^{-1})	*T* (°C)	ΔG° (kJ mol^{-1})
$P_{164}E_{462}$	–	–	27	−37
$(E/P\text{-}30/70)_{73}E_{36}$	55	−42	27	−15
$(E/P\text{-}49/51)_{119}E_{79}$	55	−32	27	−4
$(E/P\text{-}66/34)_{115}E_{120}$	55	−8	27	–

The values of ΔG°_{mic} listed under (ii) give a better representation of the effect of the length of the E block. At constant temperature the effect of increasing the E block length is to increase ΔG°_{mic}. The increment per additional oxyethylene unit varies from $\sim +0.2$ kJ mol^{-1} for the (E/P-30/70) pair of copolymers to $\sim +0.02$ kJ mol^{-1} for the (E/P-66/34) pair. A comparable figure of ~ 0.10 kJ mol^{-1} was obtained for poly(oxyethylene) alkyl ethers with somewhat shorter E block lengths (13–53 E units)[8].

Comparison of the free energies of micellization of the different types of copolymer at a single temperature can only be semiquantitative because of the long extrapolations required in the plots in *Figure 3*. The results listed in *Table 4* were obtained by linear interpolation or extrapolation of the data of *Figure 3* to either (iii) 55°C, at which temperature all the copolymers form micelles or (iv) 27°C, for purposes of comparison with other results (see below). It can be seen that decreasing the P content of the statistical block results in a large increase in ΔG°_{mic} measured at constant temperature.

Comparison with block-copoly(oxyethylene–oxypropylene). We have recently investigated[6] the micellilization behaviour of a sample of block-copoly(oxyethylene–oxypropylene), $P_{164}E_{462}$. This copolymer has a *cmc* at 27°C of 4.1×10^{-7} mol dm^{-3}, corresponding to a free energy of micellization of $\Delta G^\circ = -37$ kJ mol^{-1}. Taken together with the extrapolated data from the present work the four results form a satisfactory sequence covering a range of P contents from 100 to 34 mol% [*Table 4* (iv)].

Enthalpy and entropy of micellization. Rounded values of ΔH°_{mic} and $T\Delta S^\circ_{mic}$ are listed in *Table 5*: since the predominant contribution to the thermodynamic quantities comes from the statistical block (see discussion of ΔG°_{mic} (iii) and (iv) and *Table 4*) the results for a given type of statistical block were amalgamated in order to reduce the effect of uncertainties in the slopes of individual sets of data (*Figure 3*). The positive values of the entropy of micellization are consistent with a predominantly hydrophobic interaction between the copolymer and water. A notable feature of *Table 5* is that large values of ΔH°_{mic} and ΔS°_{mic} are found right across the range of the block copolymers, including those based on the statistical copolymer with 66 mol% of E units. The values of ΔH°_{mic} in parentheses in *Table 5* were calculated per mole of P units in the copolymer. A corresponding value for a triblock-copoly(oxyethylene–oxypropylene) ($E_{13}P_{30}E_{13}$, enthalpy of micellization ~ 200 kJ mol^{-1} at 43°C[5]) is 7 kJ (mol of P units)$^{-1}$. These results are remarkably similar for the three block copolymers with P contents in their hydrophobic blocks in the range of 49–100 mol%, but the copolymer with the low P content (34 mol%) differs. It is likely that this is an effect of temperature, since the range for determination of ΔH°_{mic} and ΔS°_{mic} for the copolymers with 34 mol% P in their statistical blocks was considerably higher ($\sim$66°C) than those for the other copolymers ($\sim$36–46°C), with consequent changes in the structure of water and the hydrophobic effect.

Gelation

Thermally reversible gelation was observed for concentrated solutions of the block copolymers. For example, at a concentration of ~ 300 g dm^{-3} a solution of sample $(E/P\text{-}30/70)_{73}E_{60}$ gelled on warming to 42°C. Gelation temperatures for solutions of similar concentrations of all the copolymers are listed in *Table 6*. There is a strong correlation between gelation temperature and cmT and conclusions drawn in the earlier discussion of the cmT can be extended to gelation. Gelation was not observed for solutions of those copolymers which did not micellize (*Table 1*).

Table 5 Enthalpy and entropy of micellization[a]

Sample	T (°C)	ΔH° [b] (kJ mol^{-1})	$T\Delta S^\circ$ (kJ mol^{-1})
$(E/P\text{-}30/70)_{73}E_n$	36	350(7)	370
$(E/P\text{-}49/51)_{119}E_n$	46	310(5)	330
$(E/P\text{-}66/34)_{115}E_n$	66	440(11)	460

[a] Estimated errors in ΔH° and $T\Delta S^\circ = \pm 50$ kJ mol^{-1}
[b] Values in parentheses are per mole of P units: see text

Table 6 Gelation temperatures of the block copolymers

Sample	c (g dm^{-3})	Gelation temperature (°C)	cmT (°C) ($c = 5$ g dm^{-3})
$(E/P\text{-}30/70)_{73}E_{36}$	300	41	30
$(E/P\text{-}30/70)_{73}E_{60}$	315	42	36
$(E/P\text{-}49/51)_{119}E_{79}$	317	49	43
$(E/P\text{-}49/51)_{119}E_{119}$	310	54	48
$(E/P\text{-}66/34)_{115}E_{95}$	282	81	65
$(E/P\text{-}66/34)_{115}E_{120}$	365	82	65
$(E/P\text{-}66/34)_{115}E_{268}$	348	92	68

Studies by polarizing microscopy showed that, for the concentration range investigated, the systems were optically isotropic in both sol and gel states. Immediately below the gelation temperature it seems likely the systems consist of packed spherical micellar particles. On raising the temperature the degree of swelling of the micellar fringe is progressively reduced. Gelation may be due to either the formation of a closed-packed colloidal crystal or more likely the formation of a static network of worm-like structures by the coalescence of micellar particles. In future studies we hope to distinguish between these possibilities by n.m.r.

Solubilization

The capacity of the micellar solutions to solubilize a related statistical copolymer was tested as follows.

1. The light scattered from a solution of block copolymer $(E/P\text{-}30/70)_{73}E_{60}$ ($c = 13.6$ g dm^{-3}, $cmT = 36$°C, cloud temperature = 93°C) and statistical copolymer $(E/P\text{-}66/34)_{100}$ ($c = 0.62$ g dm^{-3}, cloud temperature = 48°C) was observed as the solution was heated. The scattering profile was essentially identical with that of a solution of the block copolymer alone, indicative of solubilization of the statistical copolymer.
2. The light scattered from a solution of block copolymer $(E/P\text{-}66/34)_{100}E_{104}$ ($c = 21.0$ g dm^{-3}, $cmT = 67$°C, cloud temperature = 95°C) and statistical copolymer $(E/P\text{-}66/34)_{100}$ ($c = 0.17$ g dm^{-3}, cloud temperature = 48°C) was observed as the solution was heated. The solution clouded on reaching 48°C and remained cloudy up to 95°C.
3. Solutions of block copolymer $(E/P\text{-}30/70)_{73}E_{60}$ ($c = 103.0$ g dm^{-3}, 2 cm^3) and statistical copolymer $(E/P\text{-}66/34)_{100}$ ($c = 0.12$ g dm^{-3}, 20 cm^3) were mixed at 68°C. At this temperature the block copolymer solution was micellar and the statistical copolymer solution was cloudy. The mixture remained cloudy at 68°C and on heating to 95°C.

The results show that solubilization of a statistical copolymer in related block copolymer micelles is possible provided that the cloud temperature of the statistical copolymer exceeds the cmT of the block copolymer and that micellization is effected from a molecular solution at a temperature below the cloud temperature of the statistical copolymer.

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REFERENCES

1 Brown, R. A., Masters, A. J., Price, C. and Yuan, X.-F. in 'Comprehensive Polymer Science, Vol. 2' (Eds C. Booth and C. Price), Pergamon Press, London, 1989
2 Attwood, D. and Florence, A. T. 'Surfactant Systems', Chapman and Hall, London, 1983
3 Prasad, K. N., Luong, T. T., Florence, A. T., Paris, J., Vaution, C., Seiller, M. and Puisieux, F. *J. Colloid Interface Sci.* 1979, **69**, 225
4 Zhou, Z. and Chu, B. *Macromolecules* 1988, **21**, 2548
5 Reddy, N. K., Fordham, P. J., Attwood, D. and Booth, C. *J. Chem. Soc., Faraday Trans.* 1990, **86**, 1569
6 Ding, J.-F., Attwood, D., Price, C. and Booth, C. *Eur. Polym. J.* 1991, **27**, 901
7 Deng, Y., Ding, J., Yu, G., Mobbs, R. H., Heatley, F., Price, C. and Booth, C. *Polymer* 1992, **33**, 1959
8 Reddy, N. K., Foster, A., Styring, M. G. and Booth, C. *J. Colloid Interface Sci.* 1990, **136**, 588