

# Effect of chain length on the micellization and gelation of block copoly(oxyethylene/oxybutylene/oxyethylene) $E_m B_n E_m$

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Three triblock copoly(oxybutylene/oxyethylene)s,  $E_{58}B_{17}E_{58}$ ,  $E_{71}B_{28}E_{71}$  and  $E_{132}B_{53}E_{132}$ , with similar composition (75–80 wt% E) but different chain lengths, were prepared by sequential anionic copolymerization, and their micellar and gelation properties in aqueous solution were determined. The methods used were light scattering intensity, photon correlation spectroscopy and gel permeation chromatography, together with observation of gelation. Measurements were made at 30°C over the full concentration range from dilute solution into the gel. The lower and upper temperature boundaries of the gel regions were identified. Phase separation was observed in dilute solutions of the copolymer of longest chain length ( $E_{132}B_{53}E_{132}$ ). Critical micelle and gel concentrations decreased markedly as chain length was increased, and micellar weights and sizes increased.

(Keywords: micellization; gelation; block copolymers; chain length; oxyethylene; oxybutylene)

## INTRODUCTION

Oxyethylene/oxypropylene and oxyethylene/oxybutylene block copolymers (e.g.  $E_m P_n E_m$  and  $E_m B_n E_m$ , where E represents an oxyethylene unit, P an oxypropylene unit and B an oxybutylene unit) form thermally reversible gels in concentrated aqueous solution. Copolymers such as  $E_{106}P_{69}E_{106}$  (F127), which, at suitable concentrations, form gels at temperatures between ambient and body temperature, are of interest in the development of implants for the controlled release of drugs, offering the possibility of *in situ* gelation of injected solutions<sup>1–4</sup>. The block copolymers form micelles in aqueous solution and gelation involves aggregation of these associates rather than single molecules<sup>5–12</sup>. In solutions of moderate concentration, there is evidence that multimicellar aggregates are formed, and that gelation involves these entities<sup>6,11–14</sup>.

As explained previously<sup>12</sup>, the transfer reaction in the anionic polymerization of propylene oxide leads to copolymers that contain diblock copolymeric impurities with a relatively high oxypropylene content. Moreover, the molecular compositions of commercial  $E_m P_n E_m$  copolymers can be complicated by other factors. For example, samples of F127 from various sources examined in our laboratory had bimodal gel permeation chromatography (g.p.c.) curves and molecular-weight distributions<sup>15</sup>. Recent studies have shown that the second component can be (predominantly) either homopoly(oxyethylene) or triblock copolymer of lower molecular weight than the major component. The striking variations in results from studies of the micellization and gelation of F127 in different

laboratories<sup>5,9,16,17</sup> is probably due in large part to variation in sample composition. In this respect the nature of the impurity is important. Minor diblock components of high oxypropylene content, resulting from transfer, are more surface-active and less soluble than the bulk of the sample and greatly affect surface properties. Minor components of high oxyethylene content have little effect on properties; e.g. poly(oxyethylene) acts as an inert diluent.

It is not possible to eliminate chain transfer in the anionic polymerization of propylene oxide<sup>18</sup>, whereas transfer is not a problem in the anionic polymerization of butylene oxide<sup>19</sup> and completely difunctional poly(oxybutylene) can be readily prepared. Consequently, it is possible to prepare block copolymers with fairly uniform compositions. In comparison with  $E_m P_n E_m$  copolymers,  $E_m B_n E_m$  copolymers are better materials for study of micellization and gelation behaviour.

The present study concerns the micellization and gelation behaviour of a series of three triblock copolymers  $E_m B_n E_m$  with similar overall compositions, 75–80 wt% E. The background to the preparative method has been discussed recently<sup>10</sup>, and a detailed study of one of the copolymers discussed here,  $E_{58}B_{17}E_{58}$ , has been reported elsewhere<sup>12</sup>. Other studies of  $E_m B_n E_m$  copolymers have concentrated on the technology of surface activity<sup>20–22</sup> or on surface tension reduction<sup>23</sup>.

## EXPERIMENTAL

### Block copolymers

Each of the block copolymers was prepared by sequential anionic polymerization in essentially the same way. The method is briefly indicated below for copolymer

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**Table 1** Molecular characteristics of the block copolymers<sup>a</sup>

Copolymer	$w_{oe}$	$x_{oe}$	$M_n$	$M_w$	$w_{POE}$
E <sub>58</sub> B <sub>17</sub> E <sub>58</sub>	0.80	0.88	6400	7000	0.02
E <sub>71</sub> B <sub>28</sub> E <sub>71</sub>	0.76	0.84	8000	8800	0.18
E <sub>132</sub> B <sub>53</sub> E <sub>132</sub>	0.75	0.83	15 500	17 500	0.26

<sup>a</sup> $w_{oe}$  = weight fraction oxyethylene in copolymer;  $x_{oe}$  = mole fraction oxyethylene in copolymer;  $M_n$  = number-average molecular weight from n.m.r.;  $M_w$  = weight-average molecular weight from  $M_n$  and  $M_w/M_n \sim 1.1$  from g.p.c.;  $w_{POE}$  = weight fraction poly(oxyethylene) impurity

E<sub>71</sub>B<sub>28</sub>E<sub>71</sub>, together with characterization data. Full details of the preparation of copolymer E<sub>58</sub>B<sub>17</sub>E<sub>58</sub> have been reported previously<sup>12</sup>.

Initiator solution was prepared by dissolving freshly cut potassium in freshly distilled diethylene glycol. A portion of this solution served to initiate the polymerization of 1,2-butylene oxide in an ampoule under vacuum conditions at 50°C for 3 days and then at 75°C until polymerization was complete. The molecular weight calculated from the preparative conditions was  $M_n = 2230$ . A portion was removed for analysis. Chain structure and chain length were investigated by <sup>13</sup>C nuclear magnetic resonance (n.m.r.) spectroscopy (Bruker AC300E spectrometer operated at 75.5 MHz, 0.6 g cm<sup>-3</sup> solutions in CDCl<sub>3</sub>). Assignments were taken from ref. 19. The butylene oxide added exclusively head to tail and all end-groups were secondary hydroxyl with no evidence of unsaturation (no transfer). The intensities of resonances from end-group carbons were equivalent to those from carbons assigned to the oxyethylene/oxybutylene junctions (i.e. those originating from the initiator). The number of oxybutylene units added per initiator molecule was determined from the ratio of the intensity of resonances originating from the backbone carbon atoms in the B units relative to those from backbone carbon atoms in the EB junctions. The value so obtained was 28.0 B units, corresponding to a molecular weight (including the initiator residue) of  $M_n = 2120$ . The molecular weight of the poly(oxybutylene) was further investigated by gel permeation chromatography (tetrahydrofuran (THF) eluant, calibration with poly(oxyethylene) (POE) standards). The g.p.c. curve showed a narrow peak ( $M_w/M_n < 1.1$ ). The molecular weight at the peak (as if POE) was  $M_{pk} \sim 2200$ , in good agreement with the result from n.m.r.

The bulk of the poly(oxybutylene) was used to initiate the polymerization of ethylene oxide at about 10°C raised to 70°C over a period of two weeks until conversion was complete. The composition of the copolymer was determined by <sup>13</sup>C n.m.r. (conditions as described above) from the relative intensities of resonances associated with the carbons of the ethyl side-group and the methylene and methine carbons of the backbone. The mole fraction of E units added was found to be  $x_{oe} = 0.86$ , as expected, which corresponds to 86 E units per end-block, and a weight fraction of oxyethylene in the copolymer of  $w_{oe} = 0.80$  (expected,  $w_{oe} = 0.81$ ). Comparison of the intensities associated with carbon atoms in end-groups (which were all -CH<sub>2</sub>OH) and EB junctions indicated an excess of end-groups, consistent with the presence of poly(oxyethylene) in the sample, presumably initiated by moisture introduced at the second stage of the

preparation. Aqueous g.p.c. (pure water eluant, see later for details) served to confirm the presence of poly(oxyethylene) impurity. Correction for the homopolymer (about 18 wt%) reduced the number of E units per end-block from 86 to 71. The overall molecular weight was  $M_n = 8000$  and the overall weight fraction  $w_{oe} \sim 0.76$ . G.p.c. with THF eluant was used, as described above, to determine a narrow molecular-weight distribution for the copolymeric component ( $M_w/M_n \sim 1.1$ ) with a molecular weight  $M_{pk} \sim 8500$ , in good agreement with the result from n.m.r. Values of  $M_n = 8000$  and  $M_w = 8800$  were adopted. The block copolymer was denoted E<sub>71</sub>B<sub>28</sub>E<sub>71</sub>.

Molecular characteristics of the three copolymers are summarized in Table 1. The good agreement between the results of the two methods of characterization (n.m.r., g.p.c.) illustrated above was reproduced for all the samples. With the exception of sample E<sub>58</sub>B<sub>17</sub>E<sub>58</sub>, the samples contained significant fractions of poly(oxyethylene) impurity. Correction was made for this material in calculating the concentrations of the block copolymers in solution.

#### Light scattering intensity

Static light scattering (intensity light scattering) was carried out using a Malvern 7027 photometer with vertically polarized incident light of wavelength 488 nm supplied by a 2 W argon-ion laser. Solutions were clarified by ultrafiltration ( $\times 3$ ) through 0.22  $\mu$ m Millipore filters. Intensities of scattered light from solutions at 30°C were measured either at angles of 45°, 90° and 135° to the incident beam or, for solutions of copolymer E<sub>132</sub>B<sub>53</sub>E<sub>132</sub> at 11 angles in the range 30°–150°. Equilibration times of at least 10 min were allowed for dilute solutions, and at least 30 min for concentrated solutions.

#### Photon correlation spectroscopy

Dynamic light scattering (photon correlation spectroscopy, p.c.s.) was carried out with the Malvern 7027 autocorrelator using 60 linearly spaced channels with a far-point delay of 1024 sample times. Measurements of light scattered from solutions at 30°C were made at an angle of 90° to the incident beam. Solutions were clarified as described above. Equilibration times of at least 10 min were allowed for dilute solutions, and at least 30 min for concentrated solutions. Diffusion coefficients were determined from a single-exponential fit of the correlation curve. Hydrodynamic radii were calculated from measured diffusion coefficients by means of the Stokes–Einstein equation. Analysis of the polydispersity of micellar size was carried out by the method of cumulants<sup>24</sup>.

#### Refractive index increment

The specific refractive index increment at 30°C was determined by use of an Abbé 60/ED precision refractometer. The results for the three copolymers could not be distinguished. A value of  $dn/dc = 0.138 \pm 0.003$  cm<sup>3</sup> g<sup>-1</sup> was obtained from combined data. The refractive index of poly(oxyethylene) is very similar to that of the copolymer, e.g. 0.135 cm<sup>3</sup> g<sup>-1</sup> at 25°C<sup>25</sup>, and, as a consequence, light scattering was not affected by heterogeneity of refractive index.

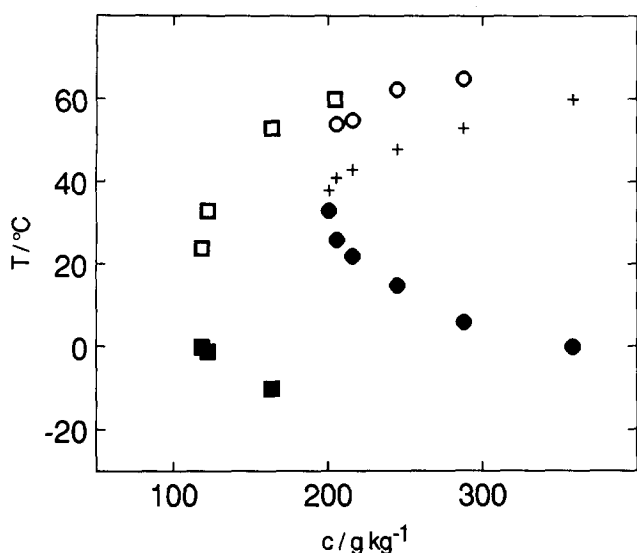


Figure 1 The sol-gel behaviour of copolymers  $E_{58}B_{17}E_{58}$  (●, ○) and  $E_{71}B_{28}E_{71}$  (■, □) in water. The points represent the temperatures at which the solutions either gel (●, ■) or become mobile (○, □) on raising the temperature. The crosses (+) indicate the onset of syneresis in the gels of copolymer  $E_{58}B_{17}E_{58}$  (not observed for copolymer  $E_{71}B_{28}E_{71}$ )

Aqueous gel permeation chromatography

Four TSK-gel PW columns (G3000 to G6000) were used with water eluant at 25°C and a flow rate of 0.5 cm<sup>3</sup> min<sup>-1</sup>. Solutions of concentration 5–7 g dm<sup>-3</sup> were injected via a 100 mm<sup>3</sup> loop. Dimethylacetamide was used as internal marker (elution volume 38.5 cm<sup>3</sup>) to compensate for any fluctuations in flow rate. Calibration was with poly(oxyethylene) standards.

Gel-sol behaviour

A solution of the block copolymer was enclosed in a small tube and observed over a range of temperatures (-10 to 70°C). The change from a mobile to an immobile system (or vice versa), determined by inverting the tube, served to define the sol-gel transition temperature (to ±1 K). Separation of water from the gel (syneresis) was observed towards the high-temperature limit of the gel region: otherwise the system was homogeneous.

RESULTS AND DISCUSSION

Solubility and gelation

The sol-gel and liquid-liquid phase behaviours of the block copolymer in water are summarized in Figures 1 and 2. The two copolymers of low molecular weight (see Figure 1) had critical gel concentrations and temperatures as follows:

Copolymer	$E_{58}B_{17}E_{58}$	$E_{71}B_{28}E_{71}$
$c_{gel}$ (g kg <sup>-1</sup> )	200	118
$T_{gel}$ (°C)	30–40	0–25

Above the critical gel concentration, the sol-gel behaviour depended on temperature and sample. For example, on raising the temperature of a solution of  $E_{58}B_{17}E_{58}$  of concentration 206 g dm<sup>-3</sup> from 0°C, the system first gelled ( $T_{gel} = 26°C$ ), then showed syneresis (separation of water from the gel) ( $T_{syn} = 41°C$ ), and

finally became mobile again ( $T_{sol} = 54°C$ ). Syneresis was not definitely observed in the gel of sample  $E_{71}B_{28}E_{71}$ ; otherwise the behaviour was similar. The copolymer of highest molecular weight ( $E_{132}B_{53}E_{132}$ , see Figure 2) had complicated sol-gel properties, since phase separation overlapped with gelation and both overlapped with freezing. The lower critical solution temperature was well below -10°C (the solutions froze at -10 to -15°C), and observations of clouding due to phase separation were limited on that account. The critical gel concentration was  $c_{gel} \sim 50$  g kg<sup>-1</sup> and the critical gel temperature ranged from below -10°C to 45°C. As indicated in Figure 2, clouding was observed on raising the temperature of the gel. It is clear from Figures 1 and 2 that the gelation temperature was sensitive to molecular length, but that the solution temperature was not, lying in the range 60 ± 10°C for all three copolymers.

The low solubility of copolymer  $E_{132}B_{53}E_{132}$  meant that studies of its micellization behaviour in dilute solution were confined to very dilute solutions. In contrast, the other two copolymers were soluble over a wide concentration range and their solutions could be studied without undue complication up to the critical gel concentration and beyond.

Micellization and surface properties

Light scattering intensity. Values of the light scattering function  $c/(S_{90}-S_{90,0})$  for dilute solutions are plotted against concentration in Figure 3. In the absence of micellization, this light scattering function should have values of 4, 8 and 11 g dm<sup>-3</sup> as  $c \rightarrow 0$ , corresponding to molecular solutions of the copolymers with  $M_w \sim 17\ 500, 8800$  and  $7000$  respectively. The low values obtained (see Figure 3) indicate predominantly micellar solutions. The clear upturn with decreasing concentration observed in the scattering function of copolymer  $E_{58}B_{17}E_{58}$  is evidence that a significant proportion of that copolymer was in its molecular state in its most dilute solutions.

Approximate values for the critical concentration for

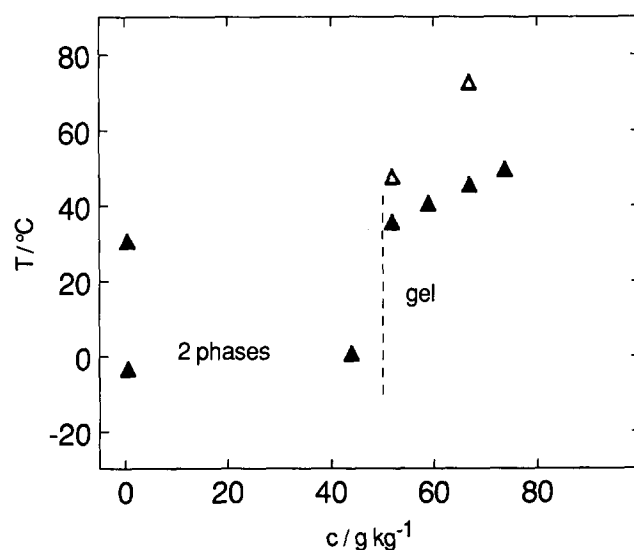
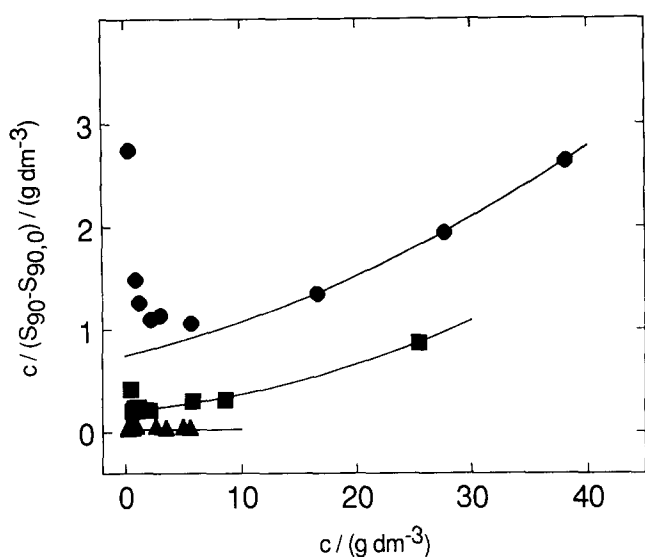
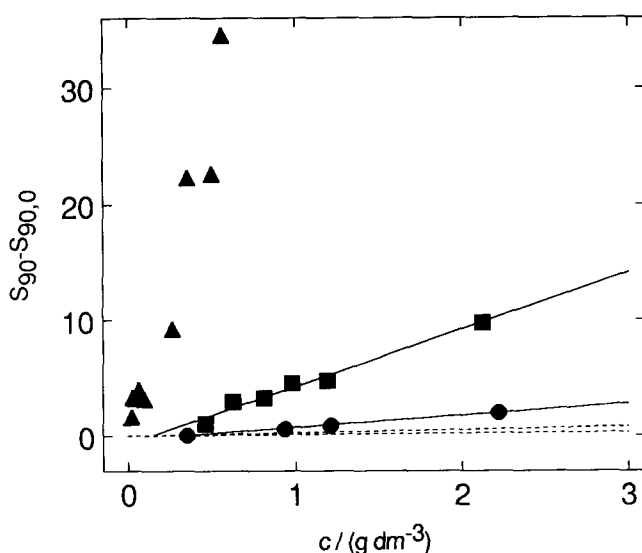


Figure 2 The phase and sol-gel behaviour of copolymer  $E_{132}B_{53}E_{132}$  in water. The full triangles (▲) represent the temperatures at which the solutions cloud on raising the temperature (phase separation). Above the concentration indicated by the broken line (i.e. > 50 g kg<sup>-1</sup>) the system is a gel from its freezing point ( $T \sim -10$  to  $-15°C$ ) to the temperature at which it becomes mobile (△)



**Figure 3** Light scattering function,  $c/(S_{90}-S_{90,0})$ , versus concentration,  $c$ , for aqueous solutions of block copolymers  $E_{58}B_{17}E_{58}$  (●),  $E_{71}B_{28}E_{71}$  (■) and  $E_{132}B_{53}E_{132}$  (▲) at 30°C.  $S_{90}$  and  $S_{90,0}$  represent intensities of light scattered at 90° from solution and from solvent respectively, relative to scattering from the benzene standard. The concentration scale for copolymer  $E_{132}B_{53}E_{132}$  is expanded 10 times



**Figure 4** Light scattering function,  $(S_{90}-S_{90,0})$ , versus concentration,  $c$ , for aqueous solutions of block copolymers  $E_{58}B_{17}E_{58}$  (●),  $E_{71}B_{28}E_{71}$  (■) and  $E_{132}B_{53}E_{132}$  (▲) at 30°C.  $S_{90}$  and  $S_{90,0}$  represent intensities of light scattered at 90° from solution and from solvent respectively, relative to scattering from the benzene standard. The full lines are the least-squares straight lines through the points. The broken lines (calculated) represent scattering from solutions of unassociated copolymers  $E_{58}B_{17}E_{58}$  (lower) and  $E_{132}B_{53}E_{132}$  (upper)

micelle formation (*CMC*) were determined by linear extrapolation of low values of  $(S_{90}-S_{90,0})$  versus  $c$  to a line representing the scattering from unassociated copolymer (see Figure 4). Values of the *CMC* obtained in this way for copolymers  $E_{58}B_{17}E_{58}$  and  $E_{71}B_{28}E_{71}$  are listed in Table 2. It has been shown previously<sup>12</sup> that, in favourable circumstances, this method gives results in fair agreement with those determined from surface tension measurements. However, in the case of copolymer  $E_{132}B_{53}E_{132}$ , the low *CMC* could not be defined with any accuracy in this way (see Figure 4). An alternative approach is defined below.

The micelles of copolymers  $E_{58}B_{17}E_{58}$  and  $E_{71}B_{28}E_{71}$  were fairly small (radius < 10 nm by all methods; see Table 2) and the light scattering theory applicable to small solutes was used to determine their average molecular weights. In support of this procedure, the dissymmetries measured for the dilute micellar solutions were very near to unity. It was assumed that light scattering from the molecular solution was essentially the same as that from pure solvent, and the molecular weight of the micelles obtained from:

$$K(c-CMC)/(S_{90}-S_{90,0}) = 1/M_w + 2A_2(c-CMC) + 3A_3(c-CMC)^2 + \dots$$

where  $K$  allows for the optical properties of the system (including the refractive index increment) and the reference standard. In the analysis, the experimental results for concentrations in the range where molecular dissociation was insignificant ( $c > 10 \text{ g dm}^{-3}$  for  $E_{58}B_{17}E_{58}$ ,  $c > 2 \text{ g dm}^{-3}$  for  $E_{71}B_{28}E_{71}$ ) were fitted by quadratic functions, as discussed previously<sup>12</sup>. Values of  $M_w$  and  $A_2$  are given in Table 2. Micellar aggregation numbers (see Table 2) were calculated from:

$$N = M_{w,mic}/M_{w,mol}$$

Treating the micelles as hard spheres, the second virial coefficient is given by:

$$A_2 = 16N_A\pi r_1^3/3M^2$$

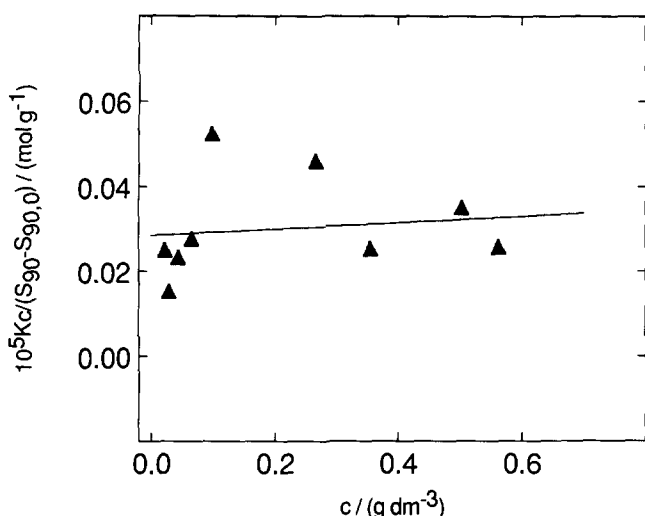
where  $r_1$  is the thermodynamic radius. Values of  $r_1$  obtained from this equation are given in Table 2.

For copolymer  $E_{132}B_{53}E_{132}$ , light scattering intensities were measured for solutions of concentration as low as  $0.02 \text{ g dm}^{-3}$  with no evidence of micellar dissociation. Accordingly, a value of the *CMC* was sought that gave a satisfactory plot of  $K(c-CMC)/(S_{90}-S_{90,0})$  versus  $c$  down to the lowest value of  $c$ , and a low value of  $A_2$  consistent with hard-sphere theory. The scatter in the data made this procedure uncertain, but a *CMC* <  $0.02 \text{ g dm}^{-3}$  was indicated, with  $A_2$  near  $10^{-6} \text{ cm}^3 \text{ g}^{-2} \text{ mol}^{-1}$ . Since the *CMC* was very low, the light scattering plots for this sample were made using  $c$  as concentration variable (see Figure 5). The pattern of scatter in the data obtained at scattering angle 90° (see Figure 5) was reproduced at other angles, indicating that

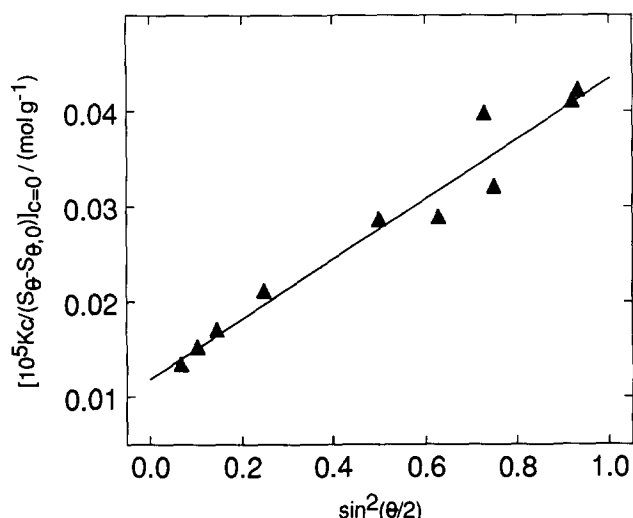
**Table 2** Micellar properties of aqueous solutions of block copolymers  $E_mB_nE_m$  at 30°C<sup>a</sup>

	Copolymer		
	$E_{58}B_{17}E_{58}$	$E_{71}B_{28}E_{71}$	$E_{132}B_{53}E_{132}$
Light scattering			
<i>CMC</i> ( $\text{g dm}^{-3}$ )	$0.30 \pm 0.03$	$0.16 \pm 0.08$	< 0.02
$10^{-5}M_w$	$0.91 \pm 0.10$	$3.6 \pm 0.3$	$70 \pm 10$
$N_w$	$13 \pm 2$	$41 \pm 5$	$400 \pm 60$
$10^4 A_2$ ( $\text{cm}^3 \text{ g}^{-2} \text{ mol}^{-1}$ )	$2.2 \pm 0.04$	$0.99 \pm 0.03$	—
$r_1$ (nm)	$5.6 \pm 2$	$10.8 \pm 3$	—
$r_g$ (nm)	—	—	$70 \pm 20$
P.c.s.			
$10^7 D_0$ ( $\text{cm}^2 \text{ s}^{-1}$ )	$4.0 \pm 0.2$	$2.7 \pm 0.1$	$0.52 \pm 0.03$
$r_h$ (nm)	$6.9 \pm 0.3$	$10.0 \pm 0.4$	$53 \pm 1$
G.p.c.			
$r_h$ (nm)	—	$11 \pm 1$	$53 \pm 5$
Hydration			
$\delta$	$10 \pm 1$	$8 \pm 1$	$49 \pm 5$

<sup>a</sup>See text for definitions of symbols



**Figure 5** Light scattering function,  $Kc/(S_{90}-S_{90,0})$ , versus  $c$  for dilute aqueous solutions of block copolymer  $E_{132}B_{53}E_{132}$ .  $S_{90}$  and  $S_{90,0}$  represent intensities of light scattered at  $90^\circ$  from solution and from solvent respectively, relative to scattering from the benzene standard. The least-squares straight line through the points is shown



**Figure 6** Light scattering function,  $[Kc/(S_\theta - S_{\theta,0})]_0$ , versus  $\sin^2(\theta/2)$  for aqueous solutions of block copolymer  $E_{132}B_{53}E_{132}$ .  $S_\theta$  and  $S_{\theta,0}$  represent intensities of light scattered at angle  $\theta$  (relative to the ongoing incident beam) from solution and from solvent respectively, relative to scattering from the benzene standard. The scattering function represents values obtained by extrapolating results for each scattering angle to zero concentration. The full line is the least-squares straight line through the points

it was mainly a consequence of error in the concentrations of the solutions, possibly as a result of filtering solutions of such low concentration.

Since the micelles of copolymer  $E_{132}B_{53}E_{132}$  were large (hydrodynamic radius  $\sim 50$  nm by g.p.c. and p.c.s., see below), data obtained over a range of angles ( $\theta$ ) were analysed. The scatter in the data did not allow construction of a satisfactory Zimm plot. Instead, values of  $Kc/(S_\theta - S_{\theta,0})$  for each angle in turn were extrapolated against  $c$  to zero concentration (see e.g. Figure 5) and then the values of  $[Kc/(S_\theta - S_{\theta,0})]_{c=0}$  were extrapolated against  $\sin^2(\theta/2)$  to zero angle (see Figure 6). The molecular weight and radius of gyration ( $r_g \equiv [(r_g^2)_z]^{1/2}$ ) found in this way (see Table 2) were  $M_w \sim (8.4 \pm 0.9) \times 10^6$  and  $r_g \sim 82 \pm 20$  nm. Additionally, the dissymmetry method was explored. Dissymmetries measured at several

concentrations were extrapolated to zero concentration ( $Z_0 = 2.0 \pm 0.2$ ) and, assuming a uniform spherical particle, the correction factor for  $90^\circ$  scattering<sup>26</sup> was obtained ( $P_{90} = 1.6$ ). This method gave a lower molecular weight ( $M_w \sim (5.6 \pm 1.1) \times 10^6$ ) and radius ( $r_g \sim 60 \pm 20$  nm) than did the angular plot, possibly as a consequence of a size distribution of clustered micelles. An average value is recorded in Table 2.

Light scattering intensities ( $S_{90} - S_{90,0}$ ) obtained over a wide concentration range are plotted against concentration in Figure 7. The maxima observed in the scattering curves of the more soluble copolymers are a consequence of interference of scattered light at moderate concentrations of scattering centres (interparticle interference). Under these circumstances, the scattering equation can be written:

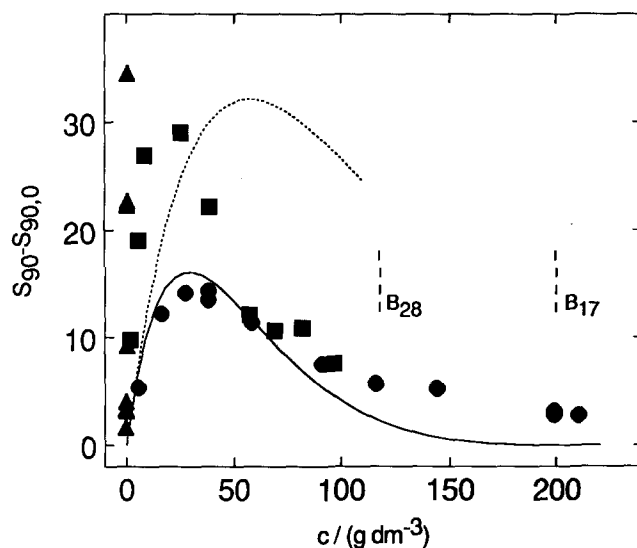
$$Kc/(S_{90} - S_{90,0}) \sim 1/Q_{90}M_w$$

where  $Q_{90}$  is the interparticle scattering factor (the intraparticle scattering factor,  $P_{90}$ , being assumed to be unity for the small micelles). For low concentrations of uniform hard spheres,  $Q_{90}$  is described by the Carnahan–Starling equation<sup>27,28</sup> based on the Percus–Yevick approximation, i.e.:

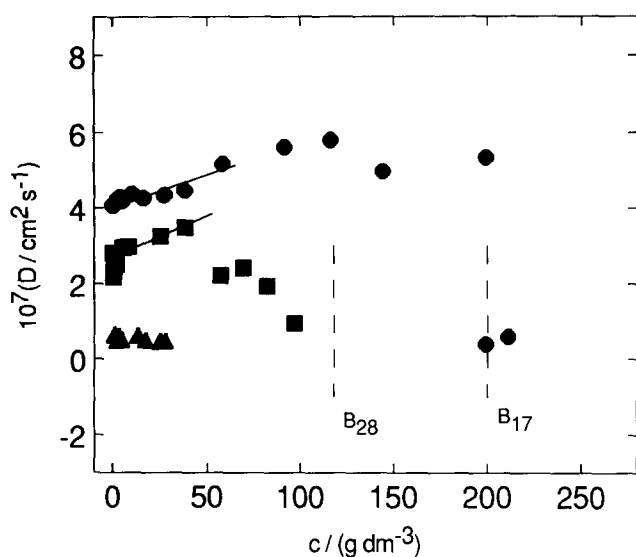
$$1/Q_{90} = [(1 + 2\phi)^2 - \phi^2(4\phi - \phi^2)](1 - \phi)^{-4}$$

where  $\phi$  is the volume fraction of equivalent hard-sphere micelles calculated from the actual volume fraction of copolymer in micelles in the system by applying a swelling factor ( $\delta_\phi$ ). A reasonable fit to the results for copolymer  $E_{58}B_{17}E_{58}$  in the concentration range 5 to  $100 \text{ g dm}^{-3}$  was obtained if it was assumed that  $\delta_\phi = 5$  (see Figure 7). The results for copolymer  $E_{71}B_{28}E_{71}$  do not fit the theory: a similar deviation has been noted for micellar solutions of P85 ( $E_{25}P_{39}E_{25}$ ) at  $50^\circ\text{C}$ <sup>11</sup>.

*Photon correlation spectroscopy.* Diffusion coefficients ( $D$ ) determined by p.c.s. are plotted against concentration in Figure 8. Diffusion coefficients for the micelles at  $c \rightarrow 0$



**Figure 7** Light scattering function,  $(S_{90} - S_{90,0})$ , versus temperature,  $T$ , for aqueous solutions of block copolymers  $E_{58}B_{17}E_{58}$  ( $\bullet$ ),  $E_{71}B_{28}E_{71}$  ( $\blacksquare$ ) and  $E_{132}B_{53}E_{132}$  ( $\blacktriangle$ ) at  $30^\circ\text{C}$ .  $S_{90}$  and  $S_{90,0}$  represent intensities of light scattered at  $90^\circ$  from solution and from solvent respectively, relative to scattering from the benzene standard. Critical gel concentrations ( $c_{gel}$ ) are indicated by the broken lines. The curves were calculated using the Carnahan–Starling equation assuming that the swelling was  $\delta_\phi = 5$  (—) and  $\delta_\phi = 2.5$  (.....)



**Figure 8** Diffusion coefficient from p.c.s.,  $D$ , versus concentration,  $c$ , for aqueous solutions of block copolymers  $E_{58}B_{17}E_{58}$  (●),  $E_{71}B_{28}E_{71}$  (■) and  $E_{132}B_{53}E_{132}$  (▲) at 30°C. The full lines are the least-squares fits to the points at  $10 < c < 50 \text{ g dm}^{-3}$ . The concentration scale for copolymer  $E_{132}B_{53}E_{132}$  is expanded 50 times. Critical gel concentrations ( $c_{\text{gel}}$ ) are indicated by the broken lines

( $D_0$ ) were obtained from the intercepts of the straight lines through the points at concentrations in the micellar range (as for extrapolation of the light scattering intensities). A linear increase of  $D$  with  $c$  has been noted for other micellar solutions<sup>7,8</sup>: at low  $c$  the effect is largely attributable to the increased probability of micelle–micelle contacts as  $c$  is increased, which has been characterized by a diffusion second virial coefficient<sup>7,8</sup>. Radii of hydration ( $r_h$ ) were calculated from  $D_0$  by means of the Stokes–Einstein equation, using a solvent viscosity of 0.6529 cP. No allowance was made for particle scattering factors: dissymmetries were near to unity for the smaller micelles so  $z$ -average values of  $D_0$  and  $r_h = [(1/r_h)_z]^{-1}$  were obtained. The indices of polydispersity of the diffusion coefficient distribution, determined by the cumulants method for the various concentrations used, were small for copolymer  $E_{58}B_{17}E_{58}$  at concentrations below  $50 \text{ g dm}^{-3}$  (variance of linewidth distribution,  $\mu_2/\Gamma^2 = 0.05 \pm 0.02$ ) but larger at higher concentrations of copolymer  $E_{58}B_{17}E_{58}$  (0.2 or higher for  $c > 80 \text{ g dm}^{-3}$ ) and for the other two copolymers over the majority of the concentration range ( $0.19 \pm 0.10$  for copolymer  $E_{71}B_{28}E_{71}$  and  $0.24 \pm 0.05$  for copolymer  $E_{132}B_{53}E_{132}$ ). The wide solute size distributions<sup>29,30</sup> of copolymers  $E_{71}B_{28}E_{71}$  and  $E_{132}B_{53}E_{132}$  observed at low concentrations may well reflect the presence of poly(oxyethylene) impurity in these samples (see Table 1). Values of  $D_0$  and  $r_h$  are listed in Table 2.

The copolymers  $E_{58}B_{17}E_{58}$  and  $E_{71}B_{28}E_{71}$  differ in their behaviour over the moderate concentration range, in that the values of the derived diffusion coefficient of copolymer  $E_{58}B_{17}E_{58}$  maintain a high value up to its critical gel concentration, whereas those of copolymer  $E_{71}B_{28}E_{71}$  fall markedly, presumably towards a low value at its critical gel concentration. A difference in behaviour was also detected in the intensity of light scattering from moderately concentrated solutions (see above). A modest decrease in  $D$  at moderate concentrations is characteristic of polymer solutions<sup>31</sup>, and is

attributable to transient entanglements. The larger decrease noted for copolymer  $E_{71}B_{28}E_{71}$  may reflect the effect of the poly(oxyethylene) impurity on the viscosity of the solvent. The sudden decrease in  $D$  at the critical gel concentration possibly reflects a transition to a system in which  $D$  is determined primarily by micellar aggregation.

**Gel permeation chromatography.** Aqueous g.p.c. curves of copolymers  $E_{71}B_{28}E_{71}$  and  $E_{132}B_{53}E_{132}$  are shown in Figure 9. The peaks at high elution volume (ca.  $30 \text{ cm}^3$ ) correspond to elution of the poly(oxyethylene) impurities. The peaks at low elution volume, ca.  $25.2$  and  $20.6 \text{ cm}^3$  respectively, correspond to elution of micelles. The tailing to the high-volume side is typical of micellar elution<sup>10,32</sup>. The apparent molecular weights on the poly(oxyethylene) calibration scale were  $M_{\text{pk}} = 9.2 \times 10^4$  ( $E_{71}B_{28}E_{71}$ ) and  $M_{\text{pk}} = 1.3 \times 10^6$  ( $E_{132}B_{53}E_{132}$ ), i.e. larger than the molecular weight of the copolymer and consistent with the elution of micelles. The intrinsic viscosity of poly(oxyethylene) calibrant in water at 25°C is given<sup>33</sup> by the equation:

$$[\eta]/(\text{cm}^3 \text{ g}^{-1}) = 0.0125 \times M^{0.78}$$

whence the elution volumes, given by:

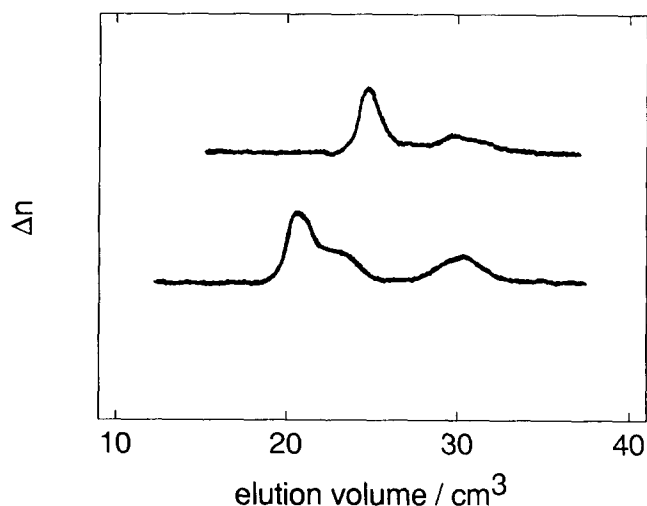
$$V_h = [\eta]M/(2.5N_A)$$

can be calculated. The corresponding hydrodynamic radii are listed in Table 2. Good agreement between hydrodynamic radii from g.p.c. and p.c.s. was expected<sup>10,32</sup>. Elution of micelles from g.p.c. was not observed for sample  $E_{58}B_{17}E_{58}$  under the conditions used in this work, in keeping with its higher CMC.

**Swelling.** The volume of anhydrous copolymer equivalent in weight to a micelle was calculated from:

$$v_a = M_{\text{w,mic}}/N_A\rho$$

where  $\rho$ , the density of the copolymer, was assumed to be  $1.1 \text{ g cm}^{-3}$ . Comparison with the swollen volume ( $v_s$ ) calculated from averaged values (Table 2, p.c.s.) of  $r = 7, 10$  and  $53$  for micelles of copolymers  $E_{58}B_{17}E_{58}$ ,  $E_{71}B_{28}E_{71}$  and  $E_{132}B_{53}E_{132}$  respectively, assuming sphericity, gave the swelling ratios ( $\delta = v_s/v_a$ ) of 8–10



**Figure 9** Aqueous g.p.c. curves for  $E_{71}B_{28}E_{71}$  and  $E_{132}B_{53}E_{132}$ : refractive index difference  $\Delta n$  (arbitrary scale) versus elution volume ( $\text{cm}^{-3}$ )

for the smaller micelles and about 50 for the larger micelles (see Table 2). Assuming that swelling is restricted to the oxyethylene block, the usual scaling of swelling to chain length for a good solvent would predict an increase of  $(132/58)^{0.6} \sim 1.6$  in radius or  $(132/58)^{1.8} \sim 4.4$  in volume on going from  $E_{58}B_{17}E_{58}$  to  $E_{132}B_{53}E_{132}$ , which is comparable with the experimental result.

*Comparison with other results.* There are no comparable systematic studies of the effect of chain length on the micellization and gelation properties of a series of oxyethylene/oxybutylene triblock copolymers ( $E_mB_nE_m$ ) of constant composition. Results for oxyethylene/oxypropylene triblock copolymers ( $E_mP_nE_m$ ) containing 80 wt% oxyethylene (as in this investigation) have been considered. The molecular characteristics of the commercially available copolymers quoted in the manufacturers' literature vary. Representative values are<sup>34</sup>:

Copolymer	F68	F88	F98	F108
$M_n$	8750	11 250	13 750	16 250
Formula	$E_{80}P_{30}E_{80}$	$E_{102}P_{39}E_{102}$	$E_{125}P_{47}E_{125}$	$E_{148}P_{56}E_{148}$

Considering initially F68, the very wide range of values of critical micelle concentrations reported<sup>8,17,35-37</sup> for this copolymer (e.g. from 0.002 to  $>100 \text{ g dm}^{-3}$  at 20–25°C) makes it clear that different workers have observed different effects. Generally, reliance can be placed on investigations that combine more than one technique, i.e. surface tension and light scattering intensity or photon correlation spectroscopy, but not dye or iodine absorption, for which depletion of the absorbant is a problem<sup>17,36,38</sup>. Agreement is by no means complete even between investigations of the micellization behaviour of F68, which meet this criterion<sup>8,37</sup>. Of course, impurities in commercial  $E_mP_nE_m$  copolymers may cause problems, as mentioned in the introduction to this paper and described in detail elsewhere<sup>7,39</sup>. Unfortunately, few results are available concerning the micellization behaviour of the other members of the '80 wt%' series, and none meet the criterion suggested above. This is the general situation; reliable results have been reported for isolated  $E_mP_nE_m$  copolymers (e.g. F127, P85, L64) but not for any series of  $E_mP_nE_m$  copolymers of constant composition.

Vadnere *et al.*<sup>40</sup> have reported gelation temperatures for the '80 wt%' series of copolymers at several concentrations. Selected values are as follows:

	$E_{80}P_{30}E_{80}$	$E_{102}P_{39}E_{102}$	$E_{125}P_{47}E_{125}$	$E_{148}P_{56}E_{148}$
$c \text{ (g kg}^{-1}\text{)}$	430	250	250	300
$T_{\text{gel}} \text{ (}^\circ\text{C)}$	55	45	30	20

Qualitatively, the effect of an increase in molecular weight of the '80 wt%'  $E_mP_nE_m$  copolymers ( $M_n$  from 8750 to 16 250) is comparable to that found in the present work for  $E_mB_nE_m$  copolymers ( $M_n$  from 6400 to 15 500). Quantitatively, the effect in the  $E_mB_nE_m$  series is much greater. For example:

	$E_{58}B_{17}E_{58}$	$E_{71}B_{28}E_{71}$	$E_{132}B_{53}E_{132}$
$c \text{ (g kg}^{-1}\text{)}$	220	120	50
$T_{\text{gel}} \text{ (}^\circ\text{C)}$	20	0	-10

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