

# Association and phase behaviour of statistical and block copolymers of ethylene oxide and butylene oxide in water

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Three copolymers of ethylene oxide (EO) and 1,2-butylene oxide (BO) were prepared by anionic polymerization to have similar molar masses ( $M_n \approx 7000 \text{ g mol}^{-1}$ ), molar mass distributions ( $M_w/M_n < 1.1$ ) and compositions (80 mol % oxyethylene) but different chain structures. A triblock copolymer was prepared by sequential copolymerization of EO followed by BO, and two statistical copolymers were prepared from mixed monomers, either to low (15%) or to high (93%) conversion. The disparity in reactivity ratios in the EO/BO copolymerization resulted in pronounced composition drift along the chains of the high conversion statistical copolymer, giving it the character of a block copolymer. This composition profile was checked by  $^{13}\text{C}$  n.m.r. spectroscopy. The association behaviour of the statistical copolymers in aqueous solution at 25°C was studied by dynamic and static light scattering. The low conversion statistical copolymer remained in its molecular state across the concentration range studied (up to  $100 \text{ g dm}^{-3}$ ), but the high conversion statistical copolymer associated into molecular clusters and micelles. Cloud point curves were determined for solutions of the three copolymers. The effect of association on phase behaviour is discussed. © 1997 Elsevier Science Ltd. All rights reserved.

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## INTRODUCTION

The statistical copolymerization of monomers with reactivity ratios differing by a factor of 10 or so results in marked composition drift. In anionic polymerization (living polymerization) this composition drift is manifested along the chain, so that the resulting copolymer takes on the character of a block copolymer. The association behaviour of block copolymers in selective solvents has been a topic of academic and industrial interest for many years. However, little attention has been paid to the self-association properties of blocky statistical copolymers in solution.

Most studies of the association behaviour of water-soluble block copolymers have been carried out using commercially available oxyethylene/oxypropylene triblock copolymers,  $E_m P_n E_m$ . (Here E represents an oxyethylene unit and P an oxypropylene unit.) The current state of this work can be judged from recent publications and the references contained therein<sup>1–10</sup>. Much of our recent work has been concerned with oxyethylene/oxybutylene block copolymers.  $E_m B_n$  and  $E_m B_n E_m$  copolymers (B represents an oxybutylene unit) are available from the Dow Chemical Co.<sup>11–14</sup>. How-

ever, most of the materials used in our studies<sup>15–26</sup> were synthesized in our laboratories. As explained previously, replacement of propylene oxide by 1,2-butylene oxide carries with it advantages in the polymerization chemistry, as well as providing B blocks of considerably enhanced hydrophobicity compared with P blocks of comparable length<sup>24</sup>.

The present account focuses on  $B_n E_m B_n$  block copolymers and related statistical copolymers. For  $B_n E_m B_n$  copolymers in water, the picture which has emerged<sup>25</sup> is of association into micelles with soluble blocks in the fringe and most insoluble blocks looping back into the core, but with a fraction of the insoluble blocks extended into the solvent and available for an attractive (bridging) interaction with a second micelle. Secondary association of this type has also been identified in aqueous micellar solutions of mixed  $E_m B_n$  and  $B_n E_m B_n$  copolymers<sup>26</sup>,  $P_n E_m P_n$ <sup>27</sup> and  $C_n E_m C_n$  copolymers<sup>28</sup> (where  $C_n$  represents an alkyl block), and also in several organic micellar solutions<sup>29–31</sup> and has been predicted by computational methods<sup>32–35</sup>.

The incentive to study self-association of a statistical copolymer arose from cooperative work between our two laboratories. A statistical copolymer of ethylene oxide and 1,2-butylene oxide (70 mol % E, number-average molar mass,  $M_n \approx 5000 \text{ g mol}^{-1}$ ) was prepared

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by anionic polymerization using diethylene glycol as initiator. Because the reactivity ratios of ethylene oxide and 1,2-butylene oxide were known<sup>36</sup> to differ considerably ( $r_E = 4.1$ ,  $r_B = 0.17$ ) composition drift was reduced by restricting the conversion to 20 wt %. Despite this precaution, anomalous behaviour was found on heating a 25 wt % solution: i.e. clouding at 9°C, clearing at 22°C and clouding again at 28°C. The effect was tentatively attributed to the following sequence of events: phase separation of the molecular solution at 9°C, association and resolubilization at 22°C, phase separation of the associates in solution at 28°C. Similar clouding → clearing → clouding sequences have been observed in more dilute solutions of  $E_m B_n E_m$  block copolymers<sup>14,22</sup>, and related to micellisation. It was assumed that composition drift, which resulted in a higher proportion of B units at both ends of the difunctionally polymerized chain than at the centre, was sufficient to give the statistical copolymer the character of a  $B_n E_m B_n$  triblock copolymer.

With this preliminary work in mind, two statistical copolymers were prepared by anionic polymerization initiated by a difunctional initiator (diethylene glycol) so that their composition profiles were symmetrical about the central unit. The copolymers had similar overall E contents (ca. 80 mol % E) and molar masses ( $M_n \approx 7000 \text{ g mol}^{-1}$ ) but different composition profiles as a result of being polymerized to either 15 wt % conversion or 93 wt % conversion. A 80 mol % E was chosen because the copolymer with a lower proportion of E (70 mol %) investigated in preliminary work clouded at inconveniently low temperatures (see above).

In the present work clouding temperatures of aqueous solutions were determined over a wide concentration range for the two copolymers, and evidence of association in solutions of dilute to moderate concentration was sought using dynamic and static light scattering. For comparison with the clouding behaviour of the statistical copolymers, a triblock copolymer ( $B_n E_m B_n$ ) was prepared by sequential polymerization of ethylene oxide followed by butylene oxide. It has already been established that copolymers of this type associate in solution<sup>25</sup>.

## EXPERIMENTAL

### Notation

The statistical E/B copolymers were denoted by overall composition, molar mass and conversion in the polymerization. For example, copolymer EB78-7100-15% had 78 mol % E units,  $M_n = 7100 \text{ g mol}^{-1}$  and was polymerized to 15 wt % conversion. The true block copolymer prepared by sequential copolymerization is denoted  $B_{12}E_{114}B_{12}$  (83 mol % E,  $M_n = 6750 \text{ g mol}^{-1}$ ).

### Preparation of copolymers

The copolymers were prepared by anionic polymerization of ethylene oxide and 1,2-butylene oxide (1,2-epoxybutane). All reagents were distilled and dried before use, and vacuum line and ampoule techniques were used in order to minimize initiation by moisture at any stage. Initiation solutions were prepared by reacting freshly-cut potassium with diethylene glycol. A ratio  $[\text{OH}]/[\text{OK}] = 8.2$  was used to ensure a controlled rate of polymerization.

*Statistical copolymer EB78-7100-15%.* The known reactivity ratios of ethylene oxide and butylene oxide were used to calculate the proportion of ethylene oxide in the initial mixture (i.e. 44 mol %) necessary to produce a copolymer containing ca. 80 mol % E after 15 wt % conversion. The method of determining the initial conditions is outlined in the section *Triad frequency distributions from <sup>13</sup>C n.m.r.*

A portion of initiator solution (0.22 mmol diethylene glycol) was transferred by syringe into a weighed ampoule under dry nitrogen, followed by butylene oxide (70 g, 0.97 mol) and ethylene oxide (33.9 g, 0.77 mol) under vacuum. The ampoule, sealed under vacuum by a PTFE tap, was allowed to warm to room temperature, shaken to mix the contents, and placed in a water bath at 45°C. Polymerization was allowed to proceed until the conversion was ca. 15 wt %, as judged by the volume contraction (90 h), whereupon unreacted monomers were removed by evacuation at  $10^{-4}$  mmHg for 16 h. The ampoule was reweighed to confirm the conversion of monomer to copolymer (yield 15.6 g, 15 wt % conversion). The recovered copolymer was a viscous liquid at room temperature.

*Statistical copolymer EB80-6400-93%.* In this case the proportion of ethylene oxide in the initial mixture was 75 mol %. Initiator solution (3.58 mmol diethylene glycol), ethylene oxide (16.7 g, 0.380 mol) and butylene oxide (8.9 g, 0.124 mol) were transferred to an ampoule which was sealed under vacuum and placed in a water bath as described above, but the copolymerization was allowed to proceed for 7 days at 65°C before evaporating residual monomer. The yield was 23.8 g (93 wt % conversion). The recovered copolymer was a waxy solid at room temperature.

*Block copolymer  $B_{12}E_{114}B_{12}$ .* The sequential copolymerization of ethylene oxide followed by butylene oxide has been described in detail previously<sup>22</sup>. In the present case, initiator solution (6.4 mmol diethylene glycol) and ethylene oxide (32.2 g, 0.73 mol) were transferred to an ampoule and polymerized completely (6 days) to form the E-block precursor. The temperature was increased in stages throughout this polymerization (eventually to 80°C) in order to avoid crystallization of the polymer. A small portion was removed for analysis (see below). Butylene oxide (0.90 g, 0.15 mol) was then transferred under vacuum into the ampoule and the copolymerization completed (80°C, 14 days). This copolymer was a brittle crystalline solid.

### Characterization by gel permeation chromatography (g.p.c.)

The g.p.c. system consisted of three  $\mu$ -Styragel columns (Waters Associates, nominal porosity from 500– $10^6$  Å) eluted by tetrahydrofuran (THF) at room temperature and a flow rate of  $1 \text{ cm}^3 \text{ min}^{-1}$ . Samples were injected via a  $100 \text{ mm}^3$  loop at a concentration  $2 \text{ g dm}^{-3}$ , and their emergence was detected by differential refractometry (Water Associates Model 410). Calibration was with poly(oxyethylene) samples of known molar mass. The g.p.c. curves gave directly values of the molar mass at the peak [ $M_{pk}$ , as if poly(oxyethylene)], and further analysis gave an estimate of width of the

**Table 1** Molecular characteristics of the copolymers

Formula	G.p.c.		N.m.r.		
	$M_{pk}/g\ mol^{-1}$	$M_w/M_n$	$M_n/g\ mol^{-1}$	mol % E	wt % E
EB78-7100-15%	7600	1.04	7100	78	69
EB80-6400-93%	6700	1.10	6400	80	71
B <sub>12</sub> E <sub>114</sub> B <sub>12</sub>	6600	1.07	6750	83	74

molar mass distribution in the form of the ratio of mass-average to number-average molar mass ( $M_w/M_n$ ). Values of  $M_{pk}$  and  $M_w/M_n$  are listed in Table 1.

#### Characterization by n.m.r.

Copolymers were dissolved in C<sub>6</sub>D<sub>6</sub> (0.1 g cm<sup>-3</sup>) and spectra were obtained by means of a Varian Unity 500 spectrometer operated at 125.7 MHz. An interval of at least 12 s was used in order to allow complete relaxation between pulses. Spectral assignments were taken from previous work<sup>37</sup>. DEPT spectral editing techniques were used to obtain CH and CH<sub>2</sub> subspectra in order to eliminate overlap of resonances from end and backbone groups<sup>37</sup>.

The <sup>13</sup>C n.m.r. spectra were used to determine number-average molar mass ( $M_n$  from integrals of end and chain groups) and average composition (i.e. mol % E) from integrals associated with backbone and side-group carbons. Values are listed in Table 1.

For the 'as prepared' block copolymer, integrals associated with carbon atoms of the hydroxyl end groups were slightly higher than those associated with carbons of the EB block junction, leading to an estimated 4 mol % homopoly(oxybutylene) in the sample, presumably initiated from adventitious moisture. Accordingly, the block copolymer was purified (four times) by equilibrating with warm hexane (55°C) and separating the solid and liquid phases after cooling to 20°C. This treatment efficiently reduced the proportion of poly(oxybutylene) below the level detectable by n.m.r. The data in Table 1 refer to the purified block copolymer.

#### Triad frequency distributions from <sup>13</sup>C n.m.r.

Triad frequency distributions were determined from the <sup>13</sup>C n.m.r. spectra of the statistical copolymers. With only one mode of addition of butylene oxide to the growing chain (head-to-tail) there are eight distinct compositional triads, i.e. the E-centred and B-centred triads EEE, EE $\vec{B}$ ,  $\vec{B}$ EE,  $\vec{B}$ E $\vec{B}$ , E $\vec{B}$ E, E $\vec{B}\vec{B}$ ,  $\vec{B}\vec{B}$ E and  $\vec{B}\vec{B}\vec{B}$ . (Here the arrow denotes head-to-tail.) For an infinite chain, the sum of the triad probabilities must be unity, and the following symmetry relationships must be obeyed<sup>38</sup>

$$[EE\vec{B}] = [\vec{B}EE] \quad (1a)$$

$$[E\vec{B}\vec{B}] = [\vec{B}\vec{B}E] \quad (1b)$$

$$[EE\vec{B}] + [\vec{B}EE] + 2[\vec{B}E\vec{B}] = [E\vec{B}\vec{B}] + [\vec{B}\vec{B}E] + 2[E\vec{B}E] \quad (1c)$$

where the square brackets denote probability. Hence, only four triad probabilities are independent. As described previously<sup>37</sup>, the probabilities of the E-centred triads were obtained from resonances of CH<sub>2</sub> carbons in the spectral region  $\delta_C = 70 - 71$  ppm while those of the

**Table 2** Triad sequence distributions in the statistical copolymers

Sequence	EB78-7100-15%		EB80-6400-93%	
	N.m.r.	Calculated	N.m.r.	Calculated
$\vec{B}E\vec{B}$	0.035	0.053	0.032	0.034
$\vec{B}EE + EE\vec{B}$	0.278	0.291	0.186	0.184
EEE	0.467	0.408	0.572	0.536
E $\vec{B}$ E	0.142	0.158	0.088	0.098
E $\vec{B}\vec{B}$ + $\vec{B}\vec{B}$ E	0.076	0.080	0.062	0.055
$\vec{B}\vec{B}\vec{B}$	0.002	0.010	0.060	0.098

$\vec{B}$ -centred triads were obtained from resonances of CH carbons in the region  $\delta_C = 79.5 - 80.5$  ppm. Triad probabilities obtained in this way are listed in Table 2.

Triad probabilities were also calculated according to the first-order Markov equations:

$$[EEE] = w(1 - u)^2/(u + w) \quad (2a)$$

$$[EE\vec{B}] = [\vec{B}EE] = uw(1 - u)/(u + w) \quad (2b)$$

$$[\vec{B}E\vec{B}] = u^2w/(u + w) \quad (2c)$$

$$[E\vec{B}E] = uw^2/(u + w) \quad (2d)$$

$$[E\vec{B}\vec{B}] = [\vec{B}\vec{B}E] = uw(1 - w)/(u + w) \quad (2e)$$

$$[\vec{B}\vec{B}\vec{B}] = u(1 - w)^2/(u + w) \quad (2f)$$

where  $u$  and  $w$  are, respectively, the probability of adding B given that the chain end is E and the probability of adding E given that the chain end is B. These quantities are given by

$$u = f_B/(r_E f_E + f_B) \quad (3a)$$

$$w = f_E/(r_B f_B + f_E) \quad (3b)$$

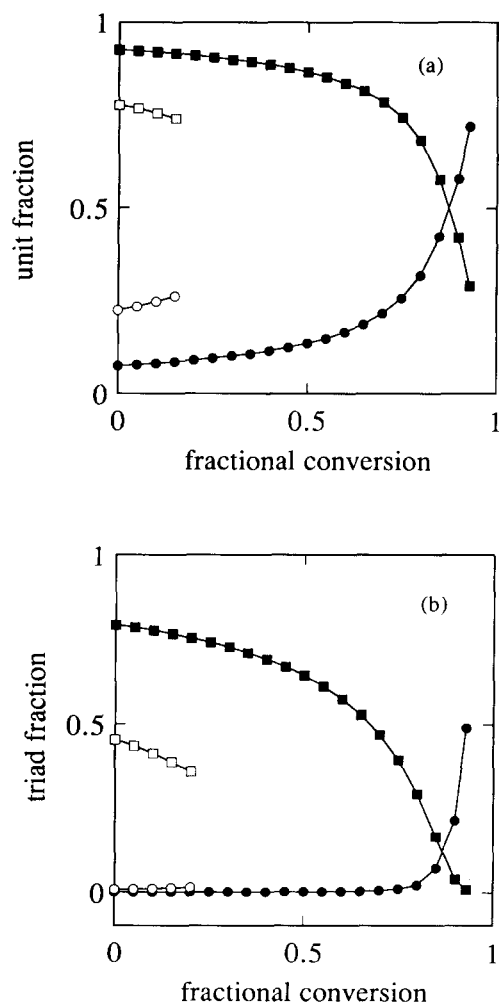
where  $r_E$  and  $r_B$  are reactivity ratios and  $f_E$  and  $f_B$  are monomer feed mole fractions.

A simple numerical procedure was employed in which the copolymerization was allowed to proceed in steps of 0.01% up to the required conversion. The composition and sequence probabilities for the copolymer formed in a step were calculated from equations (2) and (3), following which the feed composition was adjusted and the procedure repeated. The overall composition and sequence probabilities were then obtained as an average over the values for each step. The uncertainties in the calculated probabilities, estimated to be 10–20%, stemmed from the uncertainties in the reactivity ratios. Within this margin of error, the probabilities obtained from n.m.r. agreed reasonably well with the calculated values: see Table 3. The same procedure was also used to determine the initial conditions necessary to obtain a given composition at a given conversion.

Interest lies in the distribution of composition along the chain. Given the present results, this can be expressed in two ways: either as the instantaneous probabilities [E] and [B] at any point along the chain (equivalent to the mole fractions of units,  $x_B$  and  $x_E = 1 - x_B$ ), or as the instantaneous probabilities of the triads [EEE] and [BBB] at any point along the chain. Consideration of the composition profile in terms of triad probability gives a measure of the 'blockiness' of the distribution. In particular, the [BBB] profile gives a measure of the probability that the chain will interact hydrophobically with water. In this respect it is known<sup>20,22,25</sup> that short B-blocks (e.g. 4–5 B units) are sufficient for entropy-driven self-association of  $B_nE_{40}B_n$  copolymers at moderate concentrations in water at 20–50°C.

Because the chains grow in direct proportion to conversion in anionic polymerization, a plot of composition *versus* conversion is equivalent to the average composition profile along the chains. In fact, the plots of composition *versus* conversion shown in Figure 1 represent the profile along one-half of the present chains, since they were grown from a difunctional initiator.

The values of [B] are fairly constant at low conversion (see Figure 1a) and, therefore, so is the composition



**Figure 1** (a) Mole fractions and (b) triad fractions of (□, ■) oxyethylene and (○, ●) oxybutylene units in statistical copolymerizations taken to either 15% conversion (unfilled symbols) or 93% conversion (filled symbols). A plot against conversion represents the composition profile from the centre to the end of the chain

along the whole chain of copolymer EB78-7100-15%. For copolymer EB80-6400-93%, there is a rapid increase in [B] above 70% conversion, i.e. in the 25% of the chain nearest to the two ends. The values of [BBB] are essentially zero at low conversion (see Figure 1b), implying a very low probability of hydrophobic segments in copolymer EB78-7100-15%. For copolymer EB80-6400-93%, there is a sharp increase in [BBB] above 80% conversion consistent with the end 10% of the chains being essentially hydrophobic. In the same conversion range, the value of [EEE] becomes zero. We conclude that the high conversion statistical copolymer has a significant degree of triblock character. The light scattering experiments described in Results and Discussion confirm this conclusion.

#### Static and dynamic light scattering

All glassware was washed with condensing acetone vapour immediately before use. Solutions were clarified by filtering through Millipore Millex filters (Triton free, 0.22  $\mu\text{m}$  porosity, sometimes 0.1  $\mu\text{m}$  porosity) directly into the cleaned scattering cell.

Static light scattering (SLS) intensities were measured for solutions at 25°C by means of a Malvern PCS100 instrument with vertically polarized incident light of wavelength  $\lambda = 488$  nm supplied by an argon-ion laser (Coherent Innova 90) operated at 500 mW or less. The intensity scale was calibrated against benzene. Measurements were made at angles at 45°, 90° and 135° to the incident beam. In an experiment, measurements were made on solutions at a given temperature over a range of concentration.

Dynamic light scattering (DLS) measurements were made on solutions at 25°C by means of the Malvern instrument described above combined with a Brookhaven BI 9000 AT digital correlator. Measurements of scattered light were usually made at an angle of 90° to the incident beam, but some measurements were made at smaller angles (30°, 45°).

In designing the light scattering experiments, account was taken of the small size (equivalent hard-sphere radius  $r < 20$  nm) expected for the micelles in relation to the value of the scattering vector ( $q = (4\pi n/\lambda) \sin(\theta/2)$ ,  $n$  = refractive index of medium,  $\lambda$  = wavelength of light,  $\theta$  = scattering angle). The relevant parameter for assessing intraparticle interference is the dimensionless product  $qr$ , and in our experiments  $qr$  was generally less than 0.25. The structure factor depends on the volume fraction of swollen particles as well as the mass concentration, and interparticle interference at a given mass concentration can also be quantified in terms of  $qr$ . Under our conditions, the light scattering experiments were effectively carried out at the  $qr \rightarrow 0$  limit, and errors in derived quantities (e.g. molar mass, diffusion coefficient, virial coefficients) originating from measurements taken at  $\theta = 90^\circ$  (rather than  $\theta = 0^\circ$ ) were significantly less than 1% (i.e. unimportant compared with other sources of error). At all times, experiments made using scattering angles smaller than 90° gave consistent results.

The correlation functions from dynamic light scattering (DLS) were analysed by the constrained regularized CONTIN method<sup>39</sup>, thus gaining information on the distribution of decay rates ( $\Gamma$ ). Experiment duration was in the range 10–30 min, and each experiment was repeated four or more times. The distributions of decay rates obtained were tested against changes in the

regularizer and were found to be stable. The decay rates gave distributions of apparent diffusion coefficient ( $D_{app} = \Gamma/q^2$ ) and hence of apparent hydrodynamic radius ( $r_{h,app}$ , radius of the hydrodynamically-equivalent hard sphere corresponding to  $D_{app}$ ) via the Stokes–Einstein equation

$$r_{h,app} = kT/(6\pi\eta D_{app}) \quad (4)$$

where  $k$  is the Boltzmann constant and  $\eta$  is the viscosity of water at temperature  $T$ . The basis for analysis of static light scattering (SLS) was the Rayleigh–Gans–Debye equation, used here in the form

$$I - I_s = K^*cM_w \quad (5)$$

where  $I$  is intensity of light scattered from solution relative to that from benzene,  $I_s$  is the corresponding quantity for pure solvent,  $c$  is the concentration (in  $\text{g dm}^{-3}$ ),  $M_w$  is the mass-average molar mass of the solute, and

$$K^* = (4\pi^2/N_A\lambda^4)(n_B^2/R_B)(dn/dc)^2 \quad (6)$$

where  $N_A$  = Avogadro's constant,  $n_B$  and  $R_B$  = refractive index and Rayleigh ratio of benzene, respectively, and  $dn/dc$  = specific refractive index increment. Sources of the quantities necessary for the calculations have been given previously<sup>26</sup>. The value of  $dn/dc$  for the present copolymers was  $0.134 \pm 0.002 \text{ cm}^3 \text{ g}^{-1}$  at  $25^\circ\text{C}$ , as obtained previously for aqueous solutions of comparable samples<sup>18,20</sup>.

#### Clouding temperatures

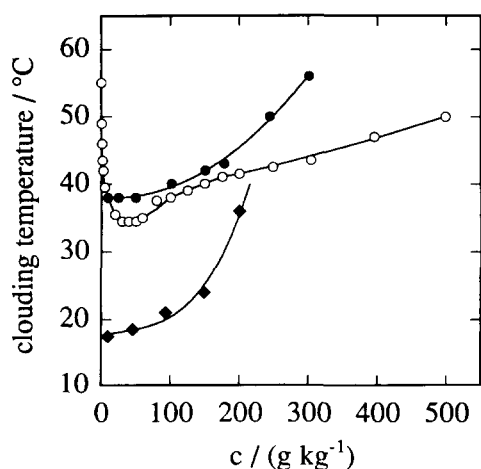
Aqueous solutions of the copolymers in sealed tubes were equilibrated at low temperature before heating slowly in a water bath until phase separation was observed by visual inspection. The experiments were repeated several times. Reproducibility was within  $\pm 1.5^\circ\text{C}$ .

## RESULTS AND DISCUSSION

#### Cloud point curves

Cloud point curves of the statistical copolymers and the triblock copolymers are shown in Figure 2.

The overall shape of the cloud point curve found for



**Figure 2** Cloud point curves for oxyethylene/oxybutylene copolymers: (○) EB78-7100-15%; (●) EB80-6400-93%; (◆)  $B_{12}E_{114}B_{12}$ . The reproducibility of the clouding temperatures was within  $\pm 1.5^\circ\text{C}$ .

copolymer EB78-7100-15% is as expected for a polymer with a lower critical solution temperature (LCST), particularly in the pronounced effect of dilution at low concentrations. The fact that the cloud point curve is not smoothly-concave downwards indicates that there is a distribution of composition, and hence solubility, among the chains, leading to effects similar to those discussed by Koningsveld and Staverman for polydisperse homopolymers<sup>40</sup>.

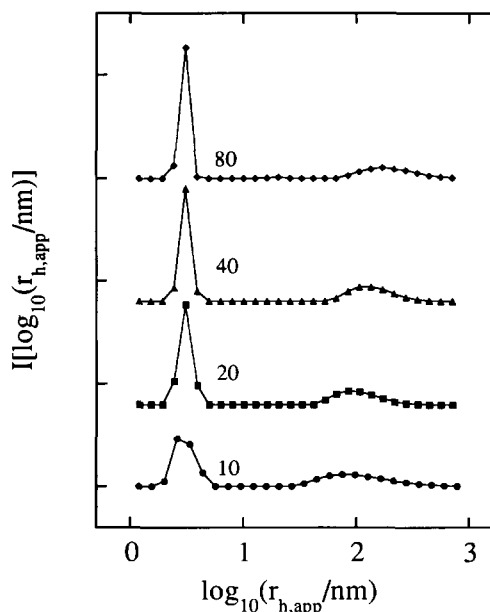
At concentrations in the range  $30\text{--}150 \text{ g (kg solution)}^{-1}$ , the cloud point curves of the two statistical copolymers are similar, but they differ at low concentration, where the cloud point curve of the high conversion copolymer (EB80-6400-93%) is flat compared with that of copolymer EB78-7100-15%, and at high concentration, where the situation is largely reversed (see Figure 2). The shape of the cloud point curve of triblock copolymer  $B_{12}E_{114}B_{12}$  at low concentration is similar to that of the statistical copolymer EB80-6400-93%, although its general level is 20 K lower. However, the clouding temperatures of the triblock copolymer solutions rise rapidly with concentrations beyond  $150 \text{ g kg}^{-1}$ , and the indication from Figure 2 is that the ranking order of clouding temperature at high concentration (i.e.  $c > 240 \text{ g kg}^{-1}$ ) is the reverse of that at very low concentration.

Interpretation of these effects requires knowledge of the state of the copolymers in solution, i.e. the extent to which they are associated. Accordingly, discussion of Figure 2 is deferred pending presentation of results from light scattering.

Because of the low clouding temperatures of dilute solutions of the triblock copolymer, the light scattering experiments were restricted to the two statistical copolymers. However, relevant information on the micellization of other triblock copolymers ( $B_5E_{39}B_5$ ,  $B_7E_{40}B_7$ ) is available<sup>25</sup>.

#### Dynamic light scattering (DLS)

DLS measurements on solutions of the statistical



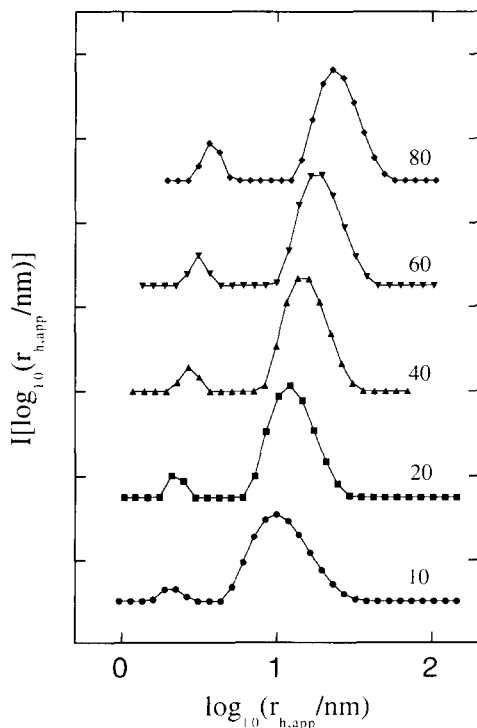
**Figure 3** Dynamic light scattering from aqueous solutions of copolymer EB78-7100-15%. Intensity-fraction distributions of logarithmic apparent hydrodynamic radius for solutions at  $25^\circ\text{C}$  and concentrations 10, 20, 40 and  $80 \text{ g dm}^{-3}$ , as indicated

copolymers were carried out at 25°C over the concentration range 10–80 g dm<sup>-3</sup>.

**Copolymer EB78-7100-15%.** Intensity fraction distributions of  $\log_{10} r_{h,app}$  obtained for 10–80 g dm<sup>-3</sup> solutions are shown in Figure 3. The peaks are assigned to molecules (peak at  $r_{h,app} \approx 3$  nm) and large particles (peak at  $r_{h,app} \approx 100$  nm). The position of the molecules peak was independent of concentration, which is consistent with no association of the copolymer in the concentration range studied.

Within the error of definition of the distributions, the relative areas under the molecules and large-particles peaks were independent of concentration (intensity fraction  $\approx 0.4$ ), which is symptomatic of an insoluble impurity in the copolymer sample. The effect must arise from a very small mass fraction of impurity in the form of large particles. Assuming uniform spheres with a density of  $\rho \approx 1$  g cm<sup>-3</sup>, the molar mass of the large particles is of the order 10<sup>9</sup> g mol<sup>-1</sup> compared with the order 10<sup>3</sup> g mol<sup>-1</sup> for the copolymer molecules themselves, hence the intensity fraction transforms (via equation (5)) to a mass fraction 10<sup>6</sup> times smaller. This approximate calculation shows that the mass fraction of impurity was very small ( $\ll 0.001$ ), and would certainly be undetectable by the analytical method (n.m.r.) used in this work. Indeed, the particles are significant in light scattering only because the scattering from unassociated molecules is weak.

It is concluded that the intensity fraction distributions of copolymer EB78-7100-15% correspond to solutions containing essentially (on a mass basis) only unassociated copolymer molecules. This result is as expected for a copolymer with an almost-constant composition profile along the chain.



**Figure 4** Dynamic light scattering from aqueous solutions of copolymer EB80-6400-93%. Intensity-fraction distributions of logarithmic apparent hydrodynamic radius for solutions at 25°C and concentrations 10, 20, 40, 60 and 80 g dm<sup>-3</sup>, as indicated

**Copolymer EB80-6400-93%.** Intensity fraction distributions of  $\log_{10} r_{h,app}$  obtained for 10–80 g dm<sup>-3</sup> solutions are shown in Figure 4. The peaks are assigned to molecules ( $r_{h,app} = 2$ –4 nm) and micelles ( $r_{h,app} \approx 10$ –20 nm). As can be seen, the molecules peak had much the same fractional intensity in all the distributions across the range of concentrations. This suggests that the association is controlled by more than one equilibrium, rather than the single closed equilibrium which is a satisfactory approximation for many copolymer–solvent systems but which, given an association number of 10 or more, requires an intensity fraction of molecules which falls rapidly as concentration is increased. This unusual feature of the present results will be discussed further later (see the section *Static light screening*).

Solutions of concentrations lower than 10 g dm<sup>-3</sup> were not investigated, and the lower limit of micelle formation (i.e. the critical micelle concentration, c.m.c.) was not detected.

For both molecules and micelles, the value of  $\log_{10} r_{h,app}$  at the peak of the distribution increased with concentration, much as found for molecules and micelles of B<sub>n</sub>E<sub>m</sub>B<sub>n</sub> triblock copolymers in a previous study<sup>25</sup>. Intensity-average values of  $D_{app}$  were calculated for both molecules and micelles by integrating over the two peaks in the intensity distributions of decay rate. The concentration dependence of apparent diffusion coefficient (in dilute solution) can be expressed as

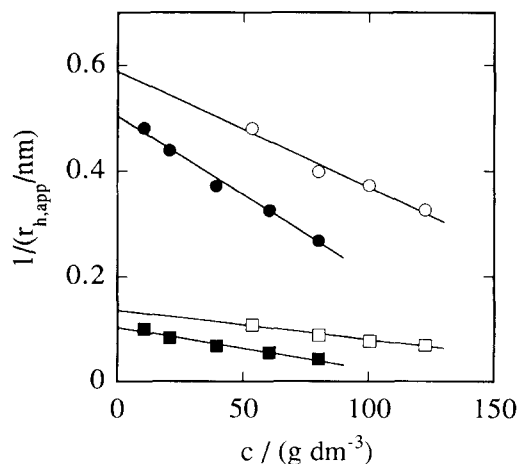
$$D_{app} = D_0(1 + k_d c) \quad (7)$$

where the expansion is truncated at the second term. Parameter  $k_d$  is related to the thermodynamic second virial coefficient,  $A_2$ , through the equation<sup>41</sup>

$$k_d = 2A_2 M_w - k_f - 2v \quad (8)$$

where  $M_w$  is the mass-average molar mass,  $k_f$  is the frictional coefficient and  $v$  is the specific volume of the micelles in solution. If the quantities  $M_w$ ,  $k_f$  and  $v$  are independent of concentration, the sign of  $k_d$  depends on the sign and size of  $A_2$ , which in turn depends on the nature of the intermicellar interaction, i.e. on the micellar excluded volume.

In the present case it is convenient to plot  $1/r_{h,app}$



**Figure 5** Inverse apparent hydrodynamic radius versus concentration for (■, □) micelles and (●, ○) molecules in solutions of copolymer EB80-6400-93% (filled symbols) or B<sub>5</sub>E<sub>30</sub>B<sub>5</sub> (unfilled symbols). The data for copolymer B<sub>5</sub>E<sub>30</sub>B<sub>5</sub> are taken from reference 25

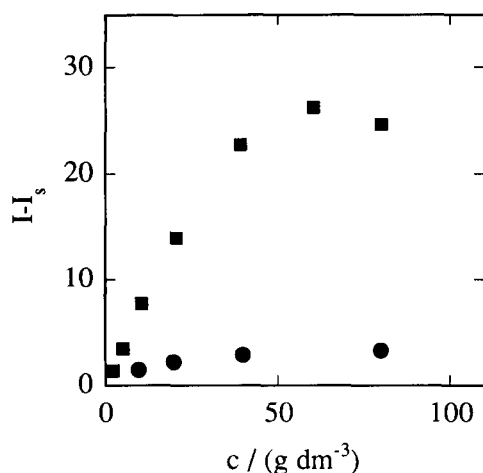
against  $c$  (rather than  $D_{app}$  against  $c$ ) because  $1/r_{h,app}$  is compensated for change in solution temperature and viscosity. This allows direct comparison with results from our previous<sup>26</sup> study of  $B_nE_mB_n$  copolymers. (As mentioned in *Cloud point curves* earlier, light scattering from solutions of copolymer  $B_{12}E_{114}B_{12}$  could not be studied because of their low cloud points.) Plots  $1/r_{h,app}$  against  $c$  for molecules and micelles of copolymers EB80-6400-93% and  $B_5E_{39}B_5$  are shown in *Figure 5*. The behaviours of the high-conversion statistical copolymer and the triblock copolymers are seen to be similar. For molecules and micelles acting as hard spheres (e.g. micelles formed from diblock copolymers<sup>18,22,24</sup>) such plots have positive slopes. The negative slopes of the plots found in this work imply substantially reduced repulsive (hard sphere) contributions to the interspecies interactions, and possibly attractive contributions.

An attractive contribution to the intermicellar interaction is consistent with the micelles having a fraction of their B-rich blocks extended into the solvent and available for interaction, either with B-rich blocks from chains originating from a second micelle or by entering the core of a second micelle. An attractive contribution to the intermolecular interaction is consistent with the formation of small molecular associates in solution. The existence of molecular association in itself provides an explanation for the high intensity of scattering from molecules across the whole concentrated range, since scattering intensity depends on the product  $cM_w$  (see equation (5)). Similar modes of interaction have been investigated experimentally and/or theoretically<sup>29-35</sup> including  $B_nE_nB_n$  copolymer systems<sup>25,26</sup>.

#### Static light scattering

*Intensity plots.* Static light scattering data for solutions of the two statistical copolymers are plotted as scattering function  $I - I_s$  versus concentration in *Figure 6*. The scattering intensities measured for copolymer EB78-7100-15% are corrected for the intensity fraction of scattering from impurity (ca. 0.4). As explained in the section *Dynamic light scattering* earlier, the concentration does not require correction on this account.

Maxima in intensity versus concentration are expected



**Figure 6** Excess light scattering intensity ( $I - I_s$ ) versus concentration for aqueous solutions of copolymers (●) EB78-7100-15% and (■) EB80-6400-93%. The data for solutions of copolymer EB78-7100-15% are corrected for scattering from impurities (see text)

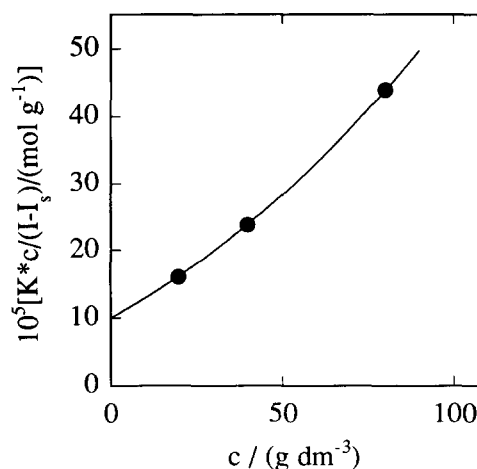
for moderately concentrated solutions, and this effect, attributable to interparticle interference, is seen in the results for both copolymers. Given two copolymers of almost the same molar mass and composition, the levels of scattering intensity seen in *Figure 6* provide an indication of the extent of association of the two solutes in aqueous solution, i.e.

$$\text{EB80-6400-93\%} \gg \text{EB78-7100-15\%}$$

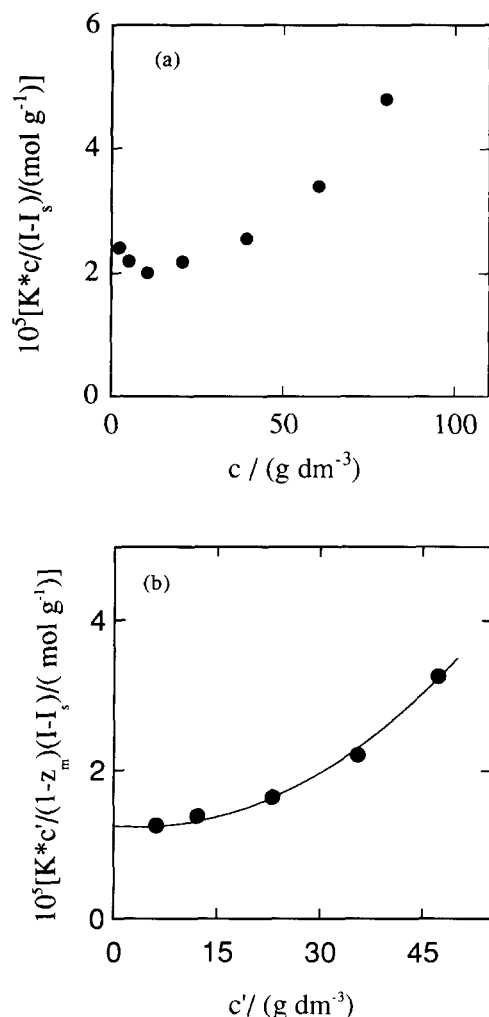
This result is consistent with the conclusions drawn from the dynamic light scattering experiments described in the section *Dynamic light scattering* i.e. that copolymer EB80-6400-93% formed micelles (and molecular associates) while copolymer EB78-7100-15% remained as molecules.

*Copolymer EB78-7100-15%.* A Debye plot for copolymer EB78-7100-15% is shown in *Figure 7*. The intensities were corrected for impurity by assuming a constant fractional contribution of 0.4 from that source, whilst the concentrations were uncorrected (see the section *Dynamic light scattering*). Because of the low intensities involved, results for solutions of low concentration were very scattered and were not considered in this analysis. The curve fitted to the data points in *Figure 7* is a quadratic. This provided a useful means of arriving at an acceptable intercept on the ordinate, and thereby a measure of the molar mass of the solute: i.e.  $M_w \approx 10\,000 \text{ g mol}^{-1}$ . This value of  $M_w$  is rather higher than that of  $7500 \text{ g mol}^{-1}$  expected from the characterization data listed in *Table 1* but is consistent with a molecular solution, since uncertainty arises from the low scattering intensities measured, as well as the additional correction for impurity.

*Copolymer EB80-6400-93%.* The Debye plot for copolymer EB80-6400-93% (see *Figure 8*) is more difficult to interpret. The upturn at low concentrations is suggestive of micellar dissociation at concentrations approaching a critical micelle concentration (c.m.c.) However, as described in the section *Dynamic light scattering*, the DLS results are not consistent with a simple closed association, in that molecules or small molecular clusters were detected across the concentration range



**Figure 7** Debye plot for aqueous solutions of copolymer EB78-7100-15% at 25°C. The curve through the points is a quadratic. See text for definitions of  $K^*$ ,  $I$  and  $I_s$



**Figure 8** Debye plots for copolymer EB80-6400-93% in aqueous solution of 25°C. (a) Uncorrected plot and (b) plot corrected using  $c_{m,app}$ . Note that  $c' = c - c_{m,app}$ , where  $c_{m,app}$  is the apparent concentration of molecules, and  $z_m$  is the intensity fraction of scattered light attributable to molecules as distinct from micelles. The curve through the points is a quadratic. See text for definition of  $K^*$ ,  $I$  and  $I_s$ .

10–80 g dm<sup>-3</sup>. Similar results have been found for certain triblock copolymers in selectively poor solvents for the end blocks, e.g. polystyrene/polyisoprene/polystyrene copolymer in heptane<sup>31</sup> and B<sub>n</sub>E<sub>m</sub>B<sub>n</sub> copolymers in water<sup>25</sup>. In those studies DLS data were used to correct the Debye plot and obtain a satisfactory value for the mass-average molar mass of the micelles<sup>25,31</sup>, and this procedure was followed in the present case.

Intensity fractions of scattering attributable to molecules ( $z_m$ ) were obtained as area fractions from the intensity distributions of  $\log_{10} r_{h,app}$  (see Figure 4). The error in  $z_m$  was large, because the number of data points defining the molecules peaks was generally no more than four or five. If the molecules were unassociated and scattering was ideal then, at a given copolymer concentration ( $c_m$ ), the contribution from molecules to the excess scattering would be

$$z_m(I - I_s) = K^* c_m M_m \quad (9)$$

where  $M_m$  is the known mass-average molar mass of the molecules. Because the solution is not ideally dilute, the actual concentration and molar mass (i.e. an average

**Table 3** Intensity and apparent mass fractions of molecules in solutions of copolymer EB80-6400-93%

$c/\text{g dm}^{-3}$	$z_m$	$I - I_s$	$c_{m,app}/\text{g dm}^{-3}$	$w_{m,app}$
80.0	0.134	24.6	31.8	0.40
60.3	0.094	26.2	23.7	0.39
39.2	0.080	22.7	17.5	0.45
20.6	0.070	13.9	9.4	0.45
10.5	0.054	7.7	4.0	0.38

over unassociated and clustered forms) cannot be obtained from the experiment. However, apparent values of the concentration of molecules ( $c_{m,app}$ , as if they were unassociated and in ideally dilute solution) could be calculated from equation (9) in the form

$$z_m(I - I_s) = K^* c_{m,app} M_m \quad (10)$$

and these apparent concentrations were used in the determination of micellar molar mass.

Relevant data for construction of a corrected Debye plot for micelles alone are listed in Table 3. Also listed are values of the apparent mass fraction of molecules, i.e.

$$w_{m,app} = c_{m,app}/c \quad (11)$$

This parameter was constant at  $0.41 \pm 0.05$ , which served as a convenient basis for smoothing the values of  $c_{m,app}$ . In a similar analysis of light scattering intensities from solutions of copolymer B<sub>7</sub>E<sub>40</sub>B<sub>7</sub><sup>25</sup>,  $w_{m,app}$  was found to vary with  $c$ , so the present result is regarded as nothing more than a useful coincidence.

The corrected plot of  $K^* c' / [(1 - z_m)(I - I_s)]$  versus  $c'$  where  $c' = (c - c_{m,app})$  is shown in Figure 8b. The curve through the data points is a quadratic fit, and is unguided by theory. Because of the use of apparent values of the concentration of molecules in calculating  $c'$ , the concentration dependence of the corrected Debye function must be interpreted with caution. However, we note that a low slope of the Debye function at low concentration, i.e. a small positive (or small negative) value of  $A_{2,app}$ , and a low concentration dependence of the Debye function overall, are both consistent with the negative concentration dependence of the diffusion coefficient described in the section *Dynamic light scattering*. The ordinate intercept, which pertains to the infinitely dilute (ideally dilute) micellar state and is not subject to the same reservation as the slope, gives a mass-average molar mass of micelles of copolymer EB80-6400-93% in aqueous solution at 25°C:

$$M_w = 80\,000 \text{ g mol}^{-1} \quad (\text{estimated uncertainty: } \pm 20\%)$$

and a corresponding mass-average association number (i.e.  $M_w$  (micelles)/ $M_w$  (molecules)) of

$$N_w = 12 \pm 2$$

#### Phase diagram

In principle, the solubility of a copolymer in a solvent depends on its molar mass and composition but not on its chain architecture. This is because the interaction parameter is determined (in the van Laar or Flory-Huggins approximation) by the sum of the individual pair-interactions of chain units and solvent molecules.



For block copolymers which associate efficiently the simple rule breaks down because the phase behaviour of a solution of associates will differ from that of a solution of molecules. This effect is particularly clear in recent results obtained for E/B copolymers with similar overall compositions but different architectures and chain lengths which give rise to different modes and extents of micellization: e.g. in the following clouding temperatures ( $T_c$ ) found<sup>24-26</sup> for 20 g kg<sup>-1</sup> aqueous solutions:

Diblock	$E_{38}B_{12}$	$T_c > 95^\circ\text{C}$
Triblock	$B_5E_{39}B_5$	$T_c = 43^\circ\text{C}$
	$B_7E_{40}B_7$	$T_c = 26^\circ\text{C}$
	$B_{12}E_{76}B_{12}$	$T_c = 9^\circ\text{C}$

Turning to the present systems, the clouding temperature of statistical copolymer EB80-6400-93% in 20 g kg<sup>-1</sup> aqueous solution ( $T_c = 38^\circ\text{C}$ ) is similar to that of triblock copolymer  $B_5E_{39}B_5$ . The clouding temperature of block copolymer  $B_{12}E_{114}B_{12}$  in 20 g kg<sup>-1</sup> aqueous solution ( $T_c = 17^\circ\text{C}$ ) lies between those of triblock copolymers  $B_7E_{40}B_7$  and  $B_{12}E_{76}B_{12}$ , which is consistent (as expected) with a much greater sensitivity of solubility to B-block length compared with E-block length.

It is known that diblock copolymer  $E_{38}B_{12}$  is fully micellized in 20 g kg<sup>-1</sup> solutions at low temperatures, with the micelles interacting effectively as hard spheres (i.e. through a repulsive interaction)<sup>24</sup>. In contrast, 20 g kg<sup>-1</sup> solutions of the triblock copolymers<sup>25</sup> and copolymer EB80-6400-93% all contain significant fractions of molecules and/or molecular clusters at all concentrations and temperatures studied. Moreover, the solutions of the triblock copolymers contain micelles which interact attractively, most probably through a bridging mechanism<sup>25,26</sup>. Attractive interactions involving molecular clusters and micelles may well be an important factor determining the cloud points of the solutions of associated copolymers.

The relationship of the cloud point curve of the 'uniform statistical' copolymer EB78-7100-15% to that of the 'tapered triblock' copolymer EB80-6400-93% is difficult to discuss in detail because the comparison is between molecular and associated systems. The near coincidence of the cloud point curves of the two copolymers at moderate concentrations is interesting, but is probably ascribable to a balance of effects in that concentration range. The relatively high cloud points of copolymer EB78-7100-15% at extreme dilution can be ascribed to the lower molar mass of molecules of that copolymer in comparison with the higher molar mass of associates of copolymer EB80-6400-93%. The relatively high cloud points of copolymer EB80-6400-93% in the more concentrated solutions (unfortunately outside the range of the light scattering experiments) are consistent with substantial association into micelles, with a consequent increase in solubility, whereas solutions of copolymer EB78-7100-15% remain molecular over the whole concentration range. An increase in solubility on micellization is, of course, a familiar concept in surfactant chemistry, e.g. in connection with the Krafft point<sup>42</sup>, and has been documented in light scattering studies on E/P<sup>43</sup> and E/B<sup>14,22</sup> copolymers. The rapid rise in clouding temperature with concentration found for the 'true triblock' copolymer  $B_{12}E_{114}B_{12}$  beyond  $c \approx 150$  g kg<sup>-1</sup> is consistent with that explanation.

## CONCLUDING REMARKS

This study has underlined the care which must be taken in selecting statistical copolymers for study of solution properties in a potentially selective solvent. The EB system presents a stringent test, since poly(oxyethylene) and poly(oxybutylene) differ markedly in their solubilities in water, and the reactivity ratios of their monomers are significantly different, giving rise to so much composition drift that a high conversion statistical copolymer has the characteristics of a block copolymer. On the basis of present information it is not possible even to say that the cloud point curve of the 15%-conversion copolymer is unaffected by composition drift. Further experiments involving a number of low-conversion copolymers would be needed to settle that point. With regard to statistical copolymers of ethylene oxide and propylene oxide, which are of interest as model systems in the definition of parameters in the theory of block copolymer association<sup>44,45</sup> and phase behaviour<sup>46</sup>, we note that the requirements in that system are much less severe because the reactivity ratios are closer together (compare  $r_E = 4.1$ ,  $r_B = 0.17$  with  $r_E = 3.0$ ,  $r_P = 0.27$ )<sup>36,47</sup> and the hydrophobicity of a P unit is about one-quarter that of a B unit<sup>24</sup>.

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