

# Effect of end group on the micelle properties of diblock copolymers of ethylene oxide and 1,2-butylene oxide

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Copolymers of ethylene oxide and 1,2-butylene oxide ( $E_{18}B_{10}$ ,  $E_{43}B_9$ ,  $E_{40}B_{10}$ ,  $E_{90}B_{10}$ ,  $E_{96}B_{18}$  and  $E_{184}B_{18}$ , E = oxyethylene unit, B = oxybutylene unit, subscripts denote number-average chain lengths) with B blocks terminated by hydroxy groups (denoted  $E_mB_nH$ ) were methylated to provide copolymers having the same chain length and composition but with B blocks terminated by methoxy groups (denoted  $E_mB_nM$ ). Micelle properties of the M copolymers were determined by dynamic and static light scattering (hydrodynamic radius, association number, thermodynamic radius) and the values obtained compared with those for the H copolymers, most of which had been published previously. The results for copolymer  $E_{18}B_{10}M$  in solution at 40 °C were consistent with the formation of worm-like micelles, the micelles of the other copolymers being spherical, including  $E_{18}B_{10}H$  in solution at 40 °C and  $E_{18}B_{10}M$  in solution at 30 °C. For micelles of the  $B_{18}$  copolymers, methylation reduced the values of all properties by ca. 10%. For micelles of the  $B_9$ – $B_{10}$  copolymers, the effect of methylation was to reduce the hydrodynamic radius by ca. 10%, but to increase the association number by ca. 25% and thermodynamic radius by ca. 10%. The explanation of these effects takes into account the increased hydrophobicity of the methylated B blocks, the highly stretched state of the  $B_{18}$  blocks in their micelles, and the probability that water will concentrate at the centre of the cores of micelles of copolymers with hydroxy-ended B blocks. For copolymers forming spherical micelles, the effect of methylation on association number is equivalent to raising the temperature of the solution by ca. 10 °C. For micelles of copolymer  $E_{18}B_{10}$ , the effect of methylation is to lower the temperature of the sphere-to-worm transition from 40–50 °C ( $E_{18}B_{10}H$ ) to 30–40 °C ( $E_{18}B_{10}M$ ).

## 1 Introduction

Recently we have investigated the micellisation and micelle properties of diblock, triblock and cyclic-block copolymers of ethylene oxide (EO) and 1,2-butylene oxide (BO).<sup>1,2</sup> Particular attention has been paid to diblock copolymers prepared by sequential oxyanionic polymerisation of EO followed by BO, the resulting copolymers being denoted  $E_mB_n$ , where E denotes an oxyethylene unit,  $OCH_2CH_2$ , B an oxybutylene unit,  $OCH_2CH(C_2H_5)$ , and the subscripts denote number-average block lengths. Because of the slow reaction of EO with a secondary B oxyanion, carrying out the copolymerisation in reverse order, BO followed by EO, results in a broadened E-block distribution,<sup>3,4</sup> and the process is undesirable on that account. In the preferred procedure, initiation of the E block by (in our work) the monomethyl ether of diethylene glycol [2-(2-methoxyethoxy)ethanol] results in a methoxy-ended E block and, on completion of the preparation, a hydroxy-ended B block. The B block is hydrophobic, and given a sufficient B-block length the diblock copolymer will micellise in dilute aqueous solution.<sup>1</sup> The presence of a terminal hydroxy group will reduce the hydropho-

bicity of a B block, the more so if the block is short. The purpose of the work reported in this paper was to investigate possible effects on micelle properties of substituting the terminal hydroxy group by a methoxy group.

Our attention was drawn to the possibility of a significant effect of a terminal hydroxy group by recent work on micellar solutions of copolymer  $E_{86}B_{10}$ .<sup>5</sup> Small-angle neutron scattering (SANS) from aqueous micellar solutions of this copolymer showed a high proportion of  $D_2O$  in the micelle core: for example, 47 vol.%  $D_2O$  in the cores of micelles formed in 1 wt.% copolymer solution at 50 °C. This value can be compared with ca. 30 vol.% water/ $D_2O$  found for a 1 wt.% solution of copolymer  $dE_{23}P_{34}dE_{23}$  at 50 °C,<sup>6</sup> similar to that found for commercial copolymer P85 ( $E_{26}P_{40}E_{26}$ ),<sup>7</sup> and the much lower volume fractions of  $D_2O$  found for 2–5 wt.% solutions of the more hydrophobic copolymers P84 ( $E_{19}P_{43}E_{19}$ ) and P104 ( $E_{27}P_{43}E_{27}$ ) at similar temperatures.<sup>8</sup> Here P denotes an oxypropylene unit,  $OCH_2CH(CH_3)$ . Based on c.m.c. values the hydrophobicity of a B unit is six-times that of an oxypropylene (P) unit,<sup>1</sup> and consequently the unexpectedly-high proportion of water in the B core was assigned to an effect of the terminal hydroxy group of the B

block.<sup>5</sup> The central P blocks of the EPE copolymers are terminated by E blocks and loop in the P-block core.

Following previous work,<sup>9,10</sup> it was possible to methylate the OH ends of the B blocks of EB copolymers with 100% conversion and without significantly changing copolymer composition and block lengths. This paper describes the effect of such end-group methylation on micelle association number and radius as revealed by static and dynamic light scattering studies. Related studies using SANS are in progress.<sup>11</sup>

## 2 Experimental

### 2.1 Copolymers

Copolymer E<sub>43</sub>B<sub>9</sub> was prepared by sequential oxyanionic polymerisation of ethylene oxide followed by 1,2-butylene oxide following an established method.<sup>4,12</sup> Three other copolymers, E<sub>90</sub>B<sub>10</sub>, E<sub>96</sub>B<sub>18</sub> and E<sub>184</sub>B<sub>18</sub>, had been prepared in a similar way in Manchester, and copolymer E<sub>18</sub>B<sub>10</sub> (also denoted E<sub>18</sub>B<sub>9</sub><sup>13</sup> or EB 18-9 M<sup>14</sup>), was prepared in a related way under industrial conditions<sup>15</sup> at The Dow Chemical Co, Texas Operations (trade name BM45-1600). These four copolymers were used previously in light scattering studies,<sup>5,13,16</sup> while a sixth copolymer, E<sub>40</sub>B<sub>10</sub>, was a repeat preparation of a previous copolymer with the same formula which also had been studied by light scattering.<sup>17</sup>

All the copolymers were characterised by <sup>13</sup>C NMR spectroscopy for absolute molar mass and composition, and by gel permeation chromatography (GPC) for distribution width, as described elsewhere.<sup>4,12</sup> The molecular characteristics of the copolymers are listed in Table 1. As prepared, all six copolymers had methoxy-terminated E blocks and hydroxy-terminated B blocks.

The copolymers were methylated using iodomethane in Cooper's adaptation of the Williamson reaction.<sup>9,10</sup> After removal of excess reactants, the purified methylated copolymers were characterised by IR spectroscopy to confirm >99% conversion to ether. GPC confirmed no measurable change in distribution width. NMR spectroscopy was used to check the high conversion and to confirm no change in average chain length and composition (within experimental error, estimated to be ±2%). Whereas the formulae of the hydroxy-ended copolymers were determined from the chain length of the poly(E) precursor and the final composition, those of the methylated samples were necessarily determined from the spectra of the copolymers, which is a marginally less precise procedure. Overall, we confirmed that the average block lengths of the hydroxy-ended and methoxy-ended copolymers were identical within the uncertainty of the method, estimated to be ±4%. Accordingly, the formulae in Table 1 were accepted for the methylated samples. The two types of copolymer are distinguished by suffix M or H. Collectively, when convenient, the terms M copolymers and H copolymers are used.

**Table 1** Molecular characteristics of the copolymers

Copolymer	$M_n/g \text{ mol}^{-1}$ (NMR)	E (wt.%) (NMR)	$M_w/M_n$ (GPC)	$M_w^a/g \text{ mol}^{-1}$
E <sub>43</sub> B <sub>9</sub>	2540	74	1.03	2620
E <sub>18</sub> B <sub>10</sub>	1510	52	1.04	1570
E <sub>40</sub> B <sub>10</sub>	2480	71	1.04	2580
E <sub>90</sub> B <sub>10</sub>	4680	85	1.03	4820
E <sub>96</sub> B <sub>18</sub>	5520	77	1.03	5690
E <sub>184</sub> B <sub>18</sub>	9390	86	1.03	9670

<sup>a</sup> Calculated from  $M_n$  and  $M_w/M_n$ .

### 2.2 Light scattering

The light scattering methods, and their applicability to micellar solutions of the type under discussion, have been described and discussed previously.<sup>17,18</sup> The equipment, which varied slightly for measurements made over the period of the experiments, is based at present on a Brookhaven BI 200S instrument equipped with an argon-ion laser (wavelength 488 nm, usually operated at 500 mW) and fitted with a BI 9000 AT digital correlator.

Measurements were made on solutions at 20, 30 and 40 °C. In several cases the lower temperatures were omitted in order to ensure that the comparisons made were always for solutions which were predominantly micellar.

The correlation functions from dynamic light scattering (DLS) were analysed by the constrained regularised CONTIN method<sup>19</sup> to obtain distributions of decay rates ( $\Gamma$ ), hence distributions of apparent mutual diffusion coefficient [ $D_{app} = \Gamma/q^2$ ,  $q = (4\pi n/\lambda)\sin(\theta/2)$ ,  $n$  = refractive index of the solvent], and ultimately of apparent hydrodynamic radius ( $r_{h,app}$ , radius of the hydrodynamically-equivalent hard sphere corresponding to  $D_{app}$ ) via the Stokes–Einstein equation

$$r_{h,app} = kT/(6\pi\eta D_{app}) \quad (1)$$

where  $k$  is the Boltzmann constant and  $\eta$  is the viscosity of the solvent at temperature  $T$ .

The basis for analysis of static light scattering (SLS) was the Debye equation in the form

$$K^*c/(I - I_s) = 1/M_w + 2A_2c \dots \quad (2)$$

where  $I$  is the intensity of light scattered from the solution relative to that from benzene,  $I_s$  is the corresponding quantity for the solvent,  $c$  is the concentration,  $K^*$  is the appropriate optical constant,  $M_w$  is the mass-average molar mass of the solute, and  $A_2$  is the second virial coefficient (higher terms being omitted). Values of the specific refractive index increment, its temperature increment, and other quantities necessary for the calculations, have been given previously.<sup>12,13,18</sup>

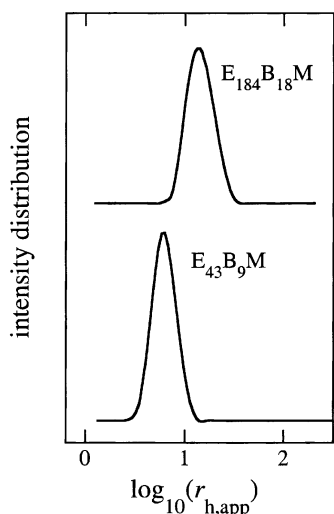
## 3 Copolymers E<sub>43</sub>B<sub>9</sub>, E<sub>40</sub>B<sub>10</sub>, E<sub>90</sub>B<sub>10</sub>, E<sub>96</sub>B<sub>18</sub> and E<sub>184</sub>B<sub>18</sub>

Results for copolymer E<sub>18</sub>B<sub>10</sub> are presented and discussed separately in Section 4. The results illustrated in this section are for methylated copolymers, those for hydroxy-ended copolymers having been described previously.<sup>5,16,17</sup>

### 3.1 Results

In Fig. 1 are shown examples of intensity distributions of apparent hydrodynamic radius obtained by DLS for 20 g dm<sup>-3</sup> aqueous micellar solutions at 40 °C of copolymers E<sub>43</sub>B<sub>9</sub>M and E<sub>184</sub>B<sub>18</sub>M. These two copolymers span the range of chain lengths considered in this section. The distributions are typical of micelles produced by closed association. The broader distribution of the micelles of E<sub>184</sub>B<sub>18</sub>M is a result of more significant intermicellar interactions caused by the expanded micelle corona of the longer E blocks. The distributions obtained for micelles of the other copolymers, and those at other temperatures, fitted this pattern.

In Fig. 2 the reciprocal of the intensity average of  $r_{h,app}$ , calculated in the CONTIN program by integration over the intensity distribution of decay rate, is plotted against copolymer concentration for copolymers E<sub>40</sub>B<sub>10</sub>M and E<sub>184</sub>B<sub>18</sub>M. Through eqn. (1),  $1/r_{h,app}$  relates directly to the apparent diffusion coefficient, but is compensated for changes in temperature and solvent viscosity. Extrapolation to  $c = 0$  gave the values of  $r_h$  listed in Table 2, together with those obtained for micelles of the other copolymers from present and



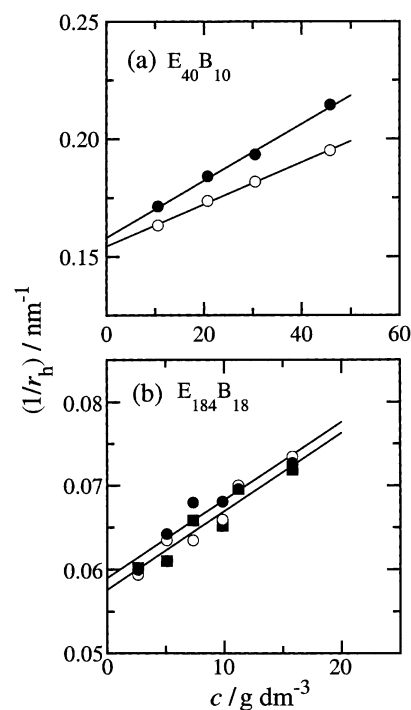
**Fig. 1** Dynamic light scattering. Normalised intensity distributions of the logarithm of apparent hydrodynamic radius for 20 g dm<sup>-3</sup> aqueous solutions at 40 °C of copolymers E<sub>43</sub>B<sub>9</sub>M and E<sub>184</sub>B<sub>18</sub>M, as indicated.

previous<sup>5,16,17</sup> work. As usually found for micelles of block poly(oxyalkylene)s in aqueous solution,<sup>1,20</sup> values of  $r_h$  were not significantly dependent on temperature.

Debye curves obtained for aqueous solutions of the copolymers are illustrated in Fig. 3 for copolymers E<sub>40</sub>B<sub>10</sub>M and E<sub>184</sub>B<sub>18</sub>M. As in previous reports which describe light scattering from solutions of the H copolymers,<sup>5,16,17</sup> the data points cannot be fitted by a straight line over the concentration range employed, but the curve expected for scattering from equivalent hard spheres based on the Percus–Yevick structure factor, as adapted for light scattering by Vrij,<sup>21</sup> can be used. As explained previously,<sup>5,16,17</sup> the method is conveniently applied by defining a thermodynamic expansion factor  $\delta_t = v_t/v_a$ , where  $v_t$  is the thermodynamic volume of the micelles (*i.e.* one of eighth of the excluded volume  $u$ ) and  $v_a$  is the anhydrous volume of the micelles

$$v_a = M_w/N_A \rho_a \quad (3)$$

where  $N_A$  is Avogadro's constant and  $\rho_a$  is the liquid density of the copolymer mixture calculated assuming mass additivity of specific volumes from published data.<sup>10</sup> To the extent that the approximation for the structure factor applies, the method is equivalent to using the virial expansion taken to its seventh



**Fig. 2** Dynamic light scattering. Concentration dependence of the reciprocal of apparent hydrodynamic radius for aqueous solutions of (a) E<sub>40</sub>B<sub>10</sub> and (b) E<sub>184</sub>B<sub>18</sub> at (■) 20, (○) 30 and (●) 40 °C. For clarity, the line for 30 °C is omitted in (b).

term but requires just two adjustable parameters, *i.e.*  $M_w$  and  $\delta_t$ . As can be seen in Fig. 3, the fit to the data points is satisfactory. Values of  $M_w$  were obtained from the intercept at  $c = 0$ . Values of the association number ( $N_w$ ) were calculated from

$$N_w = M_w/M_w^{\text{mol}} \quad (4)$$

where  $M_w^{\text{mol}}$  is taken from Table 1. These values are listed in Table 2, together with reported results for the H copolymers.<sup>5,16,17</sup> Also listed are values of the equivalent hard-sphere radius (thermodynamic radius,  $r_t$ ) calculated from the thermodynamic volume, *i.e.* from

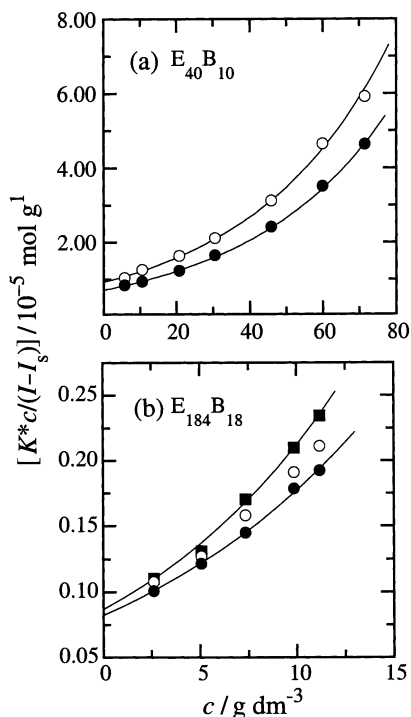
$$v_t = \delta_t v_a \quad (5)$$

Results for the two types of copolymer are compared in Fig. 4, which shows the ratios (methoxy-ended/hydroxy-ended B blocks, M/H) of micelle association numbers and the two

**Table 2** Micelle properties for E<sub>m</sub>B<sub>n</sub> copolymers in aqueous solution<sup>a</sup>

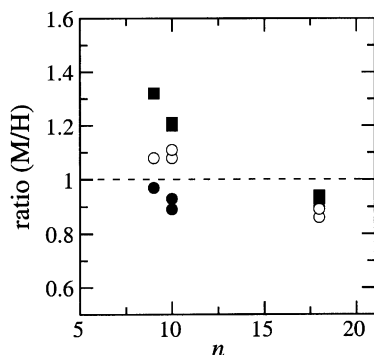
Copolymer	$T/^\circ\text{C}$	M copolymers			H copolymers <sup>b</sup>			
		$N_w$	$r_t/\text{nm}$	$r_h/\text{nm}$	$N_w$	$r_t/\text{nm}$	$r_h/\text{nm}$	
E <sub>43</sub> B <sub>9</sub>	40	50	5.4	6.7	38	5.0	6.9	
	E <sub>40</sub> B <sub>10</sub>	30	42	5.3	6.5	37	4.9	7.3
		40	54	5.7	6.3	E <sub>90</sub> B <sub>10</sub>	49	5.5
45	E <sub>96</sub> B <sub>18</sub>	27	6.5	8.8	23		5.9	9.5
30		34	7.0	8.4	31		6.5	9.5
E <sub>96</sub> B <sub>18</sub>	45	E <sub>184</sub> B <sub>18</sub>	153	13.1	13.6	163	14.8	15.5
	25		159	13.0	13.3	174	14.8	15.0
	30		163	12.8	13.3	121	18.0	19.5
	40		119	17.3	17.4	E <sub>184</sub> B <sub>18</sub>	134	18.8
25	E <sub>184</sub> B <sub>18</sub>	122	16.9	17.6	121		18.0	19.5
30		125	16.7	16.9	134		18.8	18.7

<sup>a</sup> Estimated uncertainties:  $\pm 5\%$  in  $N_w$  and  $r_h$ ;  $\pm 7\%$  in  $r_t$ . <sup>b</sup> Values for H-copolymer micelles from present work (E<sub>43</sub>B<sub>9</sub>) and from ref. 5 (E<sub>90</sub>B<sub>10</sub>), 16 (E<sub>96</sub>B<sub>18</sub> and E<sub>184</sub>B<sub>18</sub>) and 17 (E<sub>40</sub>B<sub>10</sub>).



**Fig. 3** Static light scattering. Debye plots for aqueous solutions of (a)  $E_{40}B_{10}$  and (b)  $E_{184}B_{18}$ . The data are for solutions at (■) 20, (○) 30 and (●) 40 °C. The curves through the data points are based on scattering theory for equivalent hard spheres. For clarity, the curve for 30 °C is omitted in (b).

micelle radii. The data are for solutions at 40 °C; where necessary the data for the H copolymers were interpolated to obtain values representative of solutions at 40 °C. As present interest is in the modification of the end group of the B-blocks, the plots are against B-block length. The evidence of Fig. 4 is that the length of the E block has little effect. The cluster of points at  $n = 18$  includes the six data points for copolymers  $E_{96}B_{18}$  and  $E_{184}B_{18}$ . These ratios average 0.90, *i.e.* a small reduction of *ca.* 10% in the association numbers and the radii of the micelles caused by methylation of their  $B_{18}$  blocks. The hydrodynamic radii of the micelles of the  $B_{9-10}$  M copolymers were also consistently smaller than those of their H-copolymer counterparts, by 7% on average, much the same as found for the micelles of the longer copolymers (see Fig. 4). However, for these copolymers the association numbers of the micelles of the M copolymers were significantly larger than those of their H-copolymer counterparts (average ratio = 1.24), as were their thermodynamic radii, although by a smaller percentage (average ratio = 1.09).



**Fig. 4** Properties of micelles of methoxy-ended (M) and hydroxy-ended (H)  $E_mB_n$  copolymers in aqueous solution at 40 °C. The ratio (M/H) of (■) association number, (●) hydrodynamic radius and (○) thermodynamic radius are plotted against B-block length ( $n$ ). The copolymers are  $E_{43}B_9$ ,  $E_{40}B_{10}$ ,  $E_{90}B_{10}$ ,  $E_{96}B_{18}$  and  $E_{184}B_{18}$ . The uncertainties are  $\pm 7-9\%$  in the ratios,  $\pm 4\%$  in the block length.

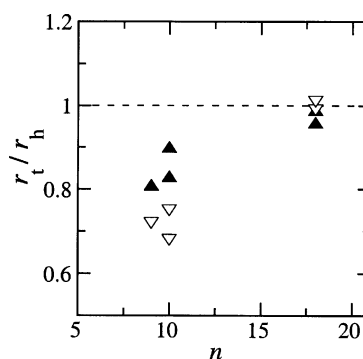
### 3.2 Micellar interaction

There is evidence from SANS from dilute solutions<sup>5,22</sup> and small-angle X-ray scattering (SAXS) from concentrated solutions<sup>5,23-25</sup> that the micelles of the H copolymers under consideration in this Section (and of closely related copolymers) are spherical at solution temperatures as high as 70 °C, and there is every reason to suppose that the M copolymers are as well. Assuming this to be so, the ratio of the thermodynamic radius to the hydrodynamic radius can be used to assess the nature of the interaction potential of the micelles in much the same way as it is used in studies of polymer coils.<sup>26</sup> If the micelles behaves as hard spheres then  $r_t/r_h = 1$ . If the micelle corona makes no contribution to the excluded volume, as in a theta solvent, then  $r_t/r_h \rightarrow 0$ . This last condition has been investigated for  $E_{40}B_{10}$  micelles in aqueous salt solution.<sup>17</sup> Values of  $r_t/r_h$  for the micelles of the M and H copolymers are plotted against B-block length in Fig. 5. Within the accuracy of determination, the micelles of the  $B_{18}$  copolymers, whether M or H, behave as hard spheres. The micelles of the  $B_{9-10}$  copolymers have softer interaction potentials, particularly those of the H copolymers. The hard-sphere nature of the micelles of the  $B_{18}$  copolymers presumably reflects their high association numbers (see Table 2) and the consequent dense packing of the E-blocks in the micelle corona.

### 3.3 Association number

The high association numbers of the  $B_{18}$  copolymers, which are rather insensitive to change in temperature (see Table 2), are typical of spherical micelles which have reached their maximum core size, *i.e.* the condition where an increase in core radius is severely limited by the adverse effect of B-block stretching. This effect has been demonstrated previously.<sup>27,28</sup> Under these circumstances, the effect of end-group modification of copolymers should be small, and the evidence (see Fig. 4) is that methylation causes a small reduction in  $N_w$ . In contrast, methylation promotes micellisation of the  $B_{9-10}$  copolymers, with a significant rise in association number.

As noted in Section 1, it is known from SANS studies that the hydroxy-ended copolymer  $E_{86}B_{10}$  forms micelles containing a significant proportion of water. As the B units are highly hydrophobic, this water is likely to be associated with the hydroxy groups. These terminal groups must be concentrated towards the centre of the micelle core, and this will create a favourable environment for solubilised water, giving an  $E_mB_nH$  micelle the character of a primitive vesicle. The effect of methylation will be to negate this effect, and at the same time to increase the hydrophobicity of the B block. If the B blocks are not overly stretched in a small micelle core, as is the case when the association number is low, as for the  $B_{9-10}$  copolymers, the increase in hydrophobicity will be the deter-



**Fig. 5** B-block length ( $n$ ) dependence of the ratio of thermodynamic radius to hydrodynamic radius ( $r_t/r_h$ ) for (▲) methoxy-ended and (▼) hydroxy-ended  $E_mB_n$  copolymers in aqueous solution at 40 °C. The copolymers are  $E_{43}B_9$ ,  $E_{40}B_{10}$ ,  $E_{90}B_{10}$ ,  $E_{96}B_{18}$  and  $E_{184}B_{18}$ . The uncertainties are  $\pm 9\%$  in the ratio,  $\pm 4\%$  in the block length.

mining factor and the association number will be increased by methylation. If the association number is at or near its upper limit, as for the  $B_{18}$  copolymers at 40 °C, stretching of the B blocks will be alleviated by the concentration of water towards the centre of the core. This mechanism is not available for the methylated copolymers, and the core radius (and so the micelle association number) must be smaller. It is intended to test this conclusion by detailed analysis of SANS experiments on H and M copolymers.<sup>11</sup>

### 3.4 Hydrodynamic radius

The ratios of hydrodynamic radii for all five copolymers lie just below unity (see Fig. 4). The copolymers under investigation have lengthy E blocks ( $>E_{40}$ ) and, unlike  $N_w$  which relates closely to core volume and thereby B block length,  $r_h$  depends mainly on the thickness of the micelle corona and so on E block length. Close correlation with the behaviour of  $N_w$  is not expected and is not found.

### 3.5 Thermodynamic radius

The intermicellar interaction potential, which controls the excluded volume and thereby contributes to the thermodynamic radius, is hard for the micelles of both  $B_{18}$  copolymers, and the change in  $r_t$  on methylation (a reduction of 10%) is in line with that in  $r_h$ . In the case of the  $B_{9-10}$  copolymers, the interaction potential of the micelles differs for the two types of copolymer, that of the H copolymers being the softer (see Section 3.2 and Fig. 5). A softer interaction potential implies a smaller excluded volume, hence a higher ratio (M/H) for  $r_t$  than for  $r_h$ .

### 3.6 Effect of E-block-length distribution

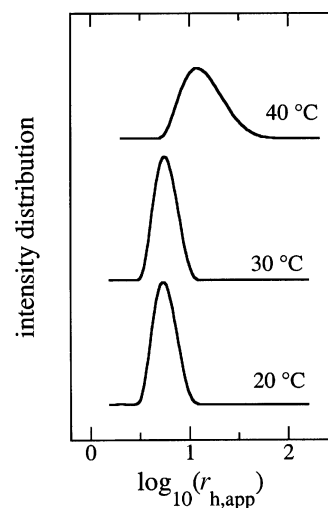
A previous study<sup>4</sup> of the properties of micelles formed from two copolymers prepared by the two monomers polymerised in different order, *i.e.*  $E_{41}B_8$  and  $B_8E_{40}$ , is related to the present study, as the B block in copolymer  $B_8E_{40}$  had a terminal methoxy group. However, as mentioned in Section 1, because of the slow initiation step polymerisation of ethylene oxide initiated by a secondary B oxyanion leads to a wide E-block distribution.<sup>3,4</sup> This being the case for copolymer  $B_8E_{40}$ , there are two effects which increase the association number and radii of its micelles compared to those of the conventional hydroxy-ended copolymer  $E_{41}B_8$ ; the wide E-block distribution and the methoxy terminal group. Assuming that the end-group effect in  $B_8E_{40}$  is similar to that in the  $B_{9-10}$  copolymers of present interest, the new results allow the two affects to be separated. The ratio of association numbers ( $B_8E_{40}/E_{41}B_8$ ) for micelles in solution at 40 °C is 2.1, compared with 1.3 for methylated and hydroxy-ended  $E_{43}B_9$ , confirming that the wide E-block distribution in  $B_8E_{40}$  is much more influential in increasing  $N_w$  than the difference in end groups. Consideration of the radii leads to the same conclusion.

## 4. Copolymer $E_{18}B_{10}$

### 4.1 Results

Examples of intensity distributions of apparent hydrodynamic radius obtained for 20 g dm<sup>-3</sup> aqueous micellar solutions of copolymer  $E_{18}B_{10}M$  are shown in Fig. 6. The distributions found for the solutions at 20 and 30 °C are narrow, and in this respect similar to those found for the other copolymers (see Fig. 1). The distribution at 40 °C is much broader and shifted to higher values of  $r_{h,app}$ . Corresponding distributions reported for solutions of  $E_{18}B_{10}H$  were narrow for solutions at both 25 and 40 °C.<sup>13</sup>

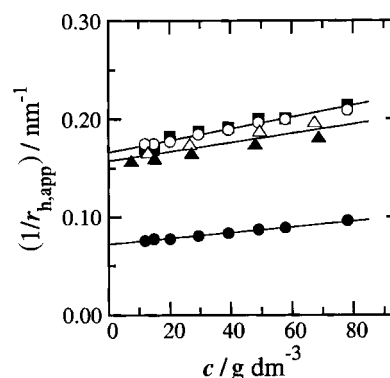
Values of the reciprocal of the intensity average of  $r_{h,app}$  found for micelles of copolymer  $E_{18}B_{10}M$  are plotted against



**Fig. 6** Dynamic light scattering. Normalised intensity distributions of the logarithm of apparent hydrodynamic radius for 20 g dm<sup>-3</sup> aqueous solutions of copolymer  $E_{18}B_{10}M$  at the temperatures indicated.

copolymer concentration in Fig. 7. Data for copolymer  $E_{18}B_{10}H$  taken from ref. 13 are included. To avoid complexity, one averaged line is drawn through the data points for  $E_{18}B_{10}M$  at 20 and 30 °C, and likewise through the data points for  $E_{18}B_{10}H$  at 25 and 40 °C. Extrapolation to  $c = 0$  of individual straight lines fitted to the data gave the values of  $r_h$  listed in Table 3.

Debye curves obtained for aqueous solutions of copolymer  $E_{18}B_{10}M$  are illustrated in Fig. 8. As discussed in Section 3.1, the data points are fitted with curves expected for scattering

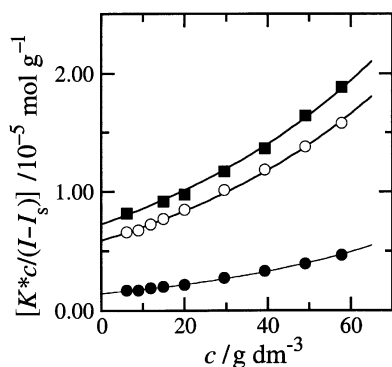


**Fig. 7** Dynamic light scattering. Concentration dependence of the reciprocal of apparent hydrodynamic radius for aqueous solutions of copolymer  $E_{18}B_{10}M$  at (■) 20, (○) 30 and (●) 40 °C, and for copolymer  $E_{18}B_{10}H$  at (△) 25 and (▲) 40 °C. For clarity, single lines are drawn through the data points at 20 and 30 °C for  $E_{18}B_{10}M$ , and at 25 and 40 °C for  $E_{18}B_{10}H$ .

**Table 3** Micelle properties for copolymer  $E_{18}B_{10}$  in aqueous solution<sup>a</sup>

$T/^\circ\text{C}$	$E_{18}B_{10}M$			$E_{18}B_{10}H^b$		
	$N_w$	$r_t/\text{nm}$	$r_h/\text{nm}$	$N_w$	$r_t/\text{nm}$	$r_h/\text{nm}$
20	88	4.9	6.1			
25				70	4.4	6.3
30	108	5.4	5.9			
40	440	9.0	13.6	110	5.4	6.5

<sup>a</sup> Estimated uncertainties:  $\pm 5\%$  in  $N_w$  and  $r_h$ ;  $\pm 7\%$  in  $r_t$ . <sup>b</sup> Values for  $E_{18}B_{10}H$  micelles from ref. 13.



**Fig. 8** Static light scattering. Debye plots for aqueous solutions of  $E_{18}B_{10}$ . The data are for solutions at (■) 20, (○) 30 and (●) 40 °C. The curves through the data points are based on scattering theory for equivalent hard spheres.

from equivalent hard spheres. The micelles in solution at 40 °C are not spherical (see Section 4.3) but, as seen in Fig. 8, the fit is satisfactory for purposes of extrapolating and deriving the required quantities in the usual way. Values of the association number ( $N_w$ ) and the thermodynamic radius (equivalent hard-sphere radius,  $r_t$ ) are listed in Table 3, together with results reported for copolymer  $E_{18}B_{10}H$ .<sup>13</sup>

#### 4.2 Spherical micelles

The results for  $E_{18}B_{10}M$  at 30 °C and corresponding interpolated values for  $E_{18}B_{10}H$  can be compared and discussed in the manner set out in Section 3. The ratios (M/H) are 1.30 for  $N_w$ , 0.92 for  $r_h$  and 1.15 for  $r_t$ . These ratios plot onto Fig. 4 in essentially the same way as the those for the micelles of the other  $B_{9-10}$  copolymers. The ratios of the two radii ( $r_t/r_h$ ) for the individual copolymers are 0.91 for  $E_{18}B_{10}M$  and 0.73 for  $E_{18}B_{10}H$ , in agreement with the data points for the  $B_{9-10}$  copolymers in Fig. 5. It is clear that the micelles formed from  $E_{18}B_{10}M$  at 20 and 30 °C and from  $E_{18}B_{10}H$  at 25 and 40 °C have similar properties to those of the copolymers discussed in Section 3, *i.e.* they can be characterised as spherical and the differences in properties can be explained as described in Section 3.

#### 4.3 Worm-like micelles

It remains to explain the high values of the association number and radii of the micelles of methylated copolymer  $E_{18}B_{10}M$  in aqueous solution at 40 °C (see Table 3). Coincidentally with this work, SANS was used in a preliminary investigation of the micelle properties of the hydroxy-ended copolymer  $E_{18}B_{10}H$  in dilute aqueous solution (10 g dm<sup>-3</sup>) over a wide temperature range.<sup>22</sup> Those results showed unequivocally that  $E_{18}B_{10}H$  micelles are spherical in solutions at 40 °C and below, but are worm-like at higher temperatures, the temperature of the transition from spherical to elongated geometry being in the range 40–50 °C.

The results we have for the association numbers of the spherical micelles of the  $B_{9-10}$  copolymers, as set out in Tables 2 and 3, indicate that the effect of methylation is roughly equivalent to the effect of raising the temperature by 10 °C. So far as micelle geometry is concerned, it can be argued that a dilute solution of copolymer  $E_{18}B_{10}M$  at 40 °C is equivalent to one of  $E_{18}B_{10}H$  at 50 °C, and consequently that worm-like micelles will form in each case.

Assuming no water in the core of the spherical  $E_{18}B_{10}M$  micelles at 30 °C then, given the specific volume of poly(oxybutylene)<sup>10</sup> and  $N_w = 108$ , the core volume is 134 nm<sup>3</sup> and the core radius is 3.17 nm. If the same core radius held for a worm-like micelle at 40 °C, for which  $N_w = 440$

(core volume 549 nm<sup>3</sup>), the contour length would be 17 nm. However, the  $B_{10}$  blocks are highly stretched in the spherical micelle core at 30 °C,<sup>5</sup> but will be more relaxed in an elongated core, reducing the core radius towards the radius of gyration ( $r_g$ ) of an unperturbed  $B_{10}$  block, *i.e.* *ca.* 0.8 nm at 30 °C.<sup>29</sup> A core radius of twice  $r_g$  would lead to a contour length of *ca.* 70 nm for the  $E_{18}B_{10}M$  micelles at 40 °C. The contour length obtained from SANS for worm-like micelles of  $E_{18}B_{10}H$  at 60 °C is 150 nm.<sup>22</sup>

## 5. Conclusions

(i) As prepared the B blocks of  $E_mB_n$  copolymers are terminated by hydroxy groups (copolymers denoted  $E_mB_nH$ ), but the end groups can be methylated with effectively 100% conversion (copolymers denoted  $E_mB_nM$ ).

(ii) H and M copolymers having E block lengths of 40 units or more ( $E_{43}B_9$ ,  $E_{40}B_{10}$ ,  $E_{90}B_{10}$ ,  $E_{96}B_{18}$  and  $E_{184}B_{18}$ ) form spherical micelles. When the B-block is long ( $B_{18}$ ) the effect of methylation is to reduce the micelle association number and the radii by *ca.* 10%. When the B block is short (*ca.*  $B_{10}$ ) the effect is to reduce the hydrodynamic radius by a similar amount, but to increase the association number by *ca.* 25% and thermodynamic radius by *ca.* 10%. These effect can be explained taking into account the increased hydrophobicity of the methylated B blocks, the highly stretched state of the  $B_{18}$  blocks in their micelles, and the probability that water will concentrate at the centre of the cores of micelles of copolymers with hydroxy-ended B blocks.

(iii) In solution at 30 °C, copolymers  $E_{18}B_{10}H$  and  $E_{18}B_{10}M$  form spherical micelles and the effect of end-group substitution is identical to that established for the other copolymers with  $B_{10}$  blocks. In solution at 40 °C, the properties of the micelles of copolymer  $E_{18}B_{10}H$  fit to this pattern but those of  $E_{18}B_{10}M$  do not, the association number and the radii having remarkably high values. This is attributed to the formation of worm-like micelles.

(iv) For the copolymers with  $B_{10}$  blocks forming spherical micelles, the effect of methylation on association number is equivalent to raising the temperature of the solution by *ca.* 10 °C. For micelles of copolymer  $E_{18}B_{10}$ , the effect of methylation is to lower the temperature of the sphere-to-worm transition from 40–50 °C ( $E_{18}B_{10}H$ ) to 30–40 °C ( $E_{18}B_{10}M$ ).

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