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# Mixed micelles of block copolymers of ethylene oxide and 1,2-butylene oxide. Solutions and gels of triblock BEB plus diblock EB copolymers studied by light scattering and rheology†

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Because of the hydrophobic end blocks, micelles of triblock BEB copolymers (E denotes an oxyethylene unit, B an oxybutylene unit) formed in aqueous solution show effects attributable to intermicellar bridging. The formation of mixed micelles with a diblock EB copolymer reduces but does not eliminate the effect. Light scattering methods applied to dilute solutions have been used to show that this is the case for mixed micelles of $B_{12}E_{114}B_{12}$ and $E_{43}B_{11}$ (the subscripts denote block lengths). This work focuses on 20 wt% aqueous solutions and on the effect of mixing on properties relating to the gel state, *i.e.* dynamic storage modulus ($G'$) and yield strength ($\sigma_y$). There are two contributory factors determining the gel properties: micelle bridging and micelle packing, with just the latter operative for a diblock gel. Increasing the proportion of diblock copolymer in the mixture reduces the contribution from micelle bridging. Considering 20 wt% solutions at 5 °C, the diblock copolymer solution does not gel at this temperature and values of $G'$ and $\sigma_y$ fall away monotonically to zero. For 20 wt% solutions at 25 °C, the diblock copolymer solution does gel at this temperature and values of $G'$ and $\sigma_y$ pass through minima as the system is changed from 100% triblock to 100% diblock copolymer.

## 1. Introduction

The properties of aqueous micellar solutions of triblock copolymers of ethylene oxide and 1,2-butylene oxide with hydrophobic end blocks are affected by micellar bridging.[1] We denote these copolymers $B_nE_mB_n$, where E represents an oxyethylene unit, $OCH_2CH_2$, B a 1,2-oxybutylene unit, $OCH_2CH(C_2H_5)$, and $n$ and $m$ are block lengths in the chain units. Because the bridges are dynamic in nature, the effect is that of a weak attractive interaction between micelles. At a given temperature, the strength of the interaction depends on the number of bridges between micelles,[2] which in turn depends on the E and B block lengths of the copolymer, as summarised by Liu *et al.*[3] For a given BEB copolymer the number of bridges between micelles can be reduced by forming mixed micelles of the triblock copolymer with a diblock EB copolymer, as a diblock copolymer cannot bridge. This technique has been used to modify the properties of aqueous solutions of associative thickeners, *e.g.* hydrophobically-modified ethoxylated urethanes (HEUR polymers) in mixtures with ionic or nonionic surfactants with comparable alkyl chain lengths.[4]

This paper describes the modulus and yield strength of 20 wt% aqueous gels of triblock copolymer $B_{12}E_{114}B_{12}$, diblock copolymer $E_{43}B_{11}$, and mixtures of the two. A previous study of solutions of triblock $B_{12}E_{76}B_{12}$ and diblock $B_8E_{41}$ copolymers has shown that mixed micellisation is readily achieved in systems of this type.[5] However, it was thought wise to use light scattering to confirm mixed micellisation, as well as to check that the micellar parameters (association number, radius) are consistent with spherical (or near spherical) micelles.

With regard to the properties of the gel, it must be borne in mind that the presence of bridging and the formation of a dynamic network do not preclude a packing mechanism for formation of a structured gel at an appropriate concentration. Indeed, packing into a liquid-crystalline (mesophase) structure would be expected when the repulsive component of the intermicellar interaction becomes dominant as the concentration is increased and the micelles move closer together. This point has been made previously in the interesting report on the properties of aqueous solutions of copolymer $P_{15}E_{156}P_{15}$.[6] In this respect it is known that a 20 wt% aqueous solution of $B_{12}E_{114}B_{12}$ at 20 °C forms a hard cubic gel with face-centred cubic (fcc) structure.[7] We use the term 'hard' to denote a gel with high modulus and yield stress, as introduced by Hvidt and coworkers.[8] As shown in this work, a 20 wt% aqueous solution of diblock copolymer $E_{43}B_{11}$ also forms a hard gel at 20 °C. The structure of this diblock gel has not been determined, but solutions of related copolymers at comparable concentrations have an fcc structure.[9]

## 2. Experimental

Copolymers $B_{12}E_{114}B_{12}$ and $E_{43}B_{11}$ were prepared by sequential oxyanionic polymerisation of ethylene oxide followed by 1,2-butylene oxide, using a difunctional or monofunctional initiator as appropriate. Gel permeation chromatography was used to characterise the distribution widths (polydispersity) as the ratio of mass-average to number-average molar mass, $M_w/M_n$ = 1.05 ($B_{12}E_{114}B_{12}$) and 1.03 ($E_{43}B_{11}$). $^{13}$C NMR spectroscopy was used to obtain absolute values of block

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length and composition, and to verify block architecture. Corresponding values of $M_n$ were 6740 g mol$^{-1}$ ($B_{12}E_{114}B_{12}$) and 2680 g mol$^{-1}$ ($E_{43}B_{11}$). The methods have been described previously.[1,5,10]

Clouding temperatures ($T_{cl}$) were determined by slowly heating solutions of the copolymers (0.2 °C min$^{-1}$) in small screw-cap tubes. At one degree intervals the tubes were inverted to check the mobility of the contents.

Intensities of light scattered from well-filtered dilute solutions were measured by means of a Brookhaven BI200S instrument and vertically polarised incident light of wavelength $\lambda = 488$ nm supplied by an argon-ion laser operated at *ca.* 500 mW. A Brookhaven BI9000AT digital correlator was used to acquire data for dynamic light scattering (DLS). The scattering angle for both DLS and SLS (static light scattering) was 90° to the incident beam. The data were analysed using Debye plots for SLS and the CONTIN programme for DLS. All the procedures have been described in detail elsewhere.[1,5]

Rheometric measurements were made using a Bohlin CS50 rheometer and cup-and-bob geometry under the conditions described elsewhere.[7,11] Storage ($G'$) and loss ($G''$) moduli were measured over a range of temperatures (heating rate 1 °C min$^{-1}$) with the instrument in oscillatory-shear mode at frequency $f$ = 1 Hz and strain amplitude $A \approx 0.5\%$. Yield stresses were measured at several temperatures with the instrument in continuous-shear mode and programmed to increase the shear stress in a series of logarithmically-spaced steps, allowing one minute to equilibrate at each step.

## 3. Light scattering

Light scattering measurements were made on micellar solutions of a 50 : 50 wt% mixture of the two copolymers $B_{12}E_{114}B_{12}$ and $E_{43}B_{11}$. Clouding temperatures ($T_{cl}$) determined over the concentration range $c$ = 1 to 10 wt% were in the range 24–32 °C (see Fig. 1). Consequently, measurements were carried out on solutions at 10 and 20 °C.

It is known that values of the critical micelle concentration (c.m.c.) of $E_mB_n$ and $B_nE_mB_n$ copolymers, when expressed in mol dm$^{-3}$ units, are not greatly dependent on E-block length.[12] Accordingly values of the c.m.c. of copolymer $B_{12}E_{114}B_{12}$ were estimated from those reported for copolymer $B_{12}E_{260}B_{12}$,[13] *i.e.* c.m.c. ≈ 0.03 and 0.02 g dm$^{-3}$ at 10 and 20 °C respectively after adjustment for the difference in molar mass. In a similar way, values of the c.m.c. of copolymer $E_{43}B_{11}$ were estimated from values reported for $E_mB_8$ and $E_mB_{10}$ copolymers.[12] With adjustment for the change in temperature,[12] we obtain c.m.c. ≈ 0.4 and 0.3 g dm$^{-3}$ at 10 and 20 °C respectively. Accordingly, light scattering from the 50 : 50 wt% mixture of copolymers was investigated for solutions with concentrations of 5 g dm$^{-3}$ (0.5 wt%) or greater, *i.e.* at concentrations more than ten-times the c.m.c. of the diblock copolymer, and sufficient to ensure that the solutions were essentially entirely micellar.

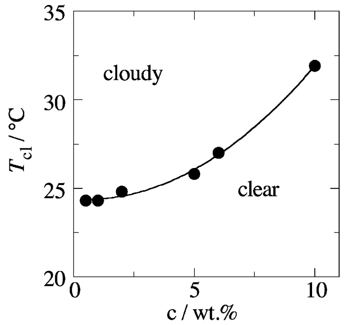

**Fig. 1** Clouding temperatures of aqueous micellar solutions of a 50 : 50 wt% mixture of copolymers $B_{12}E_{114}B_{12}$ and $E_{43}B_{11}$.

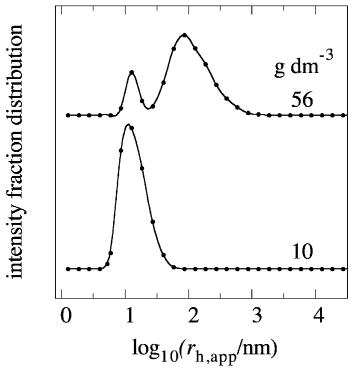

**Fig. 2** Examples of intensity fraction distributions of the logarithm of the apparent hydrodynamic radius for aqueous solutions of triblock copolymer $B_{12}E_{114}B_{12}$ mixed with 50 wt% diblock copolymer $E_{43}B_{11}$ at 20 °C. The concentrations of the solutions are indicated.

### 3.1. Hydrodynamic radius from DLS

The CONTIN procedure[14] was used to provide intensities at logarithmically-spaced values of the decay rate ($\Gamma$), and thereby corresponding distributions of the apparent mutual diffusion coefficient ($D_{app}$). The Stokes–Einstein equation,

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

where $k$ is the Boltzmann constant and $\eta$ is the viscosity of the solvent at temperature $T$, then gave values of the apparent hydrodynamic radius ($r_{h,app}$, radius of gyration of the hydrodynamically equivalent hard sphere). Intensity fraction distributions of log $r_{h,app}$ for the 50 : 50 wt% micellar solution at 20 °C are shown for two copolymer concentrations in Fig. 2. The single narrow peak at log ($r_{h,app}$) ≈ 1 found for the 10 g dm$^{-3}$ (1 wt%) solution is assigned to mixed micelles. The same peak is seen in the distribution found for the 56 g dm$^{-3}$ solution, but accompanied by a broad peak with a maximum at log ($r_{h,app}$) ≈ 2, which is assigned to bridged micellar clusters. Similar distributions have been reported for aqueous solutions of triblock $B_{12}E_{76}B_{12}$ mixed with diblock $B_8E_{41}$,[5] and for aqueous solutions of copolymer $B_{12}E_{260}B_{12}$ alone.[13] Distributions obtained for the present solutions at 10 °C (not shown) had similar distributions but a less pronounced cluster peak for the 56 g dm$^{-3}$ solution. This is as expected; water becomes a better solvent for the micelles as the temperature is lowered, and bridging (hence clustering) of micelles is reduced.

The plots in Fig. 3 show the apparent diffusion coefficient, averaged over the intensity distribution, against concentration in g cm$^{-3}$. The erratic data points for the solutions at 20 °C are for distributions with two distinct peaks (see Fig. 2) and were disregarded in constructing the quadratic curves. The

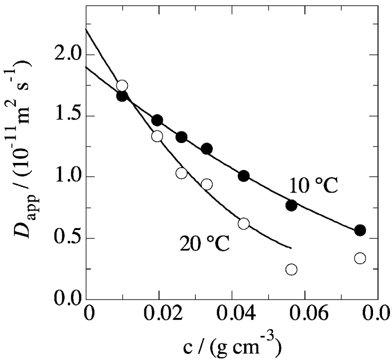

**Fig. 3** Concentration dependence of the apparent diffusion coefficient for aqueous solutions of triblock copolymer $B_{12}E_{114}B_{12}$ mixed with 50 wt% diblock copolymer $E_{43}B_{11}$. Solution temperatures are indicated. The curves are least-squares quadratic fits to the data points.

**Table 1** Micelle properties of mixed micelles of $B_{12}E_{114}B_{12}$ and $E_{43}B_{11}$ (50 : 50 wt%) from DLS and SLS[a]

| $T$/°C | $D$/$10^{-11}$ $m^2$ $s^{-1}$ | $k_D$/$cm^3$ $g^{-1}$ | $r_h$/nm | $M_w$/$10^5$ g $mol^{-1}$ | $N_w$ | $A_2$/$10^{-5}$ $cm^3$ mol $g^{-2}$ |
|---|---|---|---|---|---|---|
| 10 | 1.9 | −13 | 8.1 | 0.74 | 15 | −7 |
| 20 | 2.2 | −24 | 9.7 | 1.28 | 26 | −10 |

[a] Estimated uncertainties: $D$, $r_h$ to ±3%, $k_D$ and $A_2$ to ±10%, $M_w$ and $N_w$ to ±5%.

intercepts of the curves gave values of $D$ at $c = 0$ from which $r_h$ ($c = 0$) was calculated *via* eqn. (1). From eqn. (2) and the initial slopes of the plots, the diffusion virial coefficient ($k_D$) was calculated.

$$D_{app} = D(1 + k_D c + ......) \quad (2)$$

Values of $D$, $k_D$ and $r_h$ are listed in Table 1.

Negative values of $k_D$ have been reported for other solutions of BEB copolymers in which micelles interact attractively by bridging.[1,3,13] Parameter $k_D$ is related to the thermodynamic second virial coefficient ($A_2$) by[15]

$$k_D = 2A_2M_w - k_f - 2v, \quad (3)$$

where $k_f$ is the friction coefficient and $v$ is the specific volume of the micelles in solution. As confirmed by the results from SLS (next section), the first term in eqn. (3) is negative, so ensuring negative values of $k_D$. Values of $k_D$ found for well-micellised solutions of non-bridging EBE triblock and EB diblock copolymers are invariably positive.[12] We note that integrated van der Waals (Hamaker) attraction and polymer depletion (which can generate an attractive interaction between sterically-stabilised colloidal particles) play no significant role in dilute micellar systems. The primary cause of negative values of $k_D$ and $A_2$ is BEB chains bridging between micelles.

### 3.2. Association numbers and virial coefficients from SLS

The hydrodynamic radii of the micelles (listed in Table 1) are small compared with the wavelength of the light and intraparticle interference is not a problem. Clustering at higher concentrations changes this picture, but our attention is focused on behaviour as $c \rightarrow 0$. Debye plots obtained for the 50 : 50 wt% mixture of copolymers $B_{12}E_{114}B_{12}$ and $E_{43}B_{11}$ are shown in Fig. 4, *i.e.* plots based on

$$K^*c/(I - I_s) = 1/M_w + 2A_2c + ... \quad (4)$$

where $I$ is the intensity of light scattering from solution relative to that from benzene, $I_s$ is the corresponding quantity for the solvent, $c$ is the concentration (in g $dm^{-3}$), $M_w$ is the mass-average molar mass of the solute, $A_2$ is the second virial coefficient (a higher coefficient being neglected), and $K^*$ is the appropriate optical constant.

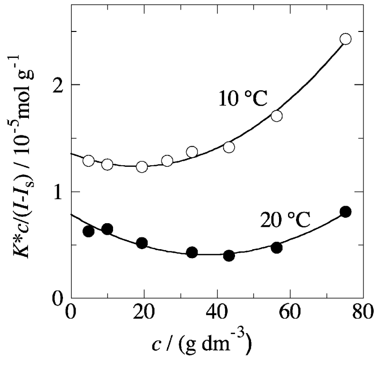

**Fig. 4** Debye plots for aqueous micellar solutions of triblock copolymer $B_{12}E_{114}B_{12}$ mixed with 50 wt% diblock copolymer $E_{43}B_{11}$. Solution temperatures are indicated. The curves through the data points are least-squares quadratic fits.

The minima seen in Fig. 4 result from competition between repulsive and attractive interactions between the micelles. The repulsive interaction, effectively a hard-sphere interaction, clearly dominates at higher concentrations where higher virial coefficients are required to describe the slope of the Debye plot. The effect of the attractive interaction between micelles, which derives from bridging, is seen at low concentrations where $A_2$ dominates.

Bridging is increased by raising the temperature, as is evident in Fig. 4 from the steeper negative initial slope of the plot for the solution at 20 °C. Water is a better solvent at low temperatures and a more-solvated E-block corona means a larger excluded volume of one micelle for another, hence the steeper positive slope at higher concentrations in the plot for the solution at 10 °C.

Values of $M_w$ from the intercepts and of $A_2$ from the initial slopes (see eqn. (4)) are set out in Table 1. Also in that table are the association numbers of the micelles calculated from

$$N_w = M_w/M_{w,mol}$$

where $M_{w,mol} = 4920$ g $mol^{-1}$ is the mass-average molar mass of the molecules in the 50 : 50 wt% mixture, in turn derived from the values of $M_n$ and $M_w/M_n$ given in Section 2. As is usually found for micelles of block-copoly(oxyalkylene)s,[12] values of $N_w$ increase with increasing temperature. The negative values of $A_2$ confirm the attractive interaction, and also the discussion in Section 3.1 regarding coefficient $k_D$: the leading term in eqn. (3) ($2M_wA_2$) dominates the negative values of $k_D$ (see Table 1).

Assuming there is no water in the spherical micelle cores, the association numbers and known densities can be used to obtain core volumes, hence core radii. At 20 °C there are 52 B blocks in the micelle core, *i.e.* a core mass of 45000 g $mol^{-1}$. Given a density of 0.97 g $cm^{-3}$,[16] the core volume is 77 $nm^3$ and the radius is 2.6 nm. A $B_{12}$ block is approximately 4.4 nm long,[17] hence spherical micelles are most probable.

### 3.3. Comparison with previous work

Liu *et al.*[3] have suggested using values of $k_D$ in a semi-quantitative way to assess the attractive contribution to the interaction between $B_nE_mB_n$ micelles caused by bridging. Their listed values for solutions at 25 °C range from −3 to −139 $cm^3$ $g^{-1}$ (see Table 1 of ref. 3). On this basis the attractive contribution to the interaction of the present mixed micelles in solution at 20 °C ($k_D = -23$ $cm^3$ $g^{-1}$) can be classified as moderate.

A direct comparison can be made with results for copolymer $B_{12}E_{260}B_{12}$[13] for which $N_w = 24$ at 20 °C, much the same as found for the present mixed micelles, but $k_D = -130$ $cm^3$ $g^{-1}$ and $A_2 = -14 \times 10^{-5}$ $cm^3$ mol $g^{-2}$, the $k_D$ value being indicative of strong bridging.[3] Compared with $B_{12}E_{260}B_{12}$, two factors count against bridging in solutions of the present mixed micelles. The shorter E-block length of $B_{12}E_{114}B_{12}$ favours looping, and the smaller number of triblock copolymers in the micelle reduces the probability of bridging. Whereas the number of triblock copolymers in a $B_{12}E_{260}B_{12}$ micelle is 24, that in the $B_{12}E_{114}B_{12}$–$E_{43}B_{11}$ mixed micelles (50 : 50 wt%, 28 no.%) is only 7.

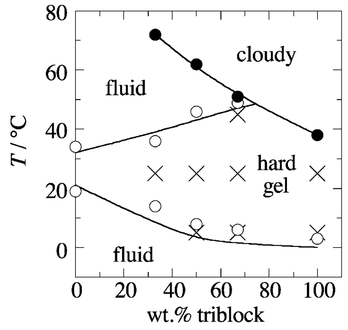

**Fig. 5** Clouding temperatures and the upper and lower limits of hard gel for 20 wt% solutions of mixed micelles of copolymers $B_{12}E_{114}B_{12}$ and $E_{43}B_{11}$. The unfilled circles show fluid/gel boundaries detected (to ±4 °C) by tube inversion. The crosses indicate gels with yield stresses greater than 40 Pa measured at 5, 25 and 45 °C.

Mixed micelles of triblock $B_{12}E_{76}B_{12}$ and diblock $B_8E_{41}$ copolymers (50 : 50 wt%) have been studied by static light scattering.[5] In that case, at a solution temperature of 25 °C, $N_w = 63$, $A_2 = -2.5 \infty 10^{-5}$ cm$^3$ mol g$^{-2}$, and $k_D = -12$ cm$^3$ g$^{-1}$. The last quantity is not quoted in ref. 5 but is available through Figure 9 of that paper. The number of triblock molecules per micelle is 19, but this value, significantly higher than that for the $B_{12}E_{114}B_{12}$–$E_{43}B_{11}$ mixed micelles, is counterbalanced by the higher association number indicating that the micelles are further apart in solution at a given mass concentration. As looping will be more important for $B_{12}E_{76}B_{12}$ compared with $B_{12}E_{114}B_{12}$, the finding that attraction in the $B_{12}E_{114}B_{12}$–$E_{43}B_{11}$ system is stronger than that in the $B_{12}E_{76}B_{12}$–$B_8E_{41}$ system can be understood.

## 4. Rheology

Copolymers $B_{12}E_{114}B_{12}$ and $E_{43}B_{11}$ and four mixtures, in proportion 100, 67, 50 and 33 wt% triblock, were used to prepare 20 wt% aqueous micellar gels. As expected in view of previous work,[5] a reduction in the proportion of triblock copolymer in the micelles resulted in an increase in clouding temperature: see Fig. 5 in Section 4.1.

### 4.1 Fluid/gel diagram

For a concentrated micellar solution with no possibility of bridging, *e.g.* an EB diblock copolymer, typical behaviour on heating from a low temperature is the sequence fluid→hard gel→fluid. In previous reports, for example ref. 10, we have used the term hard to describe a gel which is immobile in our inverted-tube test. Water becomes a poorer solvent for copolymers and micelles as the temperature is raised. The low-*T* boundary (fluid→hard gel) is associated with an increase in extent of micellisation, and so an increase in the volume fraction of micelles in the system, and the high-*T* boundary results from deswelling of the E-block corona in the poorer solvent, which causes a decrease in the volume fraction of micelles in the system.[18,19]

Characterisation of the 20 wt% solutions containing triblock copolymer by the tube-inversion method was complicated by the high viscosity of the fluids, no doubt a result of micellar bridging, which made accurate detection of fluid/gel boundaries by this method difficult. Whereas fluid/gel boundaries in solutions of EB diblock copolymers (including $E_{43}B_{11}$) can be readily detected to ±1 °C,[11,20] those in the present system could only be detected to ±4 °C. The data points so defined are shown as unfilled circles in Fig. 5.

Yield stress provided a second measure of the resistance to motion under shear stress. As carried out in our laboratories, the shear stress required to cause immobility in our tube inversion test has been shown to be 30–40 Pa.[11,20] Yield stresses ($\sigma_y$) were measured at 5, 25 and 45 °C, the values listed in Table 2 being the stresses at which the shear rate departed measurably from zero. Examples are shown in Fig. 6. Solutions with a yield stress in excess of 40 Pa are indicated by crosses in Fig. 5. The yield stresses shown in Table 2 for the 20 wt% gel of $E_{43}B_{11}$ were not measured but were estimated from the values of the storage modulus described in Section 4.2, *i.e.* that at 25 °C from the relationship established for cubic gels, $\sigma_y \approx 0.03G'$,[20–22] and those at 5 and 45 °C set equal to zero, as appropriate for a very mobile fluid.

**Table 2** Effect of composition on the yield stress of 20 wt% solutions of mixed micelles of copolymers[a] $B_{12}E_{114}B_{12}$ and $E_{43}B_{11}$

| | $\sigma_y$/Pa | | | | |
|---|---|---|---|---|---|
| $T$/°C | 100 wt% | 67 wt% | 50 wt% | 33 wt% | 0 wt%[b] |
| 5 | 310 | 150 | 70 | 6 | 0 |
| 25 | 500 | 280 | 170 | 330 | 500 |
| 45 | [c] | 60 | 5 | 8 | 0 |

[a] Compositions in wt% triblock. [b] Values estimated as described in the text. [c] Not measured: $T_{cl} \approx 38$ °C.

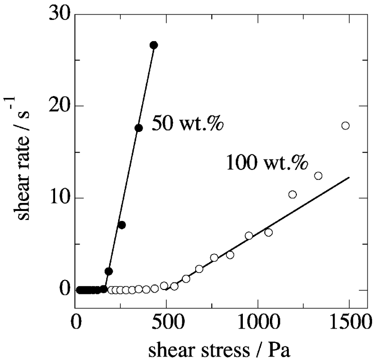

**Fig. 6** Yield stress under continuous shear for 20 wt% aqueous gels at 25 °C of mixed micelles of copolymers $B_{12}E_{114}B_{12}$ and $E_{43}B_{11}$. The proportion of triblock (wt%) is indicated.

The fluid/gel diagram for the 20 wt% gels (Fig. 5) has boundaries consistent with the results from measurement of yield stress. Indications are that the tube inversion method overestimates the fluid/gel transition temperature at the lower boundary in this system. We have no corresponding information for the high-*T* boundary. Whatever the method of measurement, it is clear that the width of the hard gel phase is decreased by incorporating diblock copolymer into the micelles, the more so as the proportion of diblock copolymer is increased.

### 4.2. Temperature dependence of modulus

Temperature scans of log ($G'$) at $f = 1$ Hz are shown in Fig. 7 for 20 wt% solutions of the unmixed copolymers $B_{12}E_{114}B_{12}$ and $E_{43}B_{11}$. Above 37 °C the modulus of the triblock copolymer is affected by clouding. The difference in width of the hard gel region, essentially that in which log ($G'$) > 3, is very obvious in this representation. Values of $G'$ for the solution of $E_{43}B_{11}$ at 5 and 45 °C (out of range in Fig. 7) were 0.3–0.1 Pa, characteristic of a Newtonian fluid.

Corresponding results for the 67 and 33 wt% mixtures are shown in Fig. 8. In each case the scan is from 5 °C to a temperature approaching the clouding point. The data from Fig. 7 for the solution of the triblock copolymer alone are included for comparison. Note the narrowing of the hard gel region as the proportion of diblock copolymer is increased, an effect also seen in Fig. 5.

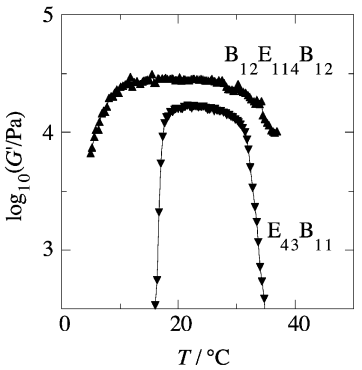

**Fig. 7** Temperature dependence of the logarithm of storage modulus determined at $f = 1$ Hz and $A \approx 0.5\%$ for 20 wt% aqueous gels of copolymers (▲) $B_{12}E_{114}B_{12}$ and (▼) $E_{43}B_{11}$.

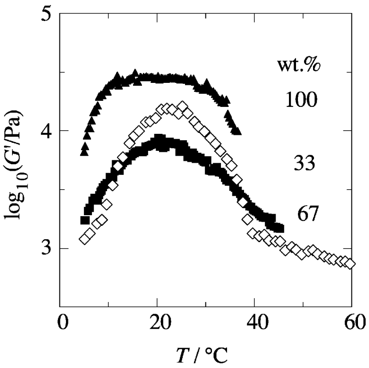

**Fig. 8** Temperature dependence of the logarithm of storage modulus determined at $f = 1$ Hz and $A \approx 0.5\%$ for 20 wt% aqueous gels of mixed copolymers $B_{12}E_{114}B_{12}$ and $E_{43}B_{11}$: (▲) 100 wt%, (■) 67 wt% and (◇) 33 wt% triblock.

For clarity, the results for the mixture with 50 wt% triblock are not shown in Fig. 8, as they overlap with those for the 67 wt% triblock. Instead *T*-scans of log ($G'$) and log ($G''$) for the 50 wt% triblock are shown in Fig. 9, where it is seen that $G'$ exceeds $G''$ at all the temperatures investigated when measurements are made at $f = 1$ Hz. That is, the gel-to-fluid transition at high temperatures is from hard to soft gel where, for convenience, we use the term soft gel to denote a complex fluid with $G' > G''$.[19] This is also the case for the mixture containing 33 wt% triblock, The solutions containing 67 and 100 wt% triblock were always hard gels in the more limited temperature range investigated. This type of soft gel also forms in related diblock systems at temperatures immediately above the hard cubic gel, and has been characterised as a defective cubic phase.[19] The high-*T* and low-*T* transitions for the 20 wt% solution of $E_{43}B_{11}$ were to sol although, as described elsewhere,[23] a soft gel is formed in the range 50–90 °C, out of range of the data in Fig. 7.

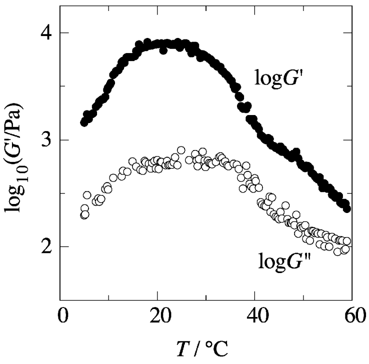

**Fig. 9** Temperature dependence of the logarithm of modulus determined at $f = 1$ Hz and $A \approx 0.5\%$ for a 20 wt% aqueous gel of mixed copolymers, $B_{12}E_{114}B_{12}$ and $E_{43}B_{11}$ (50 : 50 wt%): (●) storage modulus and (○) loss modulus.

Overall, the modulus profiles found for the solutions containing triblock copolymer resemble those found for many micellar solutions of non-bridging E–B copolymers,[11,20–22] which points to important contributions to gel properties from micelle packing at appropriate temperatures in all the systems, including 100% triblock copolymer.

### 4.3. Effect of mixing

Considering the results for the solutions at 25 °C, it is clear that the effect of mixing is to change the system from a bridged hard gel (100 wt% $B_{12}E_{114}B_{12}$) to an unbridged hard gel (100 wt% $E_{43}B_{11}$) of comparable modulus and yield stress. By contrast, for the solutions at 5 °C the corresponding effect is to change the system from a bridged hard gel to a mobile fluid. This is because solutions at 25 °C are centrally placed within the gel region across the full range of the proportion of the triblock, whereas the solutions at 5 °C lie across the low-*T* boundary of the gel region (see Fig. 5).

If, as argued in Section 3, the extent of micellisation in the system is high, it can be assumed that the copolymers enter the micelles in the same proportion as in the mixture. This being so, the number percent of triblock copolymer relates directly to the potential for forming micelle bridges. Given the data in Section 2, the solutions investigated correspond to 100, 45, 28 and 16 no.% triblock. Values of $G'$ and $\sigma_y$ obtained for the two temperatures of most interest are plotted against no.% triblock in Fig. 10. We estimate experimental errors of 10–15% in both quantities. As would be expected, at both temperatures values of the yield stress closely shadow those of the storage modulus.

Obviously we see two kinds of behaviour. For the solutions at 25 °C, the results are consistent with competing effects: (i) a

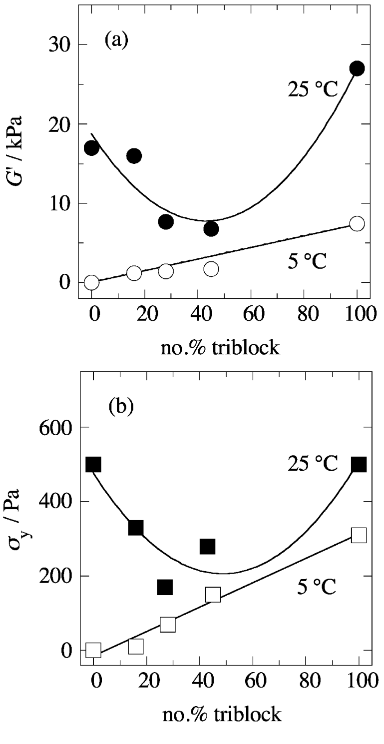

**Fig. 10** Dependence of (a) the storage modulus and (b) the yield stress on the proportion of triblock copolymer in 20 wt% gels containing mixed micelles of copolymers $B_{12}E_{114}B_{12}$ and $E_{43}B_{11}$. The modulus was measured at 1 Hz and $A \approx 0.5\%$. The gel temperatures were 25 or 5 °C, as indicated. The quadratic curves and straight lines were drawn using the least-squares procedure.

decrease in the contribution from micelle bridging as the proportion of triblock copolymer is decreased and (ii) an increase in the efficiency of packing as the proportion of diblock copolymer is increased. The curves through the data points are 'least-squares' quadratics, and it is interesting to note that the minima in $G'$ and $\sigma_y$ are at approximately 50 no.%, reflecting the symmetry of the present system which has gels with very similar properties at the two extremes.

For the solutions at 5 °C, the sole effect is a decrease in micelle bridging. In this case the data points fit reasonably well to straight lines, and it can be inferred that the properties of the gels at this temperature are determined directly by the probability of bridging. The results for the solutions at 45 °C are less useful, mainly because the intervention of clouding restricts the hard-gel range at this temperature, but also because values of $G'$ and $\sigma_y$ of the gel are much lower than those at 5 °C.

## 5. Concluding remarks

By varying the composition of mixed micelles in the system $B_{12}E_{114}B_{12}$–$E_{43}B_{11}$ we have shown that the probability of micelle bridging, hence the magnitude of the attractive intermicellar potential, is an important determinant of gel properties for triblock copolymers with hydrophobic end blocks. At the same time, the rise and fall of micelle volume fraction as temperature is increased through the hard-gel range determines the contribution of micelle packing to gel properties. At a maximum volume fraction (at $T \approx 25$ °C in the present system) this is an important effect. At a lower volume fraction (at 5 °C) packing makes a negligible contribution. The packing effect will be system specific, and substitution of diblock copolymer $E_{43}B_{11}$ by one which micellises less readily should lead to a system in which the values of the gel properties fall with the decreasing proportion of triblock copolymer at higher temperatures.

In concentrated solutions the unimers are less micellisable than in dilute solution, this being a result of the disruption of the water structure by hydration of the E-blocks, with a consequent diminution in the hydrophobic effect which drives the micellisation process.[19,24] The rise and fall in micelle volume fraction as the temperature is increased at a given copolymer concentration originates in water becoming a poorer solvent for poly(oxyethylene) blocks as the temperature is increased. In the present system it is also related to the Poisson distribution of B-block lengths in the copolymers, whereby the extent of micellisation (hence packing) and also the extent of bridging varies over a wide temperature range, contributing to the observed changes in modulus and yield stress, and to changes in related properties such as viscosity.[7,13] A Poisson number-fraction distribution[25] of B blocks with an average length of 12 units spreads from 8 to 15 B units at half-height and from 7 to 17 B units at quarter-height, and copolymers with long B blocks in the distribution will micellise at lower temperatures than those with short B blocks. The alkyl chains in HEUR and related poly(oxyethylene) dialkyl ethers are uniform in length, and protracted micellisation as the temperature is changed should not be an important effect.[4,26]

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