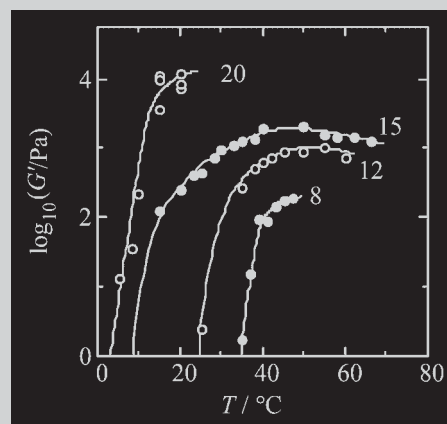


Summary: A triblock copolymer of ethylene oxide and 1,2-butylene oxide with hydrophilic central block and hydrophobic end blocks, denoted $B_{10}E_{227}B_{10}$, was prepared and characterised. The frequency dependence of dynamic modulus was determined for micellar solutions in the concentration range of 8–20 wt.-% and the temperature range of 5–70 °C, and the fluid/gel diagram was established. The results were combined with those reported previously for copolymers $B_{12}E_{227}B_{12}$ and $B_{12}E_{114}B_{12}$ to obtain insight into the effect of B-block and E-block length on the rheological properties of systems of this type. The results are discussed in terms of micelles forming bridged networks and, at higher concentrations, packing in structured gels.



Temperature dependence of the logarithm of storage modulus for aqueous solutions of copolymer $B_{10}E_{227}B_{10}$ at the concentrations (wt.-%) indicated. Conditions: $f = 1$ Hz, $A \approx 0.5\%$.

Aqueous Gels of Triblock Copolymers of Ethylene Oxide and 1,2-Butylene Oxide (Type BEB) Studied by Rheometry

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Introduction

Because of their hydrophobic end blocks, the properties of aqueous micellar solutions of triblock copolymers of ethylene oxide and 1,2-butylene oxide with hydrophobic end blocks ($B_nE_mB_n$) are affected by micellar bridging. We use E to denote an oxyethylene unit, OCH_2CH_2 , B to denote an oxybutylene unit, $OCH_2CH(C_2H_5)$, and subscripts to denote number-average block lengths in chain units. In dilute solution, but above the cmc, the copolymer chains predominantly loop in isolated micelles, but even at extreme dilution there is a finite probability of chains bridging

between micelles. Because unimers are in dynamic equilibrium with micelles, micellar bridging is transient and the effect on dilute solution properties is that of an attractive intermicellar interaction. In static light scattering experiments, strong attraction results in a negative second virial coefficient, and there is a related effect which results from dynamic light scattering together with the possibility of detecting bridged micelle clusters. The majority of light scattering studies have involved $B_nE_mB_n$ copolymers,^[1–10] but there are studies on other copoly(oxyalkylene)s, $P_nE_mP_n$,^[11–13] and $S_nE_mS_n$,^[14,15] where P denotes oxypropylene, $OCH_2CH(CH_3)$ and S denotes oxyphenylethylene,

OCH₂CH(C₆H₅). At this dilution, the effects of hydrophilic and hydrophobic block length are well understood.^[9]

Much work has been reported on the rheology of concentrated aqueous solutions of hydrophobically-modified ethoxylated urethanes (HEUR polymers), which have central E-blocks and lengthy alkyl end blocks linked via isocyanate or ether chemistry.^[16] Less has been reported for block copolymers with hydrophobic end blocks. Mortensen et al.^[12] have studied aqueous solutions of copolymer P₁₅E₁₅₆P₁₅ over a wide concentration range by static and dynamic light scattering, small-angle neutron scattering and rheology. They present evidence of unimers and unimer networks, micelles and micellar networks, and cubic and lamellar micellar gels, but gels with high elastic modulus were formed only at concentrations of $c \approx 50$ wt.-% or more, and the favoured structure at low temperatures was lamellar. We have described the rheological properties of aqueous solutions of triblock copolymers B₁₂E₁₁₄B₁₂ and B₁₂E₂₂₇B₁₂ with concentrations near to and within the gel region.^[17–19] In systems of this type, and in contrast to solutions of copolymer P₁₅E₁₅₆P₁₅,^[12] the critical micelle concentrations of the copolymers are low (<0.003 wt.-% at 25 °C),^[5] and solutions are predominantly micellar in dilute and moderately concentrated solution. Concentrated micellar solutions form gels with cubic structures, either face-centred or body-centred, depending on E-block length.^[17,19]

In this paper we describe a study of solutions of copolymer B₁₀E₂₂₇B₁₀, and compare the results with those obtained in studies of micellar solutions of copolymers B₁₂E₂₂₇B₁₂,^[18–20] and B₁₂E₁₁₄B₁₂,^[17] thus gaining direct insight into the effect of B- and E-block length on the rheological properties of aqueous B_nE_mB_n solutions.

Considering solutions of the BEB copolymers available, short E blocks favour looping in separate micelles with dynamic bridging acting as a weak attractive intermicellar potential,^[17,21] while long E blocks favour intermicellar bridging and, in solutions of moderate to high concentration, dynamic network formation.^[22] Regarding the rheological behaviour of micellar solutions, that of the short copolymers should tend towards that exhibited by weakly attractive colloids, while the long ones should tend towards that of network polymers. It is known^[17] that the dynamic moduli of solutions of copolymer B₁₂E₁₁₄B₁₂ can be scaled against frequency approximately in the manner defined by Trappe and Weitz for colloid particles, while frequency scans obtained for solutions of copolymer B₁₀E₄₁₀B₁₀ are better modelled by a combination of Maxwell elements with a distribution of relaxation times.^[22] The present copolymers with E₂₂₇ central blocks represent an intermediate case.

Experimental Part

Copolymer B₁₀E₂₂₇B₁₀ was prepared and characterised as described previously for copolymer B₁₂E₂₂₇B₁₂.^[18] Its molecular characteristics [number-average molar mass (\bar{M}_n) and

Table 1. Molecular characteristics of the copolymers. Estimated uncertainty: \bar{M}_n to $\pm 5\%$; wt.-% E to ± 1 ; \bar{M}_w/\bar{M}_n to ± 0.01 .

Copolymer	\bar{M}_n	E	\bar{M}_w/\bar{M}_n
	$\text{g} \cdot \text{mol}^{-1}$	wt.-%	
B ₁₀ E ₂₂₇ B ₁₀	11 400	87	1.06
B ₁₂ E ₂₂₇ B ₁₂	11 700	85	1.05
B ₁₂ E ₁₁₄ B ₁₂	6 740	74	1.05

wt.-% E in the copolymer from NMR spectroscopy, and ratio of weight-average to number-average molar mass (\bar{M}_w/\bar{M}_n) from gel permeation chromatography) are listed in Table 1, together with those for B₁₂E₂₂₇B₁₂ and B₁₂E₁₁₄B₁₂ reproduced from previous work.

Clouding temperatures (T_{c1}) were determined by heating solutions of the copolymers in small closed screw-cap tubes at 0.2 °C · min⁻¹.

Solutions for rheometry were prepared by weighing copolymer and water into small tubes and mixing well in the mobile state at low temperature before storing at 5 °C. Rheological properties of the solutions were determined using a Bohlin CS50 stress-controlled rheometer with Couette geometry in oscillatory mode, as described elsewhere.^[23] Storage (G') and loss (G'') moduli were measured over the frequency range of the instrument, nominally 0.003–30 Hz, for solutions at various temperatures. The strain amplitude was held at $A \approx 0.5\%$ using the autostress facility of the Bohlin software, ensuring that all measurements were within the linear viscoelastic region. The lower limit for autostress control meant that measurements of storage modulus below 1 Pa were not possible with any accuracy, i.e. for very fluid systems at low frequencies. A new solution was used for each frequency scan. It was established that the rheological response of the gels was sensitive to pretreatment under shear, much as shown previously for gels of copolymer B₁₂E₁₁₄B₁₂ under steady shear.^[17] Accordingly, a period of 30 min or more was allowed after filling the flow cell for equilibration at the test temperature before starting an experiment.

Supporting measurements of the frequency dependence of dynamic modulus were made using an ARES strain-controlled rheometer (Rheometric Scientific Ltd.) with cone-and-plate geometry and $A = 0.5\%$, as described previously.^[19] Strain sweeps were used to confirm the linear viscoelastic range, and time sweeps at $A = 0.5\%$ and $f = 1$ Hz were performed before successive frequency scans to determine times for samples to reach their equilibrium state. Equilibration times of 30 min were usually ample, but samples with concentrations and temperatures in the vicinity of the fluid-gel transition could require longer equilibration times, up to 100 min.

For the majority of solutions the results from the two instruments were in satisfactory agreement. For consistency, all the results reported in Results and Discussion were obtained using the Bohlin rheometer.

Results and Discussion

Clouding

Clouding temperatures recorded for copolymer B₁₀E₂₂₇B₁₀ in the concentration range of 2–20 wt.-% are shown in

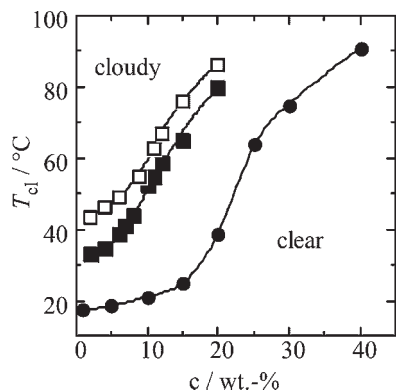


Figure 1. Clouding temperatures for aqueous solutions of copolymers (\square) $B_{10}E_{227}B_{10}$, (\blacksquare) $B_{12}E_{227}B_{12}$ and (\bullet) $B_{12}E_{114}B_{12}$. The results for copolymers $B_{12}E_{114}B_{12}$ and $B_{12}E_{227}B_{12}$ are taken from refs. ^[17] and ^[18].

Figure 1, where they are compared with the cloud-point curve reported for copolymer $B_{12}E_{227}B_{12}$.^[18] The change in B-block length from 12 to 10 units has a small effect, decreasing the clouding temperature by ca. 10 °C. The corresponding curve reported^[17] for copolymer $B_{12}E_{114}B_{12}$ is also included in Figure 1 to illustrate the much lower clouding temperatures, which result on halving the E-block length. Liu et al.^[24] have investigated the effect of E- and B-block length on the clouding temperatures of 1 wt.-% solutions of BEB copolymers, showing that T_{cl} decreases with increase in B-block length at constant E-block length, and increases with increase in E-block length at constant B-block length. The results reported here confirm that Liu's conclusions apply at higher concentrations, i.e. at a given concentration the clouding temperature is lower the more hydrophobic the copolymer. Our investigations of viscoelasticity were restricted to clear solutions below the cloud point.

Concentration and Temperature Dependence of Modulus

Concentrations in the range of 8–20 wt.-% and temperatures in the range of 5–65 °C were investigated. Values of G' at $f=1$ Hz read from frequency scans are shown in Figure 2. For a given concentration of copolymer, the value of G' increased with increase in T at low temperatures and decreased at high temperatures. Note that high temperatures were not always explored, often because clouding intervened. As expected, the maximum value of G' increased with increase in concentration. As discussed elsewhere for aqueous micellar gels of copoly(oxyalkylene)s of various block architectures,^[25,26] the onset of gelation and the associated increase in G' with increase in T at low temperatures is associated with an increase in the extent of micellisation (i.e. an increase in the fraction of unimers in micelles and so an increase in the effective volume fraction

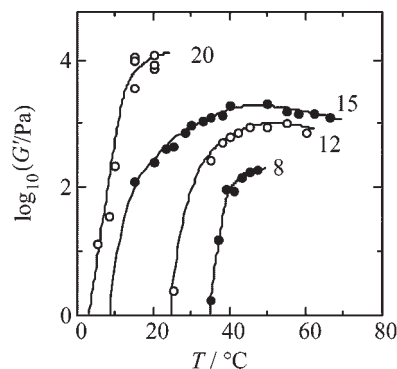


Figure 2. Temperature dependence of the logarithm of storage modulus for aqueous solutions of copolymer $B_{10}E_{227}B_{10}$ at the concentrations (wt.-%) indicated. Conditions: $f=1$ Hz, $A \approx 0.5\%$.

of micelles in the solution), and also, in the present case, with an increase in the extent of bridging. A decrease in G' with increase in T at high temperatures is associated with the water becoming a worse solvent for poly(oxyethylene), with resulting compression of the E-block corona, and thereby a decrease in the effective volume fraction of micelles in the solution. The observation of peaks in G'' at the low- T and high- T boundaries of the hard gel in a 15 wt.-% solution of copolymer $B_{12}E_{227}B_{12}$ provides another indicator of these effects.^[19]

We have used these and other results to construct a simple diagram defining the fluid and gel regions, as shown in Figure 3. As discussed previously,^[26,27] the conditions $G' > G''$ and $G' > 1$ kPa at $f=1$ Hz served to define the fluid/gel boundary. We have shown that gel defined in this way corresponds to a yield stress greater than 30–40 Pa which is sufficient to render the solution immobile in a simple inverted tube test.^[23,27] Note that the gel phase can be accessed by heating. Gelation on heating is often found for solutions of E/B copolymers of all simple architectures

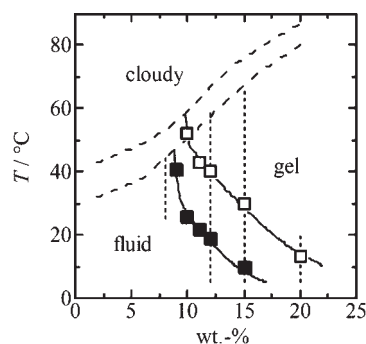


Figure 3. Phase diagrams defined by oscillatory rheometry for aqueous solutions of copolymers (\square) $B_{10}E_{227}B_{10}$ and (\blacksquare) $B_{12}E_{227}B_{12}$. Conditions were $f=1$ Hz and $A \approx 0.5\%$. The dashed curves, which indicate clouding, are taken from Figure 1. The dotted lines indicate the temperature range investigated by rheology.

(EB, EBE and BEB) under appropriate concentrations.^[28] The effect is related to the increase in the volume fraction as more micelles are formed on heating the solution. At first sight it could be thought that there is a contradiction between a high extent of micellisation at low temperatures in dilute solution (see Section 1) but not in 10–15 wt.-% solution. However, it is known^[25,29] that the micelle-unimer equilibrium is much changed when the copolymer solution is concentrated, i.e. when the H-bonded structure of water, and hence the hydrophobic effect which drives micellisation,^[30] is much reduced. The effect of mass action is opposed by this reduction in the hydrophobic effect, and in concentrated solution the B blocks are less likely to enter micelles than in 1 wt.-% solution. Moreover, the stability of the micelles of E/B copolymers, and so the extent of micellisation, is much affected by the distribution of B-block lengths, as discussed previously for BEB copolymers.^[22] Micelles (and so gels) of copolymers with alkyl blocks, e.g. HEUR copolymers and poly(oxyethylene) di- and mono-alkyl ethers,^[16,31] are stable down to low temperatures, a consequence of the high hydrophobicity and the uniformity of their alkyl chains.

Corresponding data obtained^[20] for copolymer B₁₂E₂₂₇B₁₂ are compared with those for copolymer B₁₀E₂₂₇B₁₀ in Figure 3. A change in the B-block length from 10 to 12 units is seen to have little effect on the minimum concentration for gelation (9 ± 1 wt.-%) but it does reduce the gelation temperature by 20 °C or so. These results are consistent with those for related non-bridging copolymer systems: an increase in hydrophobic-block length is known to increase the stability of the micelles (and so the gel) in water, a good solvent at low temperatures.^[32]

The sol-gel diagram for copolymer B₁₂E₁₁₄B₁₂ was not defined with the same precision.^[17] However, the minimum concentration for gel formation of micellar solutions of copolymer B₁₂E₁₁₄B₁₂ was approximately 15 wt.-%, compared with 9 wt.-% for copolymer B₁₂E₂₂₇B₁₂, consistent with a shorter E-block length, i.e. with the micelles being less swollen and micelle bridging being less important.

Frequency Dependence of Modulus

The frequency dependence of modulus for aqueous solutions of copolymer B₁₀E₂₂₇B₁₀ is illustrated by selected results.

8 wt.-%: As shown in Figure 3, at this dilution the system was a fluid at all temperatures up to the cloud point ($T_{cl} = 45$ °C). In the range of 25–35 °C, the solutions were mobile fluids over the frequency range of our measurements, see Figure 4. The straight lines drawn through the data points for the solution at 30 °C have slopes 1 ($\log G''$) and 2 ($\log G'$), values expected for fluids with short relaxation times. From 35 to 50 °C an upturn in the scan at

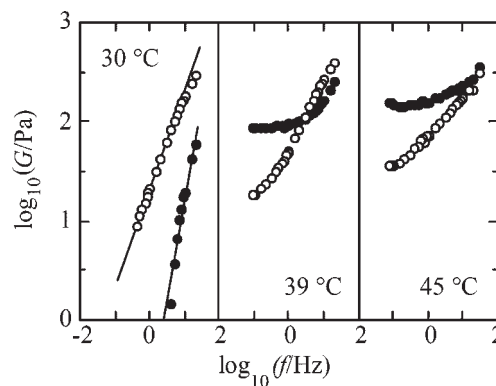


Figure 4. Log-log plot showing the frequency dependence of (●) storage and (○) loss modulus for 8 wt.-% aqueous solutions of copolymer B₁₀E₂₂₇B₁₀ at the temperatures indicated.

low frequency provided evidence of an emerging slow process, which we assign to the first formation of an elastic network through micellar bridging. This slow relaxation began to dominate the curve as temperature was increased, as illustrated by the scan for the solution at 45 °C, consistent with formation of a more robust network as micellar bridging becomes stronger as water becomes a poorer solvent at high temperature.

12 wt.-%: Solutions of this concentration changed from fluid to gel as the temperature was raised through 35–40 °C, see Figure 3. This is illustrated by the plots in Figure 5, which show that the solution at 15 °C is a mobile fluid, while that at 55 °C has a high storage modulus ($G' > 1$ kPa) characteristic of a hard gel. Just below the fluid/gel boundary ($T = 35$ °C, see Figure 5) incipient gel formation is signalled by the almost invariant dependence of G' on frequency. The values of G' measured for the 12 wt.-% solutions in the range of 40–55 °C were almost an order of

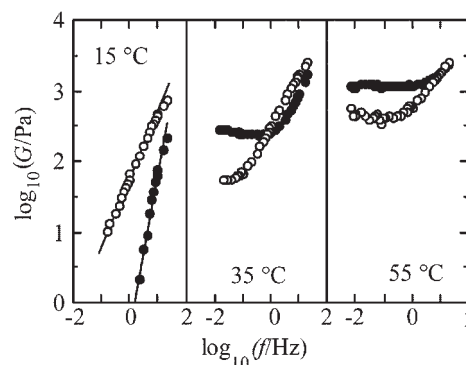


Figure 5. Log-log plot showing the frequency dependence of (●) storage and (○) loss modulus for 12 wt.-% aqueous solution of copolymer B₁₀E₂₂₇B₁₀ at the temperatures indicated. The straight lines drawn through the data points for the solution at 15 °C have slopes 1 ($\log G''$) and 2 ($\log G'$).

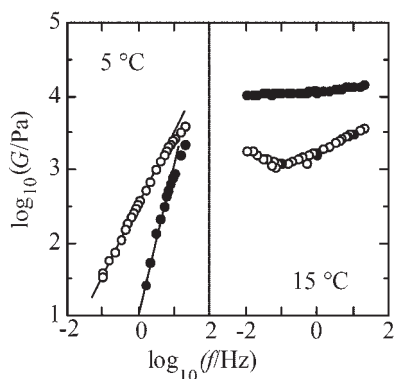


Figure 6. Log-log plot showing the frequency dependence of (●) storage and (○) loss modulus for 20 wt.-% aqueous solution of copolymer $B_{10}E_{227}B_{10}$ at the temperatures indicated. The straight lines drawn through the data points for the solution at 5 °C have slopes 1 ($\log G''$) and 2 ($\log G'$).

magnitude higher than those of the 8 wt.-% solutions in the range of 35–45 °C, see Figure 2, 4 and 5.

20 wt.-%: Solutions of concentration 15 wt.-% behaved similarly to the 12 wt.-% solutions (see Figure 2) and the frequency scans are not illustrated. Solutions of concentration 20 wt.-% were gels at all temperatures above 10 °C (see Figure 3). The scan in Figure 6 for the solution at 5 °C was that expected for a mobile fluid, while that at 15 °C (and also at 20 °C) had moduli which were weakly dependent on frequency and values of G' in excess of 10 kPa. This pattern of behaviour, i.e. a plateau value for G' and a shallow minimum in G'' , has been observed for cubic-packed structures of spherical micelles, including those of the copolymer $B_{12}E_{114}B_{12}$ and $B_{12}E_{227}B_{12}$.^[17,19] Corresponding structural information is not available for the present gels of copolymers $B_{10}E_{227}B_{10}$, but it is logical, by analogy with gels of the related copolymers, to assume cubic packing.

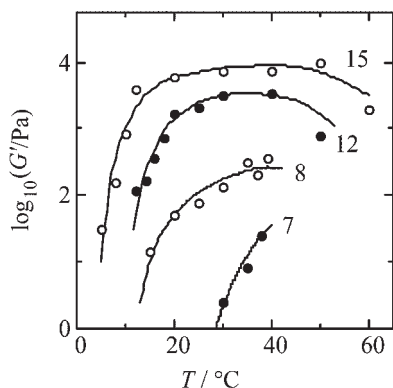


Figure 7. Temperature dependence of the logarithm of storage modulus for aqueous solutions of copolymer $B_{12}E_{227}B_{12}$ at the concentrations (wt.-%) indicated. Conditions: $f = 1$ Hz, $A \approx 0.5\%$.

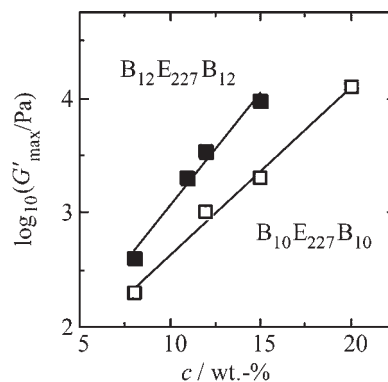


Figure 8. Maximum values of storage modulus (log scale) plotted against concentration for aqueous solutions of copolymers (□) $B_{10}E_{227}B_{10}$ and (■) $B_{12}E_{227}B_{12}$. Conditions: $f = 1$ Hz, $A \approx 0.5\%$.

Effect of B-Block Length on Modulus

Figure 7 shows the temperature dependence of storage modulus established for copolymer $B_{12}E_{227}B_{12}$.^[20] Comparison with Figure 2 confirms that the rheological properties of micellar solutions of this copolymer are very similar to those of solutions of copolymer $B_{10}E_{227}B_{10}$. The frequency scans obtained also followed similar trends with temperature.^[19,20] At comparable concentrations, maximum values of $G'(T)$ were higher for solutions of $B_{12}E_{227}B_{12}$ than for $B_{10}E_{227}B_{10}$, as shown in Figure 8 for solutions with $G'_{\max} > 100$ Pa. This is consistent with stronger intermicellar bridging by the copolymer with the longer B blocks, and with the formation of micelles with more-swollen E-block corona, and so with high exclusion volumes which favour packing at high concentrations. As can be seen, plots of $\log(G'_{\max})$ against concentration were linear for both copolymers through the concentration region from fluids with relatively high moduli to hard gels. Points for mobile fluids (out of range in Figure 8) fell well below the lines.

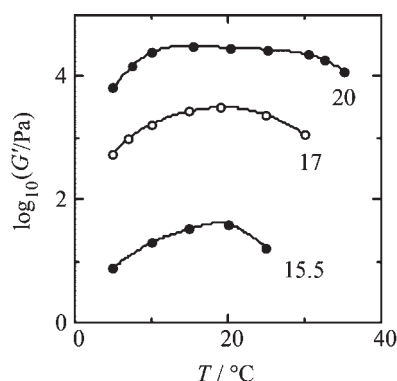


Figure 9. Temperature dependence of the logarithm of storage modulus for aqueous solutions of copolymer $B_{12}E_{114}B_{12}$ at the concentrations (wt.-%) indicated. Conditions: $f = 1$ Hz, $A \approx 0.5\%$.

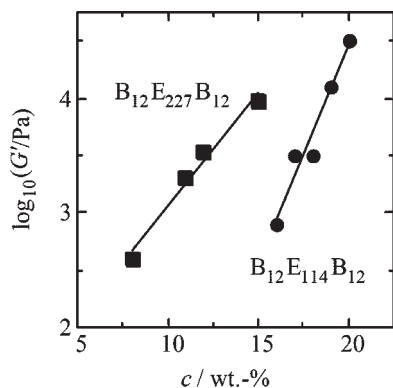


Figure 10. Maximum values of storage modulus (log scale) plotted against concentration for aqueous solutions of copolymers (■) $B_{12}E_{227}B_{12}$ and (●) $B_{12}E_{114}B_{12}$. Conditions: $f = 1$ Hz, $A \approx 0.5\%$.

Effect of E-Block Length on Modulus

Figure 9 shows examples of the temperature dependence of storage modulus established for micellar solutions of copolymer $B_{12}E_{114}B_{12}$.^[17] As illustrated by Figure 1, clouding temperatures for this copolymer were low at low concentrations, which restricted the range of solutions studied. Comparison with Figure 2 confirms that the rheological properties are similar to those of solutions of copolymer $B_{10}E_{227}B_{10}$. Also, as illustrated previously,^[17] frequency scans of modulus followed similar trends with concentration and temperature. Values of G'_{\max} ($G'_{\max} > 100$ Pa) are plotted against concentration in Figure 10, where it is seen that, at corresponding concentrations, values of G'_{\max} for micellar solutions of $B_{12}E_{114}B_{12}$ are lower than those for copolymer $B_{12}E_{227}B_{12}$. The lower values of storage modulus recorded for the copolymer with the shorter E-block length reflects the smaller intermicellar separation (centre to centre) required for bridging and the smaller effective hard-sphere volume occupied by the micelles, the latter effect of E-block length being much as found for micellar solutions of diblock EB and triblock EBE copolymers.^[26,32] As noted in Concentration and Temperature Dependence of Modulus, the smaller effective hard-sphere volume increases the minimum concentration for gelation from 9 wt.-% ($B_{10}E_{227}B_{10}$ and $B_{12}E_{227}B_{12}$) to 15 wt.-% or more ($B_{12}E_{114}B_{12}$).

Conclusion

Trappe and Weitz^[21] have shown that the dynamic moduli of colloidal suspensions in which weak short-range attractive forces act between particles, and which progressively form larger and larger clusters as concentration is increased, can be scaled against frequency to give smooth master curves for the moduli. At low-reduced frequencies

G' dominates and is almost independent of frequency while G'' passes through a minimum, a behaviour characteristic of an elastic solid. At high-reduced frequencies G'' scales as the first power of the frequency and G' takes lower values, characteristic of a mobile fluid. Overall, the behaviour differs from that of a Maxwell fluid. It was shown that the same scaling model could be applied to micellar solutions of copolymer $B_{12}E_{114}B_{12}$, at least over the frequency/composition/temperature interval investigated.^[17]

It is known from numerous studies of alkyl-terminated poly(oxyethylene)s, particularly the HEUR polymers with isocyanate-linked blocks, that the dynamic moduli of samples with lengthy E and C blocks can be modelled by a single Maxwell element.^[16] For example, the polymer $C_{16}UE_{795}UC_{16}$ (our notation), in which the C_{16} alkyl chains are urethane-linked to the E block via an isophorone diisocyanate residue (denoted U),^[16b] or urethane-linked $C_{18}E_{795}C_{18}$ prepared from octadecyl isocyanate.^[16e] A UC_{16} block is equivalent in hydrophobicity to a C_{18} chain.^[16e,33]

We were unable to fit the frequency scans for solutions of copolymers $B_{10}E_{227}B_{10}$ and $B_{12}E_{227}B_{12}$ to either of the simple models. As noted previously, the hydrophobicities of B and C chain units are in approximate ratio 6:5.^[34] Compared with C_{18} the B_{10}/B_{12} blocks (equivalent to C_{12}/C_{14}) act against strong micellar bridging. Reinforcing this, compared with E_{795} the shorter E_{227} blocks favour looping in a single micelle rather than bridging between micelles. Both these differences in molecular characteristics count against Maxwell behaviour. On the other hand, compared with $B_{12}E_{114}B_{12}$ our results indicate a more complex rheological behaviour for micellar solutions of BEB copolymers with E_{227} central blocks. More extensive work is needed in order to gain a further understanding of these complex systems.

- [1] Z. Yang, S. Pickard, N.-J. Deng, R. J. Barlow, D. Attwood, C. Booth, *Macromolecules* **1994**, *27*, 2371.
- [2] Y.-W. Yang, Z. Yang, Z.-K. Zhou, D. Attwood, C. Booth, *Macromolecules* **1996**, *29*, 670.
- [3] Z. Yang, Y.-W. Yang, Z.-K. Zhou, D. Attwood, C. Booth, *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 257.
- [4] Z.-K. Zhou, B. Chu, V. M. Nace, Y.-W. Yang, C. Booth, *Macromolecules* **1996**, *29*, 3663.
- [5] Z.-K. Zhou, Y.-W. Yang, C. Booth, B. Chu, *Macromolecules* **1996**, *29*, 8357.
- [6] Z.-K. Zhou, B. Chu, V. M. Nace, *Langmuir* **1996**, *12*, 5016.
- [7] T.-B. Liu, Z.-K. Zhou, C.-H. Wu, B. Chu, D. K. Schneider, V. M. Nace, *J. Phys. Chem. B* **1997**, *101*, 8808.
- [8] B. Chu, T.-B. Liu, C.-H. Wu, Z.-K. Zhou, V. M. Nace, *Macromol. Symp.* **1997**, *118*, 221.
- [9] T.-B. Liu, Z.-K. Zhou, C.-H. Wu, V. M. Nace, B. Chu, *J. Phys. Chem. B* **1998**, *102*, 2875.

- [10] A. Kellarakis, V. Havredaki, X.-F. Yuan, Y.-W. Yuan, C. Booth, *J. Mater. Chem.* **2003**, *13*, 2779.
- [11] Z.-K. Zhou, B. Chu, *Macromolecules* **1994**, *27*, 2025.
- [12] K. Mortensen, W. Brown, E. Jørgensen, *Macromolecules* **1994**, *27*, 5654.
- [13] H. Altinok, G.-E. Yu, S. K. Nixon, P. A. Gorry, D. Attwood, C. Booth, *Langmuir* **1997**, *13*, 5837.
- [14] S.-M. Mai, S. Ludhera, F. Heatley, D. Attwood, C. Booth, *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 567.
- [15] N. M. P. S. Ricardo, S. B. Honorato, Z. Yang, V. Castelletto, I. W. Hamley, X.-F. Yuan, D. Attwood, C. Booth, *Langmuir* **2004**, *20*, 4272.
- [16] See, for example, [16a] T. Annable, R. Buscall, R. Ettelaie, "Amphiphilic Block Copolymers: Self Assembly and Applications", P. Alexandridis, B. Lindman, Eds., Elsevier Science, Amsterdam 2000, Chapter 12; [16b] T. Annable, R. Buscall, R. Ettelaie, *Colloid Surf. A* **1996**, *112*, 97; [16c] B. Xu, A. Yetka, L. Li, Z. Masoumi, M. A. Winnik, *Colloid Surf. A* **1996**, *112*, 239; [16d] J. François, S. Maître, M. Rawiso, D. Sarazin, G. Beinert, F. Isel, *Colloid Surf. A* **1996**, *112*, 251; [16e] Q. T. Pham, W. B. Russel, J. C. Thibeault, W. Lau, *Macromolecules* **1999**, *32*, 5139.
- [17] A. Kellarakis, X.-F. Yuan, S.-M. Mai, Y.-W. Yang, C. Booth, *Phys. Chem. Chem. Phys.* **2003**, *5*, 2628.
- [18] A. Kellarakis, X.-T. Ming, X.-F. Yuan, C. Booth, *Langmuir* **2004**, *20*, 2036.
- [19] V. Castelletto, I. W. Hamley, X.-F. Yuan, A. Kellarakis, C. Booth, *Soft Matter* **2005**, *1*, 138.
- [20] A. Kellarakis, work associated with this study.
- [21] V. Trappe, D. A. Weitz, *Phys. Rev. Lett.* **2000**, *85*, 449.
- [22] D. Mistry, T. Annable, X.-F. Yuan, C. Booth, *Langmuir* **2006**, *22*, 2986.
- [23] H. Li, G.-E. Yu, C. Price, C. Booth, E. Hecht, H. Hoffmann, *Macromolecules* **1997**, *30*, 1347.
- [24] T.-B. Liu, V. M. Nace, B. Chu, *J. Phys. Chem. B* **1997**, *101*, 8074.
- [25] A. D. Bedells, R. M. Arafah, Z. Yang, D. Attwood, J. C. Padgett, C. Price, C. Booth, *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 1243.
- [26] I. W. Hamley, S.-M. Mai, A. J. Ryan, J. P. A. Fairclough, C. Booth, *Phys. Chem. Chem. Phys.* **2001**, *3*, 2972.
- [27] H. Li, G.-E. Yu, C. Price, C. Booth, J. P. A. Fairclough, A. J. Ryan, K. Mortensen, *Langmuir* **2003**, *19*, 1075.
- [28] Y.-W. Yang, Z. Ali-Adib, N. B. McKeown, A. J. Ryan, D. Attwood, C. Booth, *Langmuir* **1997**, *13*, 1860.
- [29] [29a] G.-E. Yu, Y.-L. Deng, S. Dalton, Q.-G. Wang, D. Attwood, C. Price, C. Booth, *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 2537; [29b] S. K. Nixon, S. Hvidt, C. Booth, *J. Colloid Interface Sci.* **2004**, *280*, 219.
- [30] C. Tanford, "The Hydrophobic Effect", Wiley, New York 1980.
- [31] M. Ameri, D. Attwood, J. H. Collett, C. Booth, *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 2545.
- [32] [32a] W. Mingvanish, A. Kellarakis, S.-M. Mai, C. Daniel, Z. Yang, V. Havredaki, I. W. Hamley, A. J. Ryan, C. Booth, *J. Phys. Chem. B* **2000**, *104*, 9788; [32b] C. Chaibundit, S.-M. Mai, F. Heatley, C. Booth, *Langmuir* **2000**, *16*, 9645; [32c] A. Kellarakis, W. Mingvanish, C. Daniel, H. Li, V. Havredaki, C. Booth, I. W. Hamley, A. J. Ryan, *Phys. Chem. Chem. Phys.* **2000**, *2*, 2755.
- [33] D. Mistry, T. Annable, C. Booth, *Abstr., Am. Chem. Soc.* **1999**, *218*, 156.
- [34] C. Booth, D. Attwood, *Macromol. Rapid Commun.* **2000**, *21*, 501.