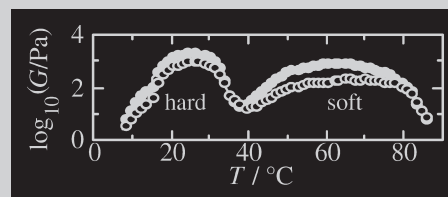


Summary: The effect of added ethanol on the rheological behaviour of aqueous solutions of diblock copolymer $E_{43}B_{11}$ (E = oxyethylene unit, B = oxybutylene unit) has been investigated. Thermally reversible sol-gel transitions were observed for concentrated solutions of the copolymer in solutions containing 0–30 wt.-% ethanol. Storage (G') and loss (G'') moduli and yield stress (σ_y) were used to define hard and soft gel phases. The introduction of 10 wt.-% ethanol did not alter the phase behaviour greatly, whereas higher ethanol concentrations had a large effect, which differed in kind from that reported for triblock copolymers of ethylene oxide and propylene oxide, type EPE.



Temperature dependence of the logarithm of (●) storage and (○) loss modulus for 20 wt.-% copolymer in 10 wt.-% ethanol.

Effect of Ethanol on the Rheological Properties of Water-Rich Gels of Diblock Copolymer $E_{43}B_{11}$

Antonios Kelarakis,¹ Vasiliki Havredaki,¹ Colin Booth*²

¹National and Kapodistrian University of Athens, Department of Chemistry, Physical Chemistry Laboratory, Panepistimiopolis, 157 71 Athens, Greece

²Department of Chemistry, University of Manchester, Manchester M13 9PL, UK

Fax: +44 161 275 4273; E-mail: colin.booth@man.ac.uk

Received: March 9, 2004; Revised: June 3, 2004; Accepted: June 7, 2004; DOI: 10.1002/macp.200400097

Keywords: aqueous ethanol; block copolymers; micelles; phase diagrams; rheology

Introduction

Many types of poly(oxyalkylene) block copolymer self associate to form micelles in dilute aqueous solutions.^[1] At higher concentrations liquid crystal mesophases are formed due to micellar packing, giving rise to interesting rheological properties. The phase behavior, microstructure and rheology of aqueous gels of $E_mP_nE_m$ copolymers have been well investigated and reviewed.^[2–6] A considerable body of work on aqueous gels of E/B copolymers has also been reviewed.^[7] Here E denotes a hydrophilic oxyethylene unit OCH_2CH_2 ; B and P denote the hydrophobic chain units oxybutylene, $OCH_2CH(C_2H_5)$, and oxypropylene, $OCH_2CH(CH_3)$ respectively, and m and n are number-average block lengths in repeat units.

One of the key factors determining the behavior of these copolymers in solution is solvent quality. This can be altered either by a change in temperature or by the addition of cosolvents or cosolutes to water. In this report we describe the effect of the addition of ethanol on the gelation and the rheological properties of aqueous gels of diblock copolymer $E_{43}B_{11}$.

Ethanol has been investigated previously as a cosolvent in solutions of several commercially-available $E_mP_nE_m$ block copolymers^[8–15] and for an E/P copolymer with two statistical blocks synthesized in our laboratory.^[16] For dilute aqueous solutions, addition of ethanol has been found to increase the critical micelle concentration (cmc) of copolymers $E_{61}P_{40}E_{61}$ (F87)^[8] and $E_{98}P_{67}E_{98}$ (F127),^[9] and, correspondingly, to increase the critical micelle temperature of F127.^[10] [The designations F87, F127, etc. are those introduced by the Wyandotte Chemical Corp. (now BASF-Wyandotte) for their Pluronic range of $E_mP_nE_m$ copolymers.] Small-angle neutron scattering (SANS) has been used to investigate the properties of micelles of $E_{37}P_{58}E_{37}$ (P105) in 8 wt.-% solutions of P105 in aqueous ethanol (0–40 wt.-%) and for 20 wt.-% ethanol over a range of temperatures (30–60 °C).^[11] All these results are consistent with aqueous ethanol being a better solvent than water. For concentrated micellar solutions the addition of ethanol has been found to increase the critical gelation concentration (cgc) for $E_{80}P_{30}E_{80}$ (F68)^[12] and F127,^[10] and to increase the critical gelation temperature (cgt) for F127.^[9,10] Recent investigations of Alexandridis and

coworkers of gel formation and structure using small-angle X-ray scattering (SAXS) and ethanol-water solutions of copolymers E₃₇P₅₈E₃₇ (P105) have been reviewed,^[13] and related investigations of E₁₀₀P₇₀E₁₀₀ (F127) in ethanol-water mixtures have been reported.^[14,15] With increase in copolymer concentration, and for solutions with 20 wt.-% ethanol or less, the mesophases reported for copolymer F127 are successively unimer/micelle solution, spherical micelles forming cubic gel, and cylindrical micelles forming hexagonal gel, the latter at copolymer concentration in excess of 60 wt.-%.^[14,15] For copolymer P105 the sequence extends at high concentration to gyroid and lamellar mesophases.^[13]

Copolymer E₄₃B₁₁ falls into the series of E_mB_n copolymers which have been closely studied by our group.^[11] In particular it is closely related to copolymers E₄₁B₈, E₄₀B₁₀ and E₅₀B₁₃. Correlations of aqueous solution properties with E and B block length allow satisfactory prediction of their values without the need for further measurement. Thus, for aqueous solution, we predict low critical micellization concentrations (e.g. cmc \approx 0.004 wt.-% at 30 °C) and moderately-high mass-average association numbers (e.g. $N_w \approx$ 50 at 30 °C). It has been shown that the gel phases of moderately-concentrated solutions of copolymers E₄₁B₈ and E₄₀B₁₀ in water at 30 °C have cubic structures, either face-centered cubic (fcc) or body-centered cubic (bcc) depending on concentration.^[17] Consequently a cubic structure is anticipated for the gels of E₄₃B₁₁ gels formed in aqueous ethanol, most likely fcc.^[17] The use of rheometry allows us to detect not only structured micellar gels, through their high storage modulus and yield strength, but also to investigate the viscoelasticity of fluids of lower storage modulus.

Experimental Part

Preparation of the Copolymer

The preparation of copolymer E₄₃B₁₁ was by sequential oxyanionic polymerization of ethylene oxide followed by 1,2-butylene oxide (systematic name 1,2-epoxybutane). The monofunctional initiator was 2-(2'-methoxyethoxy)ethanol activated by reaction with potassium metal (mole ratio OH/K \approx 10). Gel permeation chromatography (GPC) was used to confirm a narrow chain length distribution, the ratio of mass-average to number-average molar mass \bar{M}_w/\bar{M}_n being 1.03. ¹³C NMR spectroscopy was used to confirm that difunctional species were absent (triblock copolymer, polybutylene glycol which might have been initiated by adventitious moisture), i.e. that the copolymer was wholly diblock, and also to obtain the mass-fraction of E in the copolymer (0.705), the absolute value of $\bar{M}_n = 2680 \text{ g} \cdot \text{mol}^{-1}$, and the average molecular formula. Our methods have been described previously.^[18–20]

Preparation of Gels

Solutions for investigation of gelation were restricted to less than 40 wt.-% copolymer and less than 40 wt.-% ethanol in the

solvent. Solutions were prepared by weighing copolymer and water or copolymer and aqueous ethanol into small tubes and mixing, if possible, in the high-temperature mobile state before being stored for a day or more at low temperature ($T = 5 \text{ }^\circ\text{C}$). Otherwise the mixture was allowed to mix by diffusion (with occasional shaking) over a period of a week or so at 5 °C. Newly prepared samples were used for each experiment.

Tube Inversion

Samples (0.5 g) were enclosed in small tubes (internal diameter c.a. 10 mm), and observed whilst slowly heating (or cooling) the tube in a water bath within the range 0–85 °C. The heating/cooling rate was 0.5 °C · min⁻¹. The change from a mobile to an immobile system (or vice-versa) was determined by inverting the tube.

Rheometry

The rheological properties of the samples were determined using a Bohlin CS50 rheometer with water-bath temperature control. Couette geometry (bob, 24.5 mm diameter, 27 mm height; cup, 26.5 mm diameter, 29 mm height) was used for all the samples, with 2.5 cm³ sample being added to the cup in the mobile state. A trap maintained a solvent-saturated atmosphere around the cell, and evaporation was prevented at the temperatures and for the timescales investigated. Storage (G') and loss (G'') moduli were recorded across the temperature range with the instrument in oscillatory-shear mode at a frequency of 1 Hz. The choice of frequency is arbitrary, but $f = 1 \text{ Hz}$ is consistent with previous practice for T scans in our laboratory.^[7] In this mode, the samples were equilibrated for 20 min before heating at 1 °C · min⁻¹ in the range 5–85 °C. Also moduli were measured with the gels at fixed temperature across the frequency range 0.003 to 30 Hz. In both modes the strain amplitude (A) was set to a low value ($A = 0.5\%$) using the autostress facility of the Bohlin software in order to keep measurements of modulus within the linear viscoelastic region. Measurements on solutions of low modulus fell outside the range of autostress feedback and were rejected whenever A exceeded 1%. Measurements of yield stress and viscosity were made at selected temperatures with the instrument in continuous-shear mode. The instrument was programmed to increase the shear stress in a series of logarithmically-spaced steps, allowing 1 min to reach equilibrium at each step. Usually a period of 20 min was allowed for temperature equilibration before starting the program.

Results and Discussion

The solutions remained transparent to the eye during the tube-inversion experiments, $T = 0\text{--}85 \text{ }^\circ\text{C}$.

Hard-Gel Boundary by Tube Inversion

Fluid/immobile boundaries defined by tube inversion for E₄₃B₁₁ in water and in 10, 20 and 30 wt.-% aqueous ethanol are shown in Figure 1. Solutions in 40 wt.-% aqueous

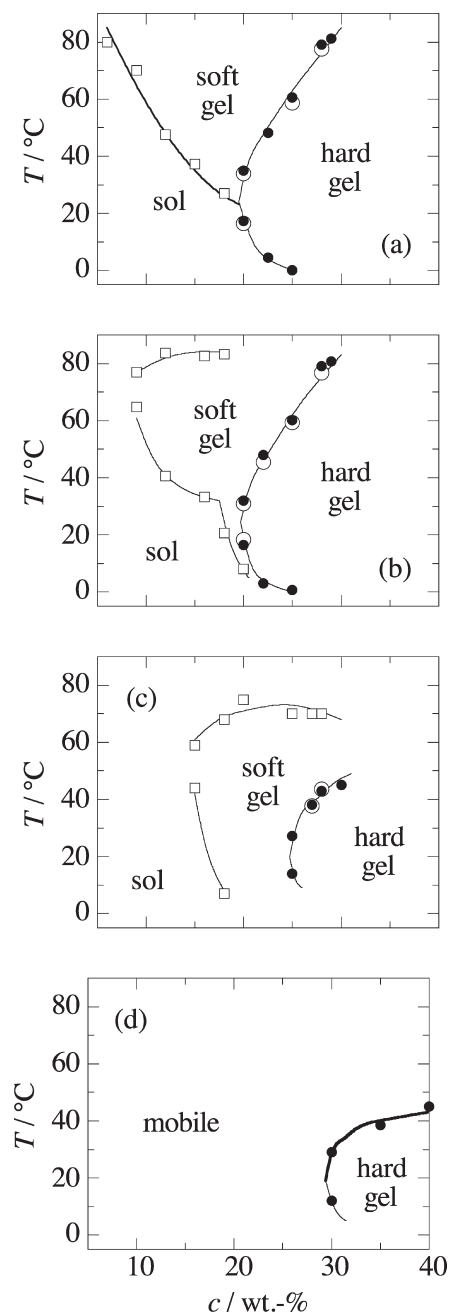


Figure 1. Phase diagrams for solutions of block copolymer $E_{43}B_{11}$ (a) in water, (b) in 10 wt.-% aqueous ethanol, (c) in 20 wt.-% aqueous ethanol, (d) in 30 wt.-% aqueous ethanol. Data points from (●) tube inversion (hard gel boundary), (○) rheometry (hard gel boundary), (□) rheometry (soft gel boundary). Solutions in 30 wt.-% aqueous ethanol were not investigated by rheometry.

ethanol did not gel at copolymer concentrations up to 40 wt.-%, the highest concentration investigated. Following Hvidt and coworkers,^[2,3] it is convenient to refer to the immobile phase as hard gel. The critical concentrations for forming the hard gel (c^*) and the related temperatures (T^*) are listed in Table 1. The introduction of 10 wt.-% ethanol does not

Table 1. Limiting conditions for hard gels of copolymer $E_{43}B_{11}$ in aqueous ethanol.

ethanol wt.-%	c^* a) wt.-%	T^* a) °C
0	19.5	24
10	19.7	24
20	24.7	20
30	29.4	19

a) c^* to ± 0.2 wt.-%, T^* to ± 2 °C.

alter c^* and T^* , but including 20 or 30 wt.-% ethanol increases c^* considerably and decreases T^* marginally.

Storage and Loss Moduli ($f = 1$ Hz)

The temperature dependence of the logarithm of storage modulus ($f = 1$ Hz, $A \leq 1\%$) is shown in Figure 2 for five concentrations of copolymer $E_{43}B_{11}$ in water and 10 wt.-% and 20 wt.-% aqueous ethanol. Because of the limited supply of copolymer, rheology was not used to define hard and soft gel boundaries for solutions in 30 wt.-% aqueous ethanol. Previous work has shown that cubic micellar gels of E_mB_n and related copolymers are immobile in our inverted-tube test when the yield strength exceeds ca. 30 Pa or, relating yield strength to storage modulus, when the storage modulus exceeds ca. 1 kPa.^[21–24] Using $G' = 1$ kPa to define the hard gel boundary leads to the data points from rheology shown in Figure 1, in good agreement with the boundary defined by tube inversion. A curious exception is the mobile solution with 25 wt.-% copolymer in 20 wt.-% ethanol, which is immobile in the inverted tube test at low temperatures (14–27 °C – see Figure 1c) where G' peaks at ca. 750 Pa but mobile at higher temperatures where G' peaks at ca. 1500 Pa. As illustrated in Figure 3 for solutions in 10 wt.-% aqueous ethanol, peak and plateau values of G' generally exceeded those of G'' .

Solutions with 28 wt.-% copolymer (Figure 2a) were hard gels ($G' \geq 1$ kPa) at low temperatures. Those in water and 10 wt.-% ethanol transformed on heating above 65 °C to mobile fluids with values of storage modulus higher than those of sol but lower than 1 kPa. It is convenient to refer to these fluids as soft gels.^[2,7] The solution in 20 wt.-% ethanol at high temperature ($T > 45$ °C) was a very-weak soft gel extending to ca. 75 °C. As explained in the section *Rheometry*, the autostress facility set at $A = 0.5\%$ was unstable at low values of G' , as can be seen in Figure 2a. We assign this solution to soft gel in the range 45–75 ± 5 °C and to sol above.

Solutions with 25 wt.-% copolymer in water and in 10 wt.-% aqueous ethanol (Figure 2b) were hard gels at low temperature which transformed on heating above 60 °C to soft gels and, for the solution in 10 wt.-% ethanol, eventually to a sol at ca. 75 °C. Sol formation was not detected

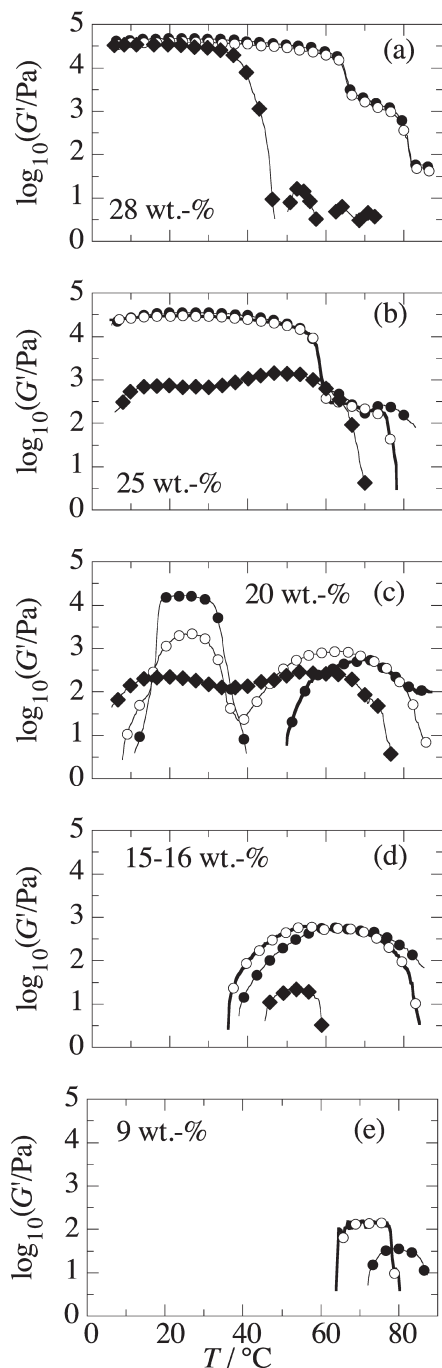


Figure 2. Temperature dependence of storage modulus ($f=1$ Hz, A set to 0.5%) for solutions of block copolymer E₄₃B₁₁. Copolymer concentrations are indicated: solvents are (●) water, (○) 10 wt.-% and (◆) 20 wt.-% ethanol. For clarity the plots show only 10% of the data points, while the curves follow all the points. In (e) values of G' for 20 wt.-% ethanol were too low to measure.

for the 25 wt.-% solution in water within the T range investigated. By tube inversion, the solution of the copolymer in 20 wt.-% ethanol was an immobile hard gel at $T=14$ – 27 °C but a soft gel at other temperatures below 65 °C. In this

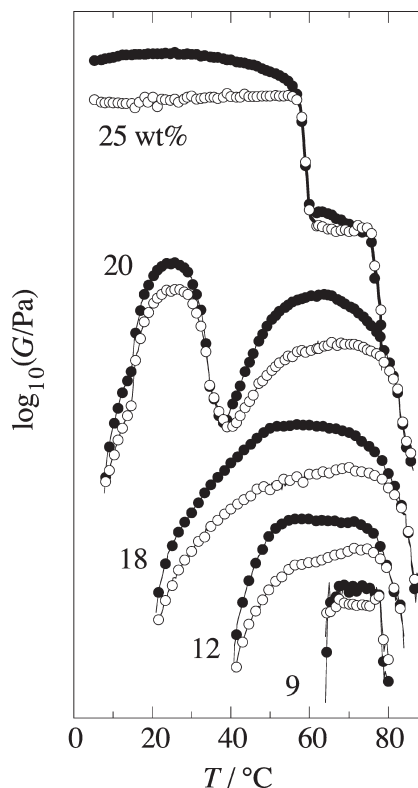


Figure 3. Temperature dependence of (filled symbols) storage modulus and (unfilled symbols) loss modulus ($f=1$ Hz, A set to 0.5%) for solutions of block copolymer E₄₃B₁₁ in 10 wt.-% aqueous ethanol. Copolymer concentrations are indicated. For clarity the curves are shifted on the ordinate; values of $\log(G)$ can be judged from Figure 2.

respect, as discussed above, the profile of $G'(T)$ for this solution is unusual.

Solutions with 20 wt.-% copolymer in water and 10 wt.-% aqueous ethanol (Figure 2c) had narrow hard-gel ranges at low temperatures, as is also evident from Figure 1. The profile of $G'(T)$ had two peaks for all three solutions, the peaks for the solution in water being clearly separated by a region of very low modulus (sol).

Solutions of concentration 15–16 wt.-% (Figure 2d) were soft gels at high temperatures, that for the copolymer in 20 wt.-% ethanol being very weak and restricted to a narrow temperature range.

At copolymer concentration 9 wt.-% (Figure 2e) soft gel was a weak feature at high temperatures for the copolymer in water and 10 wt.-% ethanol, while the solution in 20 wt.-% ethanol was a sol over the whole temperature range investigated.

The soft-gel/sol boundaries defined by T scans using oscillatory shear at $f=1$ Hz and $A \leq 1\%$ are marked in Figure 1. The diagram includes additional results for solutions not included in Figure 2. The sol at 40–50 °C found uniquely for the 20 wt.-% solution of the copolymer in water (Figure 2c) is not included in Figure 1a. A change of

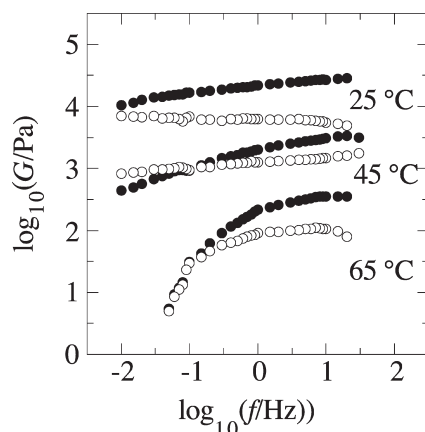


Figure 4. Frequency dependence of storage and loss moduli (A set to 0.5%) for a 22 wt.-% solution of block copolymer $E_{43}B_{11}$ in 10 wt.-% aqueous ethanol. Filled symbols denote storage modulus and unfilled symbols denote loss modulus. Solution temperatures are indicated.

frequency has little effect on the hard-gel/soft-gel boundary determined by rheometry, as values of G' for cubic hard gels are insensitive to frequency, but has a marked effect the soft-gel/sol boundary, as is illustrated by the frequency scans shown in Figure 4. This point is discussed further in the following section. However, diagrams of the type shown in Figure 1 are useful for indicating the complex viscoelasticity of micellar solutions at concentrations far below the hard gel limit.

Soft gels of the type illustrated in Figure 1–3 have been identified in aqueous micellar solutions of a wide range of block copolymers, including our own work on diblock copolymers of type E_mP_n ^[25] and E_mB_n .^[21,22,24] Soft gels at temperatures near the hard-gel boundary are assigned to defective versions of the cubic-packed hard gel, i.e. small structured domains in an overall fluid matrix. Soft gels of this type have been investigated in other laboratories, e.g. by Prud'homme et al. for low- T aqueous soft gels of copolymer F127 using small-angle neutron scattering,^[26] and by Castelletto et al. for high- T soft gels of copolymer $E_{87}B_{18}$ using SAXS.^[27] This type of soft gel is identified in Figure 3 as a narrow low- T shoulder on the $G(T)$ curve of the 20 wt.-% solution and as a distinct high- T shoulder on the $G(T)$ curve of the 25 wt.-% solution. It may well be that the broad shoulder below 40 °C on the $G(T)$ curve of the 18 wt.-% solution (see Figure 3) derives from a soft gel of similar structure. The soft gels at low concentrations and high temperatures are not so directly associated with structured hard gel, and originate in the weak attraction of spherical micelles in water or aqueous ethanol at high temperatures, where the solvent is poorer for the micelles. The transition from sol to soft gel may well occur when aggregates of spherical micelles reach a percolation threshold yielding sufficient structure to cause the characteristic rheological effect.^[23,24] Consistent with two types of soft

gel, Mallamace and coworkers have identified two mechanisms of formation, percolation or packing (structural arrest) depending on concentration and temperature, in solutions of copolymer $E_{13}P_{30}E_{13}$ (P64).^[28–30]

Effect of Frequency

Frequency scans obtained for 22 wt.-% solutions of copolymer $E_{43}B_{11}$ in 10 wt.-% aqueous ethanol are shown in Figure 4. The solution at 25 °C is centrally placed within the hard gel range for the 22 wt.-% solution (see Figure 1) and its moduli are rather insensitive to frequency. The solution at 45 °C is near the upper hard-gel boundary and the frequency scan shows the characteristic cross-over of a more viscous system. A scan obtained for a solution at 5 °C (not shown), which is near to the lower hard-gel boundary, was very similar in shape and value of modulus to that of the solution at 45 °C. These frequency scans resemble those recorded in our earlier studies of other diblock and triblock E/B copolymers forming hard gels with body-centred cubic structures.^[21,23,31–33] The insensitivity of storage modulus to frequency justifies our use of a single frequency (1 Hz) in the T scans used to confirm the hard gel boundary. The solution at 65 °C is within the soft gel range, and the frequency scan illustrates very well the sensitivity of the modulus of this solution to frequency. As a consequence, and as pointed out previously,^[21,31] temperatures at the soft-gel/sol boundary are dependent on the frequency used, and those drawn in Figure 1 give only an indication of the viscoelasticity of the three systems. Frequency scans characteristic of a stable hard gel were obtained for 30 wt.-% hard gels of the copolymer in 20 wt.-% aqueous ethanol at 5 and 25 °C.

Yield Stress

Results obtained by subjecting solutions of copolymer $E_{43}B_{11}$ to a programmed increase in shear stress are shown in Figure 5 and Table 2. The temperature was varied in order to sample the hard gel, soft gel and sol phases. The apparent yield stress ($\sigma_{y,app}$) was defined approximately as that at which the shear rate left the zero-shear rate axis. As expected, hard gels had high yield stress, sols had zero yield stress, and soft gels had low yield stress (2–30 Pa in the present experiments). As noted in previous work,^[21,31] the soft gels were destroyed by shearing after yield but reformed with passage of time, in this case regaining their maximum value of $\sigma_{y,app}$ after one hour.

Concluding Remarks

Sol-gel boundaries for the four solvents are compared in Figure 6. The effect of including 10 wt.-% ethanol in the solvent is slight, the boundaries for both hard and soft gel being similar to those found for water alone. There is difference in the high- T boundary to the soft gel region: that

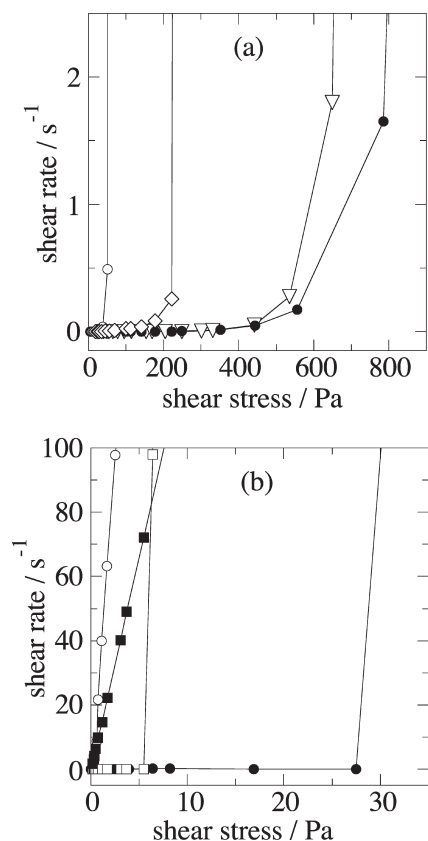


Figure 5. Dependence of shear rate on shear stress for solutions of copolymer E₄₃B₁₁ in aqueous ethanol. (a) Hard gels: 22 wt% copolymer in 10 wt% aqueous ethanol at (○) 45 °C, (●) 25 °C and (◆) 5 °C; 30 wt% copolymer in 10 wt% aqueous ethanol at (▽) 25 °C. (b) Soft gels and sols: 22 wt% copolymer in 10 wt% aqueous ethanol at (○) 85 °C, (●) 65 °C; 18 wt% copolymer in 10 wt% aqueous ethanol at (□) 65 °C and (■) 45 °C.

for the solution in 10 wt.-% ethanol is lower, bringing this feature into the range of our experiments. Also a small difference in the soft gel boundary at low temperatures is found. In contrast, the large effect of including 20 or 30 wt.-%

Table 2. Apparent yield stresses of solutions of copolymer E₄₃B₁₁.^{a)}

T °C	18 wt.-% copolymer 10 wt.-% ethanol	22 wt.-% copolymer 10 wt.-% ethanol	30 wt.-% copolymer 20 wt.-% ethanol
	$\sigma_{y,app}$ Pa		
5	–	200 (hg)	500 (hg)
25	0 (s)	400 (hg)	400 (hg)
45	2 (sg)	40 (hg)	–
65	6 (sg)	30 (sg)	–
85	0 (s)	0.3 (s/sg)	–

^{a)} s = sol; sg = soft gel; s/sg = sol/soft-gel boundary; hg = hard gel.

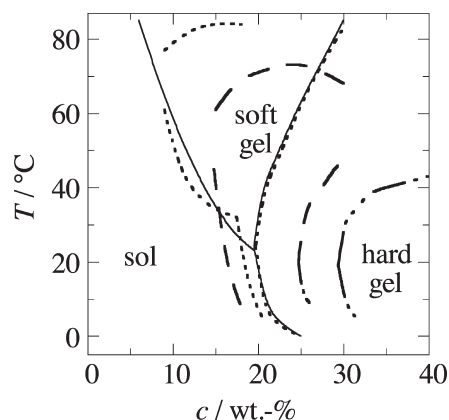


Figure 6. Comparison of gel boundaries for micellar solutions of copolymer E₄₃B₁₁ in (full curves) water, (dotted curves) 10 wt.-% ethanol, (dashed curves) 20 wt.-% ethanol, and (dot-dashed curve) 30 wt.-% ethanol.

% ethanol in the solvent is clearly seen. For the hard gels the temperatures at the high-*T* boundaries are reduced and the limiting concentrations for gel formation are increased. A similar effect is apparent for the soft gels of the copolymer in 20 wt.-% aqueous ethanol. The low-*T* boundaries are not completely defined by our experiments, but where the concentration ranges do overlap, e.g. at 25 wt.-% copolymer, the temperatures at the hard gel boundary are higher for the solution in 20 wt.-% ethanol compared with those in water.

Hard gels form when the effective volume fraction of micelles (ϕ_{eff}) acting as hard spheres exceeds a critical value at which the micelles pack. Considering raising the temperature of solutions in water alone, both upper and lower boundaries are known to be associated with the negative temperature coefficient of solubility of poly(oxyalkylene)s in water, the lower boundary through an increase in ϕ_{eff} via an increase in the extent of micellization of the copolymer, and the upper boundary through a decrease in ϕ_{eff} at constant number density of micelles caused by contraction of the E-blocks in the micelle corona in the poorer solvent.^[2,34] The increase in micelle association number associated with increase in temperature^[1,4,6] may favour formation of elongated micelles and so, in certain cases, cause a gel/fluid transition by that route.^[2] Whatever the detail, a solvent with only 10 wt.-% ethanol leaves the hard-gel boundary essentially unchanged. However, the results for higher ethanol concentrations require further discussion.

Compared with results for solutions of E₄₃B₁₁ in water, the shift of the hard gel boundaries to higher concentrations and the higher gelation temperatures at comparable concentrations at the lower boundary means that 20 and 30 wt.-% aqueous ethanol are better solvents for the copolymer than water at low temperatures. The observation that solutions of the copolymer in 40 wt.-% aqueous ethanol do not gel in the concentration range investigated fits the trend. However, if

the mechanism for dispersal of gel on heating were contraction of the E-blocks in the micelle corona, then the lower temperatures at the upper boundary imply that 20 and 30 wt.-% aqueous ethanol at, e.g., 40 °C are worse solvents for E blocks than is water at that temperature. The implication is that the temperature coefficient of solubility for E blocks in 20–30 wt.-% aqueous ethanol is significantly larger negative than in water, at least for micelles of EB copolymers at concentrations in the hard-gel range.

The evidence for hard gels of copolymer F127 (E₉₈P₆₇E₉₈) in aqueous ethanol differs from that for E₄₃B₁₁. It has been reported that the limiting concentration for gel formation (c^*) and the temperatures at the lower boundary are both increased by increasing the ethanol concentration in that system, and that the temperatures at the upper boundary are either not greatly affected^[10] or are increased.^[9] For example, for 20 wt.-% gels of F127 the temperature at the lower boundary increased from 20 °C (water) to 30 °C (20 wt.-% aqueous ethanol), while that at the upper boundary stayed approximately constant at 78–80 °C.^[10] SANS has been used to show that the association number of micelles of copolymer P105 (E₃₇P₅₈E₃₇) in 8 wt.-% solution at 60 °C decreases as the concentration of ethanol in the solvent is increased in the range 0–40 wt.-%,^[11] a result which is consistent with aqueous ethanol being a better solvent for P105 than water alone under these conditions. The effect of increasing the temperature of a 20 wt.-% micellar solution of P105 from 30 to 60 °C was an increase in association number, i.e. behaviour similar that found for an 8 wt.-% solution of the copolymer in water alone. Values of the hard sphere radius of micelles in 20 wt.-% aqueous ethanol were insensitive to temperature over the same range, again similar behaviour to that in water. Presumably the increase in micellar size resulting from the increase in association number is compensated by contraction of the E-block corona as solvent conditions worsen. Of course, it is the hard sphere radius which determines packing in the gel state. Overall, the evidence is that the temperature dependences of the properties of EPE copolymers in aqueous ethanol mirror those in water, but with 20 wt.-% aqueous ethanol a better solvent than water at low temperature (20 °C) and a marginally better solvent than water at high temperature (80 °C).

If the only determining factor was the response of the E blocks in the micelle corona to the change in solvent conditions as temperature is raised then the hard gels in the two systems, EB and EPE, should behave in a similar way. Accordingly, we seek an additional mechanism for dispersal of the E₄₃B₁₁ hard gel at moderate temperatures, and this must originate from the interaction of aqueous ethanol with the B blocks, whether in the micelle core or in the aqueous phase or both. We suppose that ethanol solvates the B blocks, the more so as the solvent becomes less structured by H-bonding as the temperature is raised, and that this favours dissociation of micelles which, combined with

deswelling of the micelle corona, causes dispersal of the hard gel. Further speculation along these lines must await a detailed investigation by scattering methods of the micellisation and micelle properties of an E_mB_n copolymer in aqueous ethanol.

Returning to Figure 6, the effect of ethanol concentration on the upper soft gel boundaries is seen to shadow that found for the upper hard gel boundaries, i.e. the boundaries shift to lower temperatures and higher concentrations as the ethanol concentration is increased. As discussed in the section *Storage and Loss Moduli*, the rheology which defines soft gel for E₄₃B₁₁ in micellar solutions of concentrations well below the hard-gel limit and at moderate to high temperatures is thought to reflect the formation loosely-structured aggregates by a percolation mechanism. Nearer the hard gel boundary the soft gel might best be described as defective hard gel. In either case the local structure must be cubic, similar to that of the hard gel, and correspondence of effects might be expected. The effect of ethanol concentration on the soft gel boundaries at low temperatures differs. At 20 °C, the concentrations at the boundary shift to lower concentrations as the ethanol concentration is increased. At this temperature aqueous ethanol is a better solvent than water and expansion of the micelle corona will increase the effective volume fraction of micelles in solution, sufficiently so that a soft gel can persist to lower concentrations than in water alone.

Acknowledgement: We thank Dr. F. Heatley and Mr. S. K. Nixon for help with the characterisation of the copolymer. Copolymer synthesis at Manchester was supported by the Engineering and Physical Science Research Council, UK.

- [1] C. Booth, D. Attwood, *Macromol. Rapid Commun.* **2000**, *21*, 501.
- [2] S. Hvidt, E. B. Jorgensen, W. Brown, K. Schillen, *J. Phys. Chem.* **1994**, *98*, 12320.
- [3] M. Almgren, W. Brown, S. Hvidt, *Colloid Polym. Sci.* **1995**, *273*, 2.
- [4] G. Wanka, H. Hoffmann, W. Ulbricht, *Macromolecules* **1994**, *27*, 4145.
- [5] K. Mortensen, in: “*Amphiphilic Block Copolymers: Self-assembly and Applications*”, P. Alexandridis, B. Lindman, Eds., Elsevier Science, Amsterdam 2000, Chapter 9.
- [6] B. Chu, Z.-K. Zhou, in: “*Nonionic Surfactants: Polyoxyalkylene Block Copolymers*”, Surfactant Science Series, Vol. 60, V. M. Nace, Ed., Marcel Dekker, New York 1996, Chapter 3.
- [7] I. W. Hamley, S.-M. Mai, A. J. Ryan, J. P. A. Fairclough, C. Booth, *Phys. Chem. Chem. Phys.* **2001**, *3*, 2972.
- [8] J. K. Armstrong, B. Chowdhry, J. Mitchell, A. S. Beezer, S. Leharne, *J. Phys. Chem.* **1996**, *100*, 1738.
- [9] N. K. Pandit, H. J. McIntyre, *Pharm. Dev. Technol.* **1997**, *2*, 181.

- [10] K.-W. Kwon, M. J. Park, J. Hwang, K. Char, *Polym. J.* **2001**, *33*, 404.
- [11] P. Alexandridis, L. Yang, *Macromolecules* **2000**, *33*, 5574.
- [12] M. Vadnere, G. Amidon, S. Lindenbaum, J. L. Haslam, *Int. J. Pharm.* **1984**, *22*, 207.
- [13] R. Ivanova, B. Lindman, P. Alexandridis, *Adv. Colloid Interface Sci.* **2001**, *89–90*, 351.
- [14] R. Ivanova, P. Alexandridis, B. Lindman, *Colloid Surf. A* **2001**, *183–185*, 41.
- [15] R. Ivanova, B. Lindman, P. Alexandridis, *J. Colloid Interface Sci.* **2002**, *252*, 226.
- [16] Y. Deng, C. Price, C. Booth, *Eur. Polym. J.* **1994**, *30*, 103.
- [17] I. W. Hamley, C. Daniel, W. Mingvanish, S.-M. Mai, C. Booth, L. Messe, A. J. Ryan, *Langmuir* **2000**, *16*, 2508.
- [18] A. D. Bedells, R. M. Arafah, Z. Yang, D. Attwood, F. Heatley, J. C. Padget, C. Price, C. Booth, *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 1235.
- [19] Z. Yang, S. Pickard, N.-J. Deng, R. J. Barlow, D. Attwood, C. Booth, *Macromolecules* **1994**, *27*, 2371.
- [20] F. Heatley, G.-E. Yu, W.-B. Sun, E. J. Pywell, R. H. Mobbs, C. Booth, *Eur. Polym. J.* **1990**, *26*, 583.
- [21] A. Kelarakis, W. Mingvanish, C. Daniel, H. Li, V. Havredaki, C. Booth, I. W. Hamley, A. J. Ryan, *Phys. Chem. Chem. Phys.* **2000**, *2*, 2755.
- [22] W. Mingvanish, A. Kelarakis, S.-M. Mai, C. Daniel, Z. Yang, V. Havredaki, I. W. Hamley, A. J. Ryan, C. Booth, *J. Phys. Chem. B* **2000**, *104*, 9788.
- [23] H. Li, G.-E. Yu, C. Price, C. Booth, J. P. A. Fairclough, A. J. Ryan, K. Mortensen, *Langmuir* **2003**, *19*, 1075.
- [24] H. Li, G.-E. Yu, C. Price, C. Booth, E. Hecht, H. Hoffmann, *Macromolecules* **1997**, *30*, 1347.
- [25] A. Kelarakis, V. Havredaki, C. Booth, *Macromol. Chem. Phys.* **2003**, *204*, 15.
- [26] R. K. Prud'homme, G. Wu, D. K. Schneider, *Langmuir* **1996**, *12*, 4651.
- [27] V. Castelletto, C. Caillet, J. Fundin, I. W. Hamley, Z. Yang, A. Kelarakis, *J. Chem. Phys.* **2002**, *116*, 10947.
- [28] L. Lobry, N. Micail, F. Mallamace, C. Liao, S.-H. Chen, *Phys. Rev. E* **1999**, *60*, 7076.
- [29] F. Mallamace, P. Gambaduro, N. Micail, P. Tartaglia, C. Liao, S.-H. Chen, *Phys. Rev. Lett.* **2000**, *84*, 5431.
- [30] S.-H. Chen, W.-R. Chen, F. Mallamace, *Science* **2003**, *300*, 619.
- [31] A. Kelarakis, V. Havredaki, K. Viras, W. Mingvanish, F. Heatley, C. Booth, S.-M. Mai, *J. Phys. Chem. B* **2001**, *105*, 7384.
- [32] A. Kelarakis, V. Havredaki, L. Dericci, G.-E. Yu, C. Booth, I. W. Hamley, *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 3639.
- [33] A. Kelarakis, V. Castelletto, C. Chaibundit, J. Fundin, V. Havredaki, I. W. Hamley, C. Booth, *Langmuir* **2001**, *17*, 4232.
- [34] A. D. Bedells, R. M. Arafah, Z. Yang, D. Attwood, J. C. Padget, C. Price, C. Booth, *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 1243.