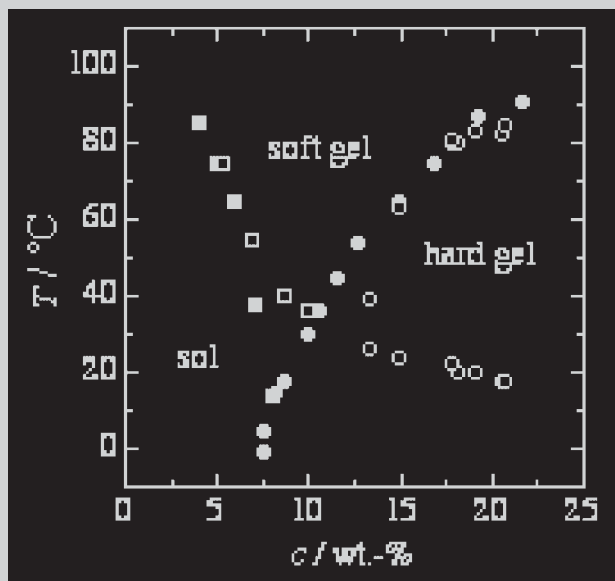


**Full Paper:** Aqueous solutions of diblock copolymers  $E_{102}P_{37}$  and  $E_{92}P_{55}$  (E = oxyethylene unit, P = oxypropylene unit) were investigated by rheometry. Storage ( $G'$ ) and loss ( $G''$ ) modulus and yield stress ( $\sigma_y$ ) were used to detect and characterise hard and soft gels in experiments which covered the concentration range 4–28 wt.-% copolymer and the temperature range 5–85 °C. Comparison is made with phase diagrams reported for other diblock copoly(oxyalkylene)s, and it is shown that the mesophase behaviour of these systems depends on the effective thickness of the E-block corona and the stability of the micelles at low temperatures.

Hard-gel boundaries (circles) and soft-gel boundaries (squares) for aqueous solutions of copolymers (○, □)  $E_{92}P_{55}$  and (●, ■)  $E_{96}B_{18}$ .



# Aqueous Gels of Diblock Oxyethylene-Oxypropylene Copolymers

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**Keywords:** aqueous solution; block copolymers; phase diagrams; rheology

## Introduction

Micellar solutions of water-soluble block copoly(oxyalkylene)s form fluids with complex rheologies and, at high enough concentration, immobile gels. Much work on these systems has centred around the  $E_mP_nE_m$  triblock copolymers available commercially from, for example, BASF (Pluronic) and Uniqema (Synperonic-PE). Here E denotes an oxyethylene unit,  $OCH_2CH_2$  and P an oxypropylene unit,  $OCH_2CH(CH_3)$ , and the subscripts denote number-average block lengths in chain units. Information on the structures and rheological properties of their mesophases can be found, for example, in ref.<sup>[1–6]</sup>

There are no corresponding studies of rheological properties published for micellar solutions of diblock copolymers of ethylene oxide and propylene oxide. In a previous study of the micellisation and micelle properties of a series of  $E_mP_n$  copolymers ( $m \approx 100$ ,  $n = 37–73$ ) in aqueous solution we defined only their hard gel boundaries.<sup>[7]</sup> In this

paper we report aspects of the rheology of solutions of two of these copolymers,  $E_{102}P_{37}$  and  $E_{92}P_{55}$ . Recently we have described small-angle X-ray scattering (SAXS) experiments which show that aqueous gels of diblock  $E_mP_n$  copolymers closely related in composition to those of present interest comprise body-centred cubic (bcc) arrays of packed spherical micelles.<sup>[8]</sup> There is related rheological and structural information for aqueous gels of other diblock copoly(oxyalkylene)s, notably copolymers of ethylene oxide and 1,2-butylene oxide,<sup>[9–13]</sup> but also copolymers of ethylene oxide and styrene oxide.<sup>[14,15]</sup>

## Experimental Part

### Copolymers

The preparation of the copolymers by sequential oxyanionic polymerisation of ethylene oxide followed by propylene oxide has been described previously, together with their purification

Table 1. Molecular characteristics of the block copolymers and micelle properties in aqueous solution.<sup>[7]</sup>

Copolymer	Composition <sup>a)</sup>	$\bar{M}_n$ <sup>a)</sup>	cmc <sup>b)</sup>	$N_w$ <sup>b)</sup>
	wt.-% E	$\text{g} \cdot \text{mol}^{-1}$	wt.-%	
E <sub>102</sub> P <sub>37</sub>	68	6630	0.015	50
E <sub>92</sub> P <sub>55</sub>	56	7240	0.006	170

<sup>a)</sup> NMR measurements.

<sup>b)</sup> At 40 °C.

and molecular characterisation.<sup>[7]</sup> Purification was needed to remove the small proportion of homopoly(oxypropylene) produced by the transfer reaction in the oxyanionic polymerisation of propylene oxide under the conditions employed.<sup>[16]</sup> Gel permeation chromatography calibrated with poly(oxyethylene) standards was used to confirm narrow chain length distributions: i.e. ratios of weight-average to number-average chain length of 1.04 without correction for instrumental broadening, estimated to reduce to approximately 1.02 after correction. This value is consistent with a Poisson distribution for the E-blocks and a somewhat wider distribution for the P blocks caused by the transfer reaction. <sup>13</sup>C NMR spectroscopy was used to obtain absolute values of number-average chain length and composition, hence the molecular formulae quoted, and to confirm the diblock architecture and sample purity. In the same study, a range of techniques was used to confirm micellisation in dilute aqueous solution, and tube-inversion was used to detect gelation in more concentrated solution. Selected results (critical micelle concentration, cmc, and mass-average association number,  $N_w$ ) are summarised in Table 1; see ref.<sup>[7]</sup> for further details.

### Rheometry

Solutions for rheometry were prepared by weighing copolymer and water into small tubes and mixing in the high-temperature mobile state before being stored for a day or more at low temperature ( $T = 5$  °C). Newly prepared samples were used for each experiment.

The rheological properties of the samples were determined using a Bohlin CS50 Rheometer. 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 cm<sup>3</sup> sample being added to the cup in the mobile state. Temperature was controlled by circulation of water from a thermostat bath. A solvent trap maintained a water-saturated atmosphere around the cell, and evaporation was not significant for the temperatures and timescales used. Storage and loss moduli were recorded across the temperature range with the instrument in oscillatory-shear mode at a frequency of 1 Hz. In this mode, the samples were heated at 1 °C · min<sup>-1</sup> in the range 5–95 °C, the temperature recorded being that of the water bath. Also moduli were measured for selected gels at fixed temperature across the frequency range 0.003 to 30 Hz. In all experiments the strain amplitude was held at ca. 0.5% using the autostress facility of the Bohlin software, the intention being that all measurements should be within the linear viscoelastic region. 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 equilibration before starting the program.

In the related tube-inversion experiments carried out previously,<sup>[7]</sup> 0.5 g samples were enclosed in small tubes (internal diameter ca. 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<sup>-1</sup>, and the temperature was held at a steady value during observation. The change from a mobile fluid to an immobile gel (or vice-versa) was determined by inverting the tube. The method is sensitive to yield stress and, for bcc gels under the conditions specified, immobility requires a yield stress 30–40 Pa.<sup>[11,12]</sup>

## Results

The plots in Figure 1 show the immobile and mobile regions of the phase diagram defined by tube inversion from previous work<sup>[7]</sup> and by storage modulus from present work as described in the section *Hard Gel*. Features which are useful in considering the results are the temperature range of the immobile gel at any given concentration and the minimum concentration for forming the immobile gel ( $c^*$ ) together with the corresponding temperature ( $T^*$ ).

In discussing the results of the rheology experiments, it is useful to distinguish three regions of rheological behaviour: hard gel, soft gel and sol. The notation is consistent with early reports of the rheology of aqueous micellar solutions of E<sub>m</sub>P<sub>n</sub>E<sub>m</sub> block copolymers<sup>[2,3]</sup> and we have used it our previous work.<sup>[9–15]</sup> Hard gel corresponds to the immobile region of the phase diagram depicted in Figure 1 and is characterised by high storage modulus and a high yield stress ( $\sigma_y$ ). Of the mobile region, those solutions with very low values of  $G'$  and  $\sigma_y$  and with  $G' < G''$  are denoted sols, and solutions with moderate values of  $G'$  and  $\sigma_y$  and with  $G' > G''$  are denoted soft gels. In presenting the results attention is focused on solutions of copolymer E<sub>102</sub>P<sub>37</sub>. The results for copolymer E<sub>92</sub>P<sub>55</sub> were similar in all respects.

### Hard Gel

The effect of concentration and temperature on the storage modulus measured at 1 Hz of 12–28 wt.-% aqueous gels of copolymer E<sub>102</sub>P<sub>37</sub> is shown in Figure 2a. It is seen that the maxima in  $G'$  increase with concentration from approximately 10 kPa ( $c = 12$  wt.-%) to approximately 60 kPa ( $c = 28$  wt.-%). The temperature at which  $G'$  fell steeply to a low value (ca. 1 kPa) served to define the limit of the hard gel. The temperature range of the hard (immobile) gel widened as concentration was increased and, as shown in Figure 1, within experimental scatter the hard-gel boundaries defined by rheometry and the immobile-gel boundaries defined by tube inversion are the same. Considering

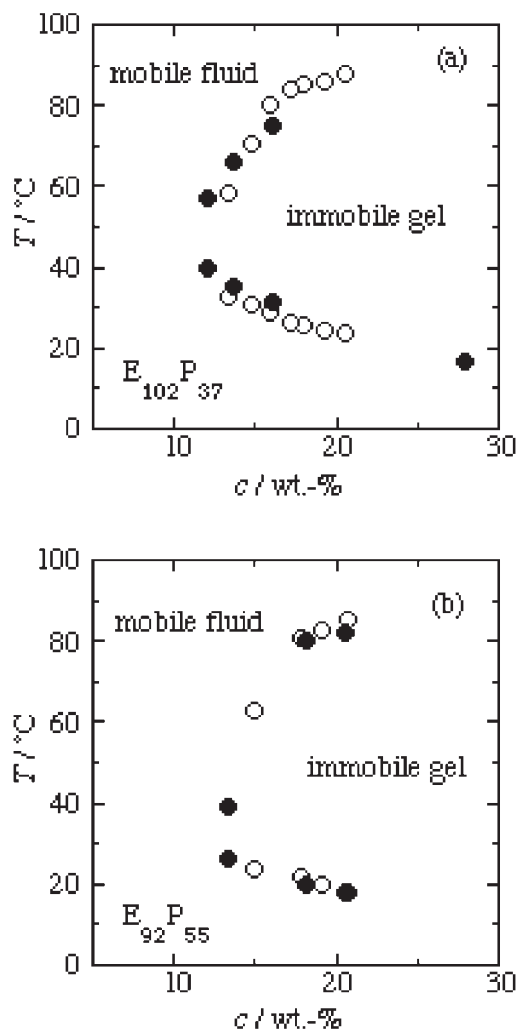


Figure 1. Gel boundaries for aqueous solutions of block copolymer (a)  $E_{102}P_{37}$  and (b)  $E_{92}P_{55}$  determined either by tube inversion (open symbols, data from ref.<sup>[7]</sup>) or by rheometry (filled symbols).

the combined data, the error in determining temperatures of the hard-gel boundary was estimated to be  $\pm 2^\circ\text{C}$ .

A comparison of values of  $\log(G')$  and  $\log(G'')$  is illustrated for the 16 wt.-% solution in Figure 2b. For this solution the transition on increasing temperature from a low value is from sol ( $G' < 0.1$  Pa) to hard gel ( $G' > 1$  kPa), while the transition at high  $T$  is from hard to soft gel ( $G' \leq 1$  kPa). The gels, both hard and soft, have  $G' > G''$ , while the sol has  $G' < G''$ . This behaviour is typical of all concentrations studied, values of  $G'$  in the high temperature soft gel phase being 1 kPa or less.

#### Soft Gel at Low Concentration

Plots of storage modulus (frequency = 1 Hz) against temperature obtained for solutions of copolymer  $E_{102}P_{37}$  below the limiting concentration for hard-gel formation ( $c^* \approx$

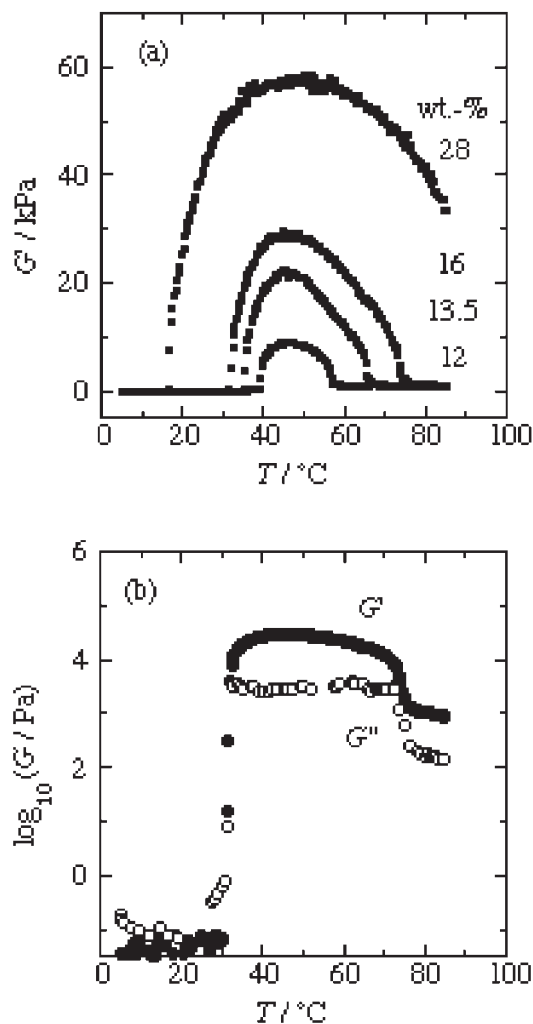


Figure 2. (a) Temperature dependence of storage modulus (frequency = 1 Hz) for aqueous solutions of block copolymer  $E_{102}P_{37}$ . Copolymer concentrations (wt.-%) are indicated. (b) Temperature dependence of logarithmic storage and loss modulus (frequency = 1 Hz) for a 16 wt.-% aqueous solution of block copolymer  $E_{102}P_{37}$ . Filled symbols denote  $\log(G')$  and unfilled symbols denote  $\log(G'')$ .

11.5 wt.-%) are shown in Figure 3a. At low temperatures the fluids are sols. The increase in modulus as temperature is increased signals formation of a soft gel, as illustrated for the 10 wt.-% gel in Figure 3b. Maximum values of  $G'$  for the soft gels of ranged from 120 (5.2 wt.-%) to 660 Pa (10 wt.-%) compared with maximum values in the range 10–60 kPa for the hard gels.

The sol/soft-gel boundaries determined for the two copolymers as the temperature at which  $G'$  (measured at 1 Hz) left the baseline (as illustrated in Figure 3a) are shown in Figure 4. The hard gel boundaries (taken from Figure 1) are included. The increase in P block length from 37 to 55 repeat units has the effect of moving both hard-gel and soft-gel boundaries to slightly lower temperatures without changing the pattern of behaviour.

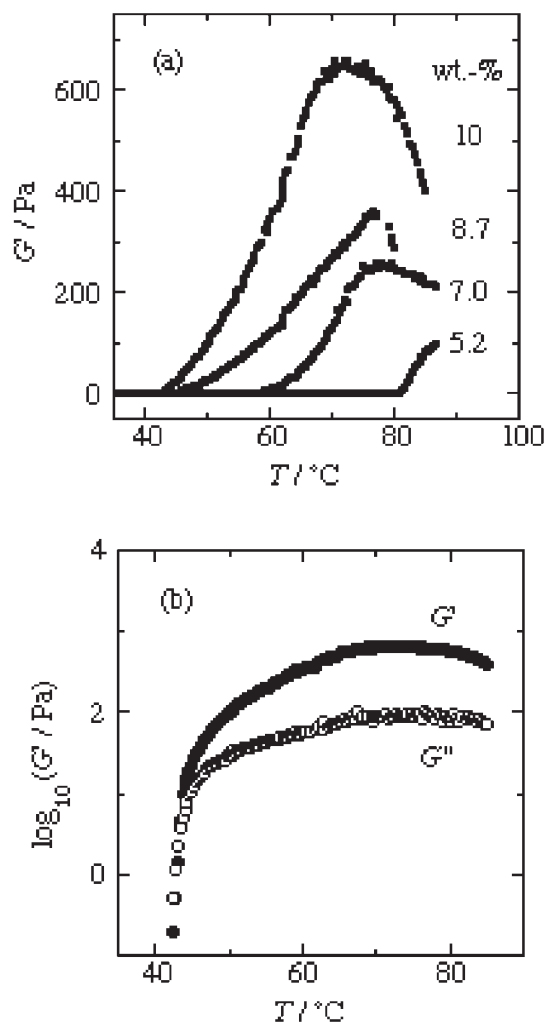


Figure 3. (a) Temperature dependence of storage modulus (frequency = 1 Hz) for aqueous solutions of block copolymer  $E_{102}P_{37}$ . Copolymer concentrations (wt.-%) are indicated. (b) Temperature dependence of logarithmic storage and loss modulus (frequency = 1 Hz) for a 10 wt.-% aqueous solution of block copolymer  $E_{102}P_{37}$ . Filled symbols denote  $\log(G')$  and unfilled symbols denote  $\log(G'')$ .

### Effect of Frequency

Values of  $G'$  determined for hard gels were constant across the frequency range accessible with our instrument; 0.01–30 Hz. This implies that the relaxation time  $\tau \rightarrow \infty$ , which would be expected for a gel of cubic-packed spheres. For hard gels near to the critical concentration  $G'$  increased slowly with frequency, presumably reaching a plateau at higher frequencies. This relative insensitivity of storage modulus to frequency measured at 1 Hz means that the hard gel boundaries defined by rheology are also insensitive to frequency. As an example results for a 12 wt.-% solution of copolymer  $E_{102}P_{37}$  at 45 °C are shown in Figure 5a. Behaviour of this kind has been observed for hard gels of related diblock copolymers,<sup>[11,13]</sup> and for triblock copoly-

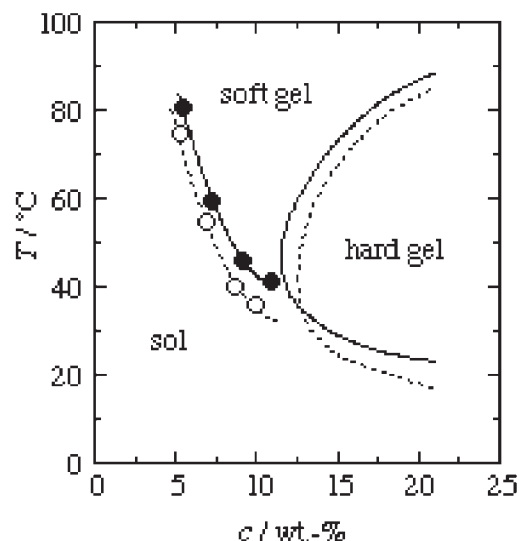


Figure 4. Mesophase boundaries for aqueous solutions of block copolymers  $E_{102}P_{37}$  (filled symbols, full curves) and  $E_{92}P_{55}$  (open symbols, dotted curves). The data points define the soft-gel/sol boundaries. The hard gel boundaries are from Figure 1.

mer  $E_{80}P_{30}E_{80}$  (F68).<sup>[17]</sup> The Cole-Cole plot of  $G''$  against  $G'$  in Figure 5b shows that the viscoelastic response of the  $E_{102}P_{37}$  gel differs markedly from that of a single Maxwell element (the dotted curve in the Figure) and points to a broad distribution of relaxation times, or an even more complex relaxation function.<sup>[17]</sup>

The effect of frequency on the soft gel was investigated only briefly, i.e. by changing from 1 Hz to 10 Hz. As found for solutions of other copolymers in the 'soft-gel' concentration range<sup>[11,13]</sup> the temperature of the sol/soft-gel boundary (defined as described in section *Soft Gel at Low Concentration*) decreased on increasing the frequency; for example by some 15 °C for a 10 wt.-% solution of copolymer  $E_{102}P_{37}$ .

### Yield Stress and Viscosity

As an example, the results of subjecting a 12 wt.-% solution of copolymer  $E_{102}P_{37}$  to a programmed increase in shear stress are set out in Table 2. The temperature was varied in order to sample the sol phase, the hard-gel phase and the soft-gel phase, as indicated in Table 2. On yield the gels fractured and the program terminated. At low temperature in the sol phase  $\sigma_y$  was zero and the Newtonian viscosity decreased with increase in temperature. As the hard-gel boundary was approached (35 °C), the viscosity increased and showed limited shear thinning. In the hard-gel phase the yield stress was high ( $\sigma_y > 100$  Pa) whilst in the soft-gel phase at higher temperatures it was low ( $\sigma_y < 20$  Pa). Similar results were obtained for other concentrations, the highest yield stress measured for a soft gel in the present experiments being 27 Pa. These values of  $\sigma_y$  are consistent

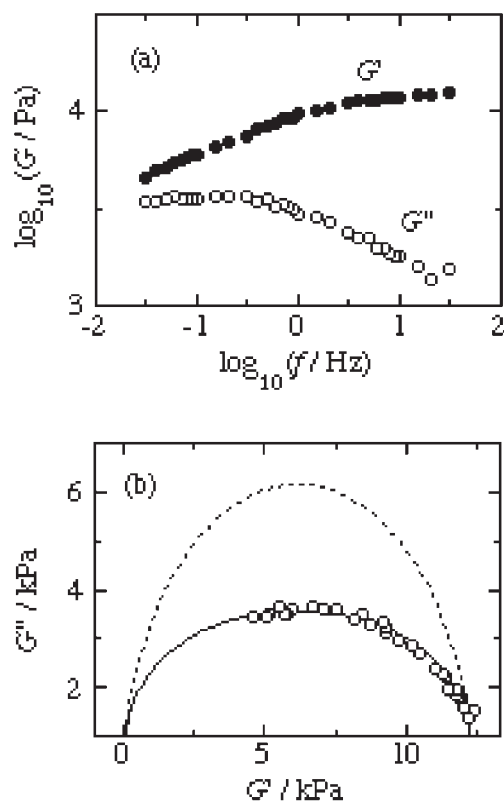


Figure 5. (a) Frequency dependence of storage and loss modulus for a 12 wt.-% aqueous solution of block copolymer  $E_{102}P_{37}$  at 45 °C. Filled symbols denote  $\log(G')$  and unfilled symbols denote  $\log(G'')$ . (b) The same data plotted as  $G''$  versus  $G'$ . The dotted curve is calculated for a single Maxwell element, i.e. from  $G'' = [G'G' - (G'')^2]^a$  where  $G'$  is the plateau value at high frequency and  $a = 0.5$ . The full curve through the data points has  $a = 0.35$ .

with the results (immobile or mobile) of the tube inversion test, i.e. the yield stress for immobility under the conditions of the test is at least 30 Pa.

The yield stresses of selected gels were measured as a function of time after fracture under shear. The hard gels showed no measurable effect, but the soft gels recovered slowly. For example, an 8 wt.-% soft gel of copolymer  $E_{102}P_{37}$  at 65 °C had  $\sigma_y \approx 0$  when measured immediately after fracture, rising to  $\sigma_y \approx 4$  Pa after equilibrating for 30 min.

## Discussion

### Hard Gel Structure

We have not determined the structures of the present gels, but 30 wt.-% aqueous gels at 25 °C of a series of  $E_mP_n$  with  $m$  in the range 91–165 and  $n$  in the range 43–105 have been studied by SAXS and found to be body-centred cubic structures formed from packed spherical micelles.<sup>[18]</sup> These copolymers include  $E_{91}P_{64}$ , which is closely related to the

Table 2. Values of yield stress and viscosity for a 12 wt.-% aqueous solution of copolymer  $E_{102}P_{37}$ .

Temperature °C	Phase	$\sigma_y$ Pa	$\eta$ mPa · s
5	sol	0	14
15	sol	0	10
25	sol	0	8
35	sol	0	40
45	hard gel	200	–
55	hard gel	125	–
65	soft gel	18	–
75	soft gel	8	–

present copolymer  $E_{92}P_{55}$ . The effective hard-sphere radius determined from unit cell dimensions for micelles of copolymer  $E_{91}P_{64}$  was  $r_{\text{gel}} \approx 12$  nm,<sup>[18]</sup> much the same as the hard-sphere radius determined from the concentration dependence of light scattering intensity (i.e. from the exclusion properties of the micelles) for copolymer  $E_{92}P_{55}$  in dilute solution at 35 °C, i.e.  $r \approx 13$  nm.<sup>[17]</sup> Against this background we assign the hard gels of copolymers  $E_{102}P_{37}$  and  $E_{92}P_{55}$  to the same structure: spherical micelles packed in a bcc structure.

### Effect of Hydrophobe Length

The solubility of the  $E_mP_n$  block copolymers in water is increased at low temperature, where water/ether-oxygen and water/water hydrogen bonding is enhanced, the latter reinforcing the hydrophobic effect,<sup>[18]</sup> but is decreased by a higher ratio of hydrophobic P units to hydrophilic E units in the molecule. Consequently, the effect of a longer P-block (at approximately constant E-block length) is to enhance the stability of the micelles at low temperatures, and thereby to stabilise the gel phases (both hard and soft) as temperature is lowered. In the present experiments, involving  $E_{102}P_{37}$  and  $E_{92}P_{55}$ , the effect was small but detectable, see Figure 4.

### Effect of Hydrophobe Composition

Comparison can be made with reported results for  $E_mB_n$  diblock copolymers, where B denotes an oxybutylene unit,  $\text{OCH}_2\text{CH}(\text{C}_2\text{H}_5)$ . A B unit is six-times more hydrophobic than a P unit,<sup>[19]</sup> and copolymers with comparable association properties require relatively short B blocks compared to  $E_mP_n$  copolymers. Such copolymers are readily prepared with high purity under laboratory conditions where there are no complications from chain transfer.<sup>[19,20]</sup> Because hard gel formation involves packing of spherical micelles, the important factor is the volume fraction of micelles, which is related to the number density and effective volume of the micelles in solution, and the latter is mainly determined by the effective thickness of the water-



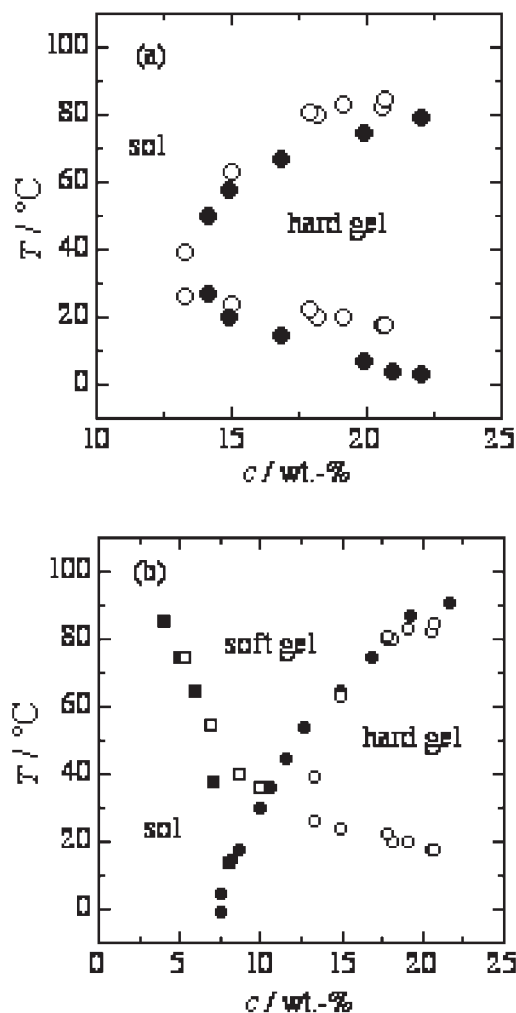


Figure 6. (a) Hard-gel boundaries for aqueous solutions of copolymers (○)  $E_{92}P_{55}$  and (●)  $E_{90}B_{10}$ . (b) Hard-gel boundaries (circles) and soft-gel boundaries (squares) for aqueous solutions of copolymers (○, □)  $E_{92}P_{55}$  and (●, ■)  $E_{96}B_{18}$ . Results for the  $E_mB_n$  copolymers are taken from ref.<sup>[11,20]</sup>

swollen E-block corona. Accordingly, a useful comparison can be made for copolymers of equivalent E-block length. In this respect copolymer  $E_{92}P_{55}$  is closely matched by copolymer  $E_{90}B_{10}$  for which a phase diagram is available.<sup>[20]</sup> Moreover, given the multiplying factor of six for a B unit, these two copolymers are closely matched with respect to hydrophobicity. Figure 6a shows that they have similar hard gel diagrams. Unfortunately the soft gel region in the phase diagram of copolymer  $E_{90}B_{10}$  was not defined.

A second copolymer which meets the criterion of similar E-block length is  $E_{96}B_{18}$ , and in this case a full phase diagram is available.<sup>[11]</sup> Comparison with results for copolymer  $E_{92}P_{55}$  is made in Figure 6b. It is clear that the phase behaviour of the two copolymers is very similar at temperatures above 50 °C, but very different at low temperatures. This applies to the soft as well as the hard gel. The

difference at low temperature arises because the  $B_{18}$  block acts effectively as a  $P_{108}$  block, with the result that the micelles of  $E_{96}B_{18}$ , and therefore the gel, are much more stable at low temperatures.

#### Soft Gel Formation at High Concentration

At concentrations above  $c^*$ , raising the temperature from a low value increases the extent of micellisation and hard gel is formed from sol when a critical volume fraction is reached. The extent of micellisation is maximised by raising the temperature further, but at the same time the poly(oxyethylene)-block corona shrinks in the poorer solvent, eventually to become the dominant effect and disrupt the gel structure, when the system becomes mobile again. As indicated in the section *Hard Gel*, this mobile phase is rheologically a soft gel. Evidence from other studies points to the probability that the soft gel in this region has a highly-defective cubic structure.<sup>[9,11]</sup>

#### Soft Gel Formation at Low Concentration

Soft gel regions (determined at frequency 1 Hz) similar to those in Figure 4 have been reported for copolymer  $S_{13}E_{60}$ ,<sup>[14]</sup> for a series of  $E_mB_{18}$  copolymers ( $m = 96-384$ , that for  $E_{96}B_{18}$  being reproduced in Figure 6b),<sup>[11]</sup> and for a series of  $B_{20}E_m$  copolymers ( $m = 430-610$ ),<sup>[13]</sup> all of which form spherical micelles in dilute solution. A closely related phase diagram has been found for a shorter diblock copolymer  $E_{41}B_8$ .<sup>[10]</sup> This type of soft gel has been assigned to weakly interacting spherical micelles.<sup>[10,11]</sup> The transition from sol to soft gel is assumed to occur when micellar aggregates reach a threshold yielding sufficient structure to cause an increase in modulus and, at a suitable frequency, the dynamic storage modulus to exceed the loss modulus. There is confirmatory information from small-angle neutron scattering for related  $E_mP_nE_m$  systems.<sup>[21,22]</sup> More complex behaviour in the soft gel region is expected if the micelles are subject to a sphere-to-rod transition at high temperatures,<sup>[2,12,23,24]</sup> and the rheological properties of this type of soft gel have been attributed to the hindered rotation of rod-like micelles.<sup>[2]</sup> The present results are consistent with spherical micelles across the whole temperature range.

## Conclusions

Above a critical concentration ( $c^* = 11-13$  wt.-%) aqueous solutions of copolymers  $E_{102}P_{37}$  and  $E_{92}P_{55}$  form hard gels. In this concentration range, when studied at frequency 1 Hz, they are sols at low temperature ( $\sigma_y = 0$ ,  $G'' < 1$  Pa,  $G' > G''$ ), hard gels at intermediate temperatures ( $\sigma_y > 100$  Pa,  $G' > 1$  kPa,  $G' > G''$ ), and soft gels at high temperatures ( $\sigma_y < 30$  Pa,  $G' < 1$  kPa,  $G' > G''$ ). Below  $c^*$  the transition on heating the solution is from sol to soft gel. The effect of an increase in

hydrophobe-block length is to stabilise micelles against dissociation at low temperatures, and thereby to move both hard and soft gel phases to lower concentrations. Comparison of gel boundaries published for copolymers with poly(oxybutylene) hydrophobes indicates a general pattern of behaviour for systems which form spherical micelles.

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