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Shear-induced orientational order in the hexagonal phase of oxyethylene/oxybutylene diblock copolymer gels

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Shear-induced orientational ordering in diblock copolymer gels of $E_{40}B_{10}$ in 0.2 mol dm^{-3} aqueous K_2SO_4, where E denotes oxyethylene and B denotes oxybutylene, was studied in the hexagonally packed rod phase at 85°C for a number of diblock copolymer concentrations. Large amplitude ($\lambda = 50\%$) oscillatory shear at a shear rate of $\omega = 10$ rad s^{-1} was applied to the gels and the degree of orientation was quantified in terms of global orientational order parameters extracted from small-angle X-ray scattering (SAXS) patterns. Shearing the gel produced a rapid drop in the dynamic shear moduli and a slower increase in orientation; up to a second rank orientation parameter of $\bar{P}_2 = 0.26$ for the highest concentration (38 wt%) diblock gel. Time-resolved SAXS measurements showed that the steady state level of orientation was established over a time-scale of 3 min. Lower concentration gels yielded lower orientation parameters from the same deformation process, and a 25 wt% gel remained unoriented. Upon cessation of shear the dynamic shear moduli recovered rapidly to their initial values, although the shear-induced anisotropy in the SAXS patterns relaxed very slowly to zero over a time-scale of over an hour. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: diblock copolymer gel; SAXS; oscillatory shear)

INTRODUCTION

Diblock copolymers in solution in a selective solvent can form gels at high concentrations when micelles pack to produce ordered structures. For example, spherical micelles can order into a cubic structure, or rod-like micelles can form a hexagonal structure. The orientation and rheology of such phases are influenced by the application of a shear field, as shown by experiments on cubic micellar phases[1]. To date, rheological measurements and experiments which probe the ordered structure, for example small-angle X-ray scattering (SAXS) or small-angle neutron scattering (SANS), have been performed separately. Here, we present results from simultaneous SAXS/rheology experiments on the hexagonal packed cylinder (hex) phase formed in gels of a diblock copolymer.

We have previously invesigated the diblock copolymer $E_{40}B_{10}$ in 0.2 mol dm^{-3} aqueous K_2SO_4, with polymer concentrations 25–38 wt%, which forms cubic micellar phases at low temperature, and then a high-temperature gel phase consisting of hexagonally packed cylinders[2]. These features were shown to be in good agreement with results from previous experiments[3].

The effects of large-amplitude oscillatory shear in inducing orientation in diblock copolymers have been studied by a number of workers. It has been commonly reported that large-amplitude oscillatory shear acts to enhance orientational ordering in a variety of phases. This is characterized by the sharpening and intensifying of peaks in small-angle scattering patterns[4–9]. It has been shown for the hex phase of both diblock[4–6] and triblock[7–9] copolymer melts that large-amplitude oscillatory shear induces orientational order of the rods in the direction of the applied shear. Nevertheless, all of these studies have expressed the observed orientation in a purely qualitative sense, and no attempt has been made to date to quantify the degree of orientation imposed by the shear field in these systems.

The principal purpose of this study was to quantitatively characterize the degree of alignment of the cylindrical 'rods' in the hex phase in $E_{40}B_{10}$ diblock copolymer gels which is induced by the application of large-amplitude oscillatory shear. The time-scales over which the orientation develops, the role of diblock concentration in determining the maximum limit of shear-induced alignment and the effects which occur upon cessation of shear were also considered. The storage and loss moduli G' and G'' were monitored throughout the shearing and relaxation process so that the rheology of the gels could be correlated to structural changes. The simultaneous SAXS and rheology measurements were performed with an X-ray rheometer which allowed confident association between the structural and orientational information yielded from the SAXS data and the dynamic mechanical properties extracted simultaneously using the rheometer.

EXPERIMENTAL

Materials

The $E_{40}B_{10}$ diblock copolymer which was employed in

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this work was identical to that used in previous studies[2,3]. The diblock copolymers were prepared by sequential anionic polymerization of the two monomers, with the E block being polymerized first[10,11], and solutions of the copolymer were then prepared in 0.2 mol dm^{-3} aqueous K_2SO_4 at $T = 60–70°C$, followed by several days storage in a refrigerator. The chain length distribution of the sample was narrow: $M_w/M_n = 1.04$, determined by gel permeation chromatography based on poly(oxyethylene) calibrants and uncorrected for instrumental spreading. The composition was assessed by nuclear magnetic resonance. The $E_{40}B_{10}$ gels used in this study contained between 25 and 38 wt% copolymer.

Rheometer

Rheological measurements were performed using a Rheometrics Solids Analyzer RSA II. The rheometer was configured with a shear sandwich geometry with apertures in the plates to permit transmission of the X-ray beam, and has been described previously[2]. Oscillatory shear deformation is applied to the sample, and the dynamic moduli G' and G'' are measured. In this work the frequency employed was $\omega = 10$ rad s^{-1} with a strain amplitude of $\lambda = 50\%$, and the rheometer plates were arranged to give a sample thickness of 0.5 mm. The temperature at which the samples were studied was 85°C, so that all of the materials were studied in the hexagonally packed rod phase, as determined in previous SAXS[2,12] and SANS[12] experiments.

For the time-resolved relaxation of orientation measurements a Couette Cell was employed, which has been described previously[13]. This device did not permit the shear moduli. Steady shear at $\omega = 6$ rad s^{-1} was applied to the $E_{40}B_{10}$ gel for 5 min, and the relaxation was monitored via orientation parameters extracted from two-dimensional X-ray diffraction patterns collected continuously for 2 h after the shearing was stopped.

Small-angle X-ray scattering

Simultaneous *in situ* SAXS and rheology experiments were performed on station 16.1 at the Synchrotron Radiation Source at the Daresbury Laboratory, Warrington, UK, using a monochromatic X-ray beam of dimension 0.3 mm × 3 mm diameter and wavelength $\lambda = 1.5$ Å. Details of the Daresbury storage ring, radiation, camera geometry and data collection electronics have been given elsewhere[14].

Scattered X-rays were collected on a multiwire gas filled area detector, which has an active area of 200 mm × 200 mm. The pixel array was set by the interfacing software to 256 × 256 and the count rate capability was 500 000 Hz. Scattering patterns from oriented specimens of wet collagen (rat-tail tendon) were used for calibration of the q scale range of the detector ($q = 4\pi \sin\theta/\lambda$, where radiation of wavelength λ is scattered through an angle 2θ). The data were corrected for background scattering from the camera and empty shear cell, sample absorption and the positional alinearity of the detector.

The relaxation experiment was performed on the high brilliance beamline at the ESRF synchrotron facility at Grenoble, France[15]. The X-ray beam, of wavelength $\lambda = 1$ Å, had a cross-section of 0.2 mm diameter at the point of intersection with the sample, and, as at the Daresbury synchrotron, a two-dimensional gas-filled detector was employed in the collection of the scattered photons.

X-ray scattering analysis

Small-angle X-ray scattering reveals information about the gel structure on a scale of ~100 Å, i.e. on the lengthscale of the hexagonal-packed cylinder structure. The anisotropy of the diffraction rings in the SAXS patterns is related to the macroscopic orientational ordering of domains containing constituent cylinders. X-ray scattering proves particularly useful for determining orientational order because a complete characterization of the orientation distribution function is possible: in contrast, only the first-order coefficient is obtainable from, for example, birefringence measurements. The area of the sample illuminated by the incident beam is large in relation to the scattering units (1 mm compared with 100 Å) and therefore the SAXS patterns provide orientational order parameters that are global averages.

In order to describe the anisotropy within the system we employ a distribution function $f(\beta)$ which denotes for a uniaxial system the probability of finding a structural unit (in this case the scattering arises from domains of hexagonally packed anisotropic micelles whose orientation is described by a vector known as the director) at an angle β to a prescribed axis; in this work the shear axis. Scattering patterns obtained with the beam incident along the shear direction confirm uniaxial symmetry, as the scattering pattern consists of a uniform ring. The orientation distribution function $f(\beta)$ that completely characterizes the orientational order as a sum of orthogonal harmonic functions can then be written as[16]:

$$f(\beta) = \sum_{n=0}^{\infty} (4n+1)\overline{P}_{2n}(\cos\beta)P_{2n}(\cos\beta) \qquad (1)$$

with the globally averaged order parameters $\overline{P}_{2n}(\cos\beta)$ being utilized here to describe the overall state of orientation. These coefficients can be extracted directly from the SAXS patterns using the azimuthal distribution of the intensity function at a fixed value of the magnitude of the scattering vector q; and a model for the scattering of a perfectly aligned system:

$$\overline{P}_2 = \frac{\overline{P}_2^{\mathrm{I}}}{\overline{P}_2^{\mathrm{m}}} \qquad (2)$$

where $\overline{P}_2^{\mathrm{I}}$ is the normalized coefficient calculated from the observed X-ray scattering and $\overline{P}_2^{\mathrm{m}}$ is the coefficient calculated from the model. In this case the model for a single unit is approximated to be an infinitely long rod, so that the orthogonal components of the scattering model are simplified to[17]:

$$\overline{P}_2^{n}(\cos\beta)^n = \frac{(2n)!}{(-1)^n 2^{2n}(n!)^2} \qquad (3)$$

and thus: $\overline{P}_2^{\mathrm{m}} = -1/2$, $\overline{P}_4^{\mathrm{m}} = 3/8$ and $\overline{P}_6^{\mathrm{m}} = -5/16$. It should be noted that a complete description of the orientation function can be obtained from the scattering data between the azimuthal angles of $\beta = 0$ and $\beta = \pi/2$, and therefore the results presented in this paper, which were determined from a complete diffraction ring of $0 < \beta \leq 2\pi$, are averaged results from each of the four quadrants of the diffraction ring.

OSCILLATORY SHEAR

Figure 1 shows diffraction patterns taken from a 38% $E_{40}B_{10}$ gel in static equilibrium at 85°C and during shearing

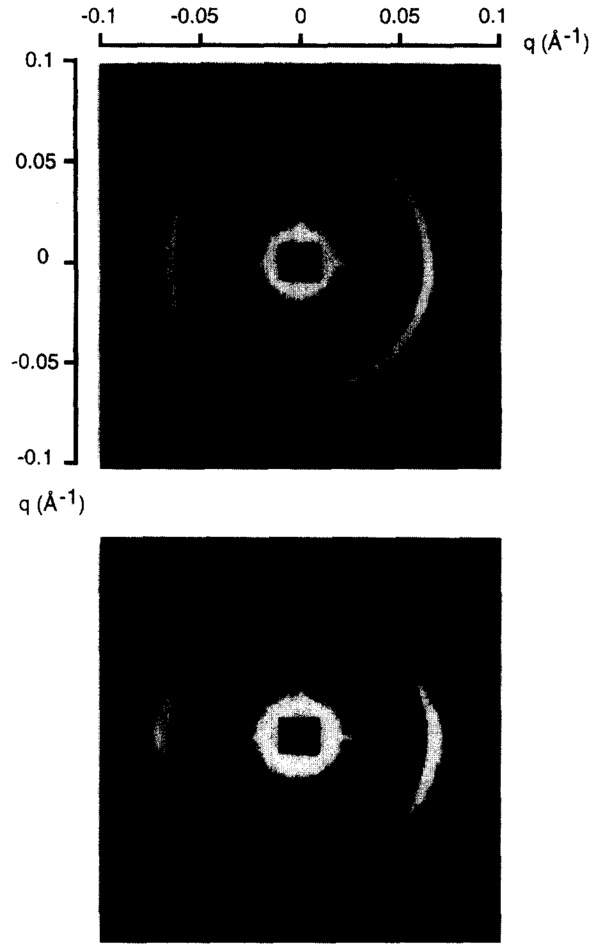

Figure 1 SAXS diffraction patterns from a 38% $E_{40}B_{10}$ diblock copolymer gel in static equilibrium (above) and during oscillatory shear at a frequency of $\omega = 10\ \mathrm{rad\ s^{-1}}$ with a strain amplitude of $\lambda = 50\%$ (below). The shear direction was vertical, and the sample temperature was 85°C in both cases

at a frequency of $\omega = 10\ \mathrm{rad\ s^{-1}}$ with a strain amplitude of $\lambda = 50\%$. It can be seen from the SAXS patterns that the principal effect of the shear field is to concentrate the intensity of the scattering in the inner diffraction ring in two arcs, centred on an axis close to the equator. This indicates a preferential alignment of the hexagonally packed rods parallel to the (vertical) shear direction. The second-order reflection is also considerably reduced in intensity in the sheared SAXS pattern, indicating a lessening of longer range positional ordering during the application of the shear field.

It should be noted that orientational order parameters were obtained by dividing the two-dimensional field of the 'raw' uncorrected data of the sheared gel by the static image. This procedure leaves a two-dimensional image which represents only the changes which have been induced by the shear field (and also necessarily incorporates all of the data correction procedures, such as background subtraction, which are used to obtain the images in *Figure 1*). This essentially uses the initial state of the hex phase gel as a normalizing condition by defining as zero the orientation function coefficients for the first diffraction pattern, which are calculated as close to zero: $\overline{P}_{2n} \ll 0.01$.

Figure 2 shows the global orientation function coefficients $\overline{P}_{2n}$ ($n = 1$–3), with the simultaneous measurements of the storage and loss moduli G' and G'', as a function of time during an oscillatory shear flow experiment. Measurements of the dynamic shear moduli were made every 30 s, which was the same length of time employed for acquisition of each SAXS image. The sample remained static in the rheometer for 2 min, corresponding to the first four data points, acquired within the linear viscoelastic region at $\lambda = 0.1\%$ strain was then subjected to large amplitude shearing for 5 min, and was finally allowed to relax for 3 min.

Both dynamic shear moduli decreased rapidly (within the 30 s data collection period) upon application of the deformation field and recovered completely upon cessation of shear within the same time-scale. By contrast, the orientation, as seen in all of the first three non-zero coefficients, showed a relatively gradual development of a shear-induced structure over a time-scale of 2–3 min. This relaxed when the shear field was removed, although the relaxation was noted to be significantly slower than that of the dynamic shear moduli.

We propose that the contrast in behaviour between the orientation and the rheology data (which is evidenced principally in terms of response time to the application and removal of the shear field) arises from the polydomain structure of the gel. The SAXS patterns result from a global average of the order within the sample, whilst the rheological measurements are more sensitive to the local defect density. We suggest that the introduction of the shear field caused a rapid increase in the defect density (and hence a rapid drop in dynamic shear moduli), whilst the orientation of the domains along the shear axis, revealed in the SAXS data, developed more slowly about the shear axis. When the shearing was stopped, the defect texture recovered rapidly as domain boundaries were annihilated, but the preferential orientation of domains relaxed much more gradually.

RELAXATION PHENOMENA

It can be seen from *Figure 2* that the orientational order did not completely disappear during the 3 min of relaxation for which it was monitored. For this reason a longer relaxation experiment was performed at the ESRF facility in Grenoble in which the sample was permitted to relax from an applied shear field for 2 h (*Figure 3*), with diffraction patterns collected every 2 min. The experimental circumstances differed slightly in that the applied shear field was steady rather than oscillatory in nature, with an applied frequency $\omega = 6\ \mathrm{rad\ s^{-1}}$. In addition, the geometry of the shearing device differed: for the dynamic shear experiments detailed above the samples were sheared between parallel plates, with the shear vector $\mathbf{v}$ in the vertical plane and the shear gradient vector $\nabla\mathbf{v}$ and the vorticity vector $\mathbf{e}$ in the horizontal plane; whereas in this experiment a Couette cell was employed, with the vorticity vector $\mathbf{e}$ in the vertical plane, and $\mathbf{v}$ and $\nabla\mathbf{v}$ in the horizontal plane. The orientation parameters were extracted from the 2D SAXS patterns in the same way as previously described, although the statistical noise in the images obtained from the ESRF detector was higher, resulting in only the first-order orientation parameter being obtainable from the SAXS patterns.

Figure 3 reveals that the relaxation of the shear aligned domains within the diblock copolymer gel was an involved procedure which lasted for some 90 min. The recovery can also be seen to be total: at the end of the relaxation the shear-induced orientation was completely eliminated. Of particular interest is the presence of two significant inflections in the $\overline{P}_2$ curve. This form of orientation inflection during

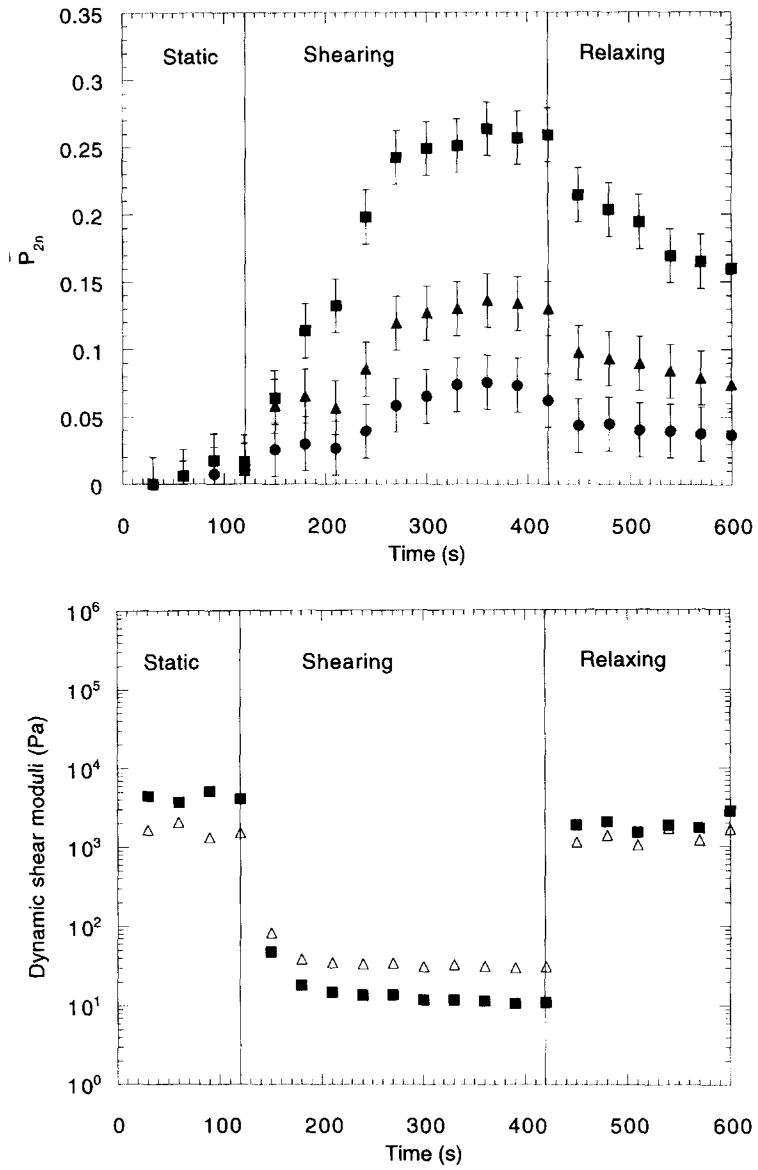

Figure 2 The development of the global orientation function coefficients $\bar{P}_{2n}$ for $n = 1$ (■), $n = 2$ (▲) and $n = 3$ (●) (above) and the dynamic shear moduli G'(■) and G'' (△) (below) with time for a 38% diblock copolymer gel at 85°C. The deformation, consisting of oscillatory shear at a frequency $\omega = 10$ rad s^{-1} with a strain amplitude of $\lambda = 50\%$, was imposed over the region shown between the solid, vertical lines. The 'static' rheology was acquired using a strain amplitude of $\lambda = 0.1\%$

relaxation subsequent to applied shear flow has been observed in nematic phases of a non-polymeric liquid crystal system (5CB)[18] and in a lyotropic liquid crystal polymer system (hydroxypropylcellulose)[19] where, in the latter case, it has been associated with the appearance of a banded texture[20].

To account for the presence of these inflections in the $\bar{P}_2$ relaxation we consider the effects of shear deformation on 'rigid rod' systems. For systems which can be described using directors for domains containing 'rigid-rods', as for the $E_{40}B_{10}$ gel considered here, the application of shear is considered to drive directors which are aligned to the shear axis out of the plane of shear[21,22], and increase the defect density within the system[23]. During this process the value of the order parameter rises as more rods within the plane of shear are aligned towards the shear axis. The annealing of energetically unfavourable shear-induced defects by the relaxation process causes a greater number of directors to re-enter the shearing plane. Finally, these directors relax into a random orientation within the shear plane. It is worth noting that the orientation patterns determined from the X-ray patterns concern only projections of the directors within the shearing plane, whilst interactions occurring in other planes remain undetected[24]. This presents a possible means by which the presence of the relaxation inflections can be understood, however the precise explanation for the presence and form of these features remains unknown.

EFFECT OF COPOLYMER CONCENTRATION

The extent of shear-induced orientational order at a fixed frequency and strain amplitude was found to increase with increasing gel concentration. *Figure 4* shows azimuthal intensity profiles for gels in the steady state subjected to large-amplitude oscillatory shear, normalized to the static patterns in each case, and reveals the increase in intensity of the equatorial arcs with increasing gel concentration. *Figure 5* shows the shear-induced orientation parameters which were extracted from each of the profiles in *Figure 4*.

In general, it can be seen from *Figures 4 and 5* that higher

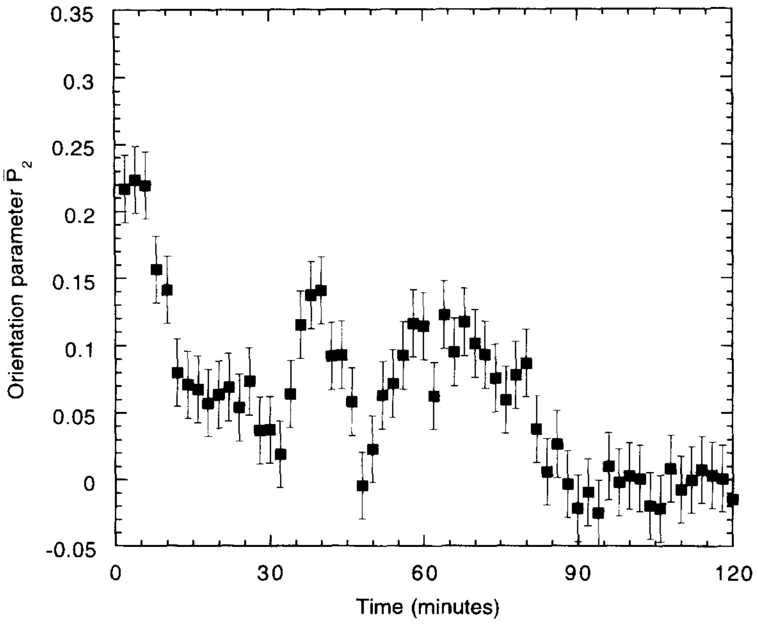

Figure 3 The global orientation parameter $\bar{P}_2$ as a function of time subsequent to the application of steady shear at a frequency $\omega = 6$ rad s^{-1} for 5 min. Time $t = 0$ s corresponds to the point at which the shearing motors were stopped

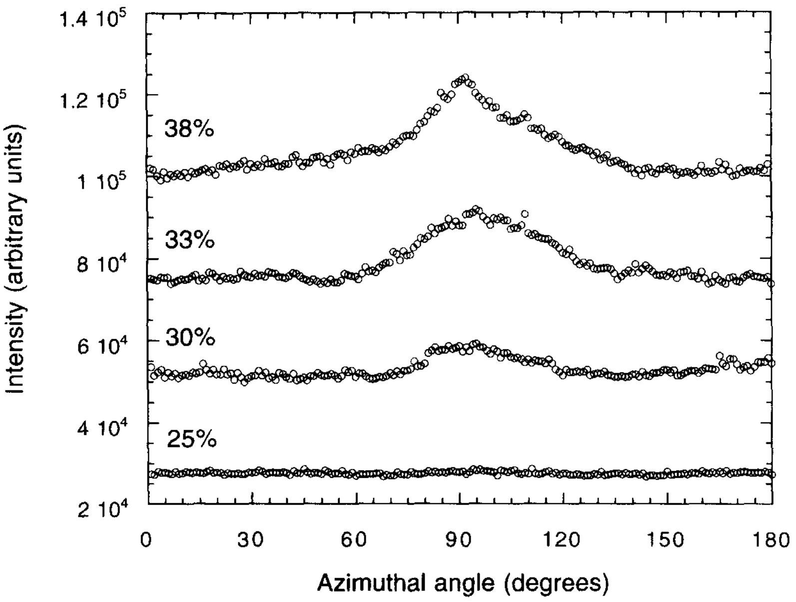

Figure 4 A plot of the semi-azimuthal distribution of intensity at the principal scattering vector for four concentrations of diblock copolymer gel as indicated. The shear induced global orientation parameters taken from these profiles are given in *Figure 5*

concentrations of copolymer led to more highly ordered structures within the sheared gel. This is understood in terms of our model that the higher density of domains of hexagonally packed rods within the more concentrated gels produced a greater number of interactions which produce co-operative alignment in the flow field[25], resulting in the more aligned structures observed (*Figure 5*). Indeed it can be seen in the case of the lowest concentration gel studied (25% $E_{40}B_{10}$), that the shear field was unable to induce any global orientation: $\bar{P}_2 = 0.00 \pm 0.01$.

SUMMARY AND CONCLUSIONS

The application of large-amplitude oscillatory shear creates globally oriented structures within the high-temperature hexagonally packed rod phase of $E_{40}B_{10}$ diblock copolymer gels. The highest value of shear induced orientation observed at $\omega = 10$ rad s^{-1} was $\bar{P}_2 = 0.26 \pm 0.01$ for the 38% gel. The maximum $\bar{P}_2$ value was lower for lower concentration gels. Higher levels of orientation were observed for more concentrated gels by reason of greater co-operative interactions in the flow field.

Time-resolved SAXS experiments indicated that this degree of orientation, where it occurred, was established over a time-scale of about 3 min for all gels that oriented. Simultaneous measurements of the dynamic shear moduli revealed different time-scales for the change in moduli measured rheologically and the structure evolution determined using SAXS. This we attribute to the different properties probed by the two techniques: the SAXS patterns

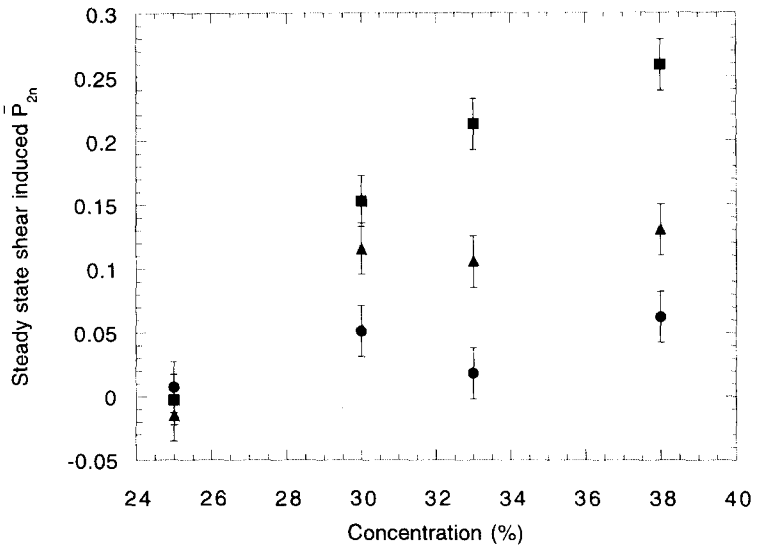

Figure 5 The global orientation function coefficients $\bar{P}_{2n}$ for $n = 1$ (■), $n = 2$ (▲) and $n = 3$ (●) induced by oscillatory shear at frequency $\omega = 10$ rad s^{-1} with a strain amplitude of $\lambda = 50\%$ in the hexagonally packed rod phase of $E_{40}B_{10}$ diblock copolymer gels as a function of copolymer concentration. The azimuthal intensity profiles from which these measurements were extracted are shown in *Figure 4*

are related to the global degree of orientation, whilst the rheological measurements are influenced to a high degree by the defect density. An order parameter of $\bar{P}_2 = 0.22 \pm 0.025$ which was induced in the 38% gel by steady shear at $\omega = 6$ rad s^{-1} was found to relax to zero over a period of 90 min. On cessation of shear, $\bar{P}_2$ did not relax monotonically, oscillations noted as a function of time may be due to banded textures formed during the relaxation process.

In summary, we have shown that the extraction of the orientational order parameters from SAXS patterns provides a method by which orientation of diblock copolymer gels can be quantified, using data for the hexagonally packed rod phase of $E_{40}B_{10}$ diblock copolymer gels. Additionally, we have shown how this technique allows relaxation processes in the gels, which are not obvious to the eye from the SAXS data, to be studied. Related to the present work, we have studied in more detail the effect of shear rate and strain amplitude on the orientational ordering of the rods hex phase of a different poly(oxyethylene)/poly(oxybutylene) gel[26].

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