

A shear induced transition of lamellar alignment in a concentrated diblock copolymer solution

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Abstract

The effect of shear on the alignment of the lamellar phase in a concentrated aqueous salt solution of a poly(oxyethylene) and poly(oxybutylene) diblock copolymer is investigated in situ using small-angle X-ray scattering (SAXS). The alignment of the lamellae is deduced from the anisotropy of the scattering patterns. It is found that the orientation of the lamellae with respect to the shear direction alters with an increase in the shear rate: the lamellae are oriented transverse to the shear direction at low shear rates, and perpendicular to the vorticity direction at high shear rates. The transition between the two lamellar alignments occurs at a critical shear rate in the range: $10 \text{ s}^{-1} < \dot{\gamma}_c < 100 \text{ s}^{-1}$. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The effect of shear on ordered microphases in block copolymer melts and solutions has aroused much recent interest [1]. A particular focus has been the effect of the shear rate and amplitude on the orientation of the lamellar phase. Koppi et al. [2] found that two orientations could be accessed in a poly(ethylene–propylene)–poly(ethylene) (PEP–PEE) diblock melt subjected to large amplitude oscillatory shear depending on the shear rate and temperature. Either perpendicular (lamellar normal along the neutral or vorticity direction) or parallel (lamellar normal along the direction of the shear gradient) orientations were observed, (see Fig. 1). A perpendicular orientation was obtained at high frequencies and high temperatures, the parallel orientation, believed to result from defect-mediated growth, was obtained otherwise [2]. The transverse orientation, which corresponds to the lamellar normal along the shear direction, is the least favourable state, and is unstable for low molecular weight diblock melts. A schematic representation of the three available orientations of the lamellae relative to the shear direction is given in Fig. 1.

The transverse orientation was observed for poly(styrene)–poly(isoprene) (PS–PI) diblock melts of intermediate molecular weight by Zhang and Wiesner [3]. They deduced this orientation using small-angle X-ray scattering (SAXS) on samples pre-sheared at high frequency and interpreted it in terms of topological constraints because of entanglements of PI. This was also noted by Fredrickson and Bates [4] who pointed out that the mechanical contrast of PS–PI (PS unentangled, PI entangled) is distinct from that for a mechanically balanced system. Patel et al. [5] and Riise et al. [6], studying PS–PI diblocks, observed the parallel orientation at high frequency and/or low temperature and the perpendicular orientation at lower frequency and/or lower temperature. Zhang et al. [7] provide a unified picture for low molecular weight PS–PI polymers, with changes in lamellar orientation explained as a function of reduced frequency. At high frequencies, they suggest that the observed parallel orientation arises from mechanical contrast between PS and PI blocks. At intermediate frequencies, lamellar interface destruction and reorganization occurs leading to a perpendicular orientation whilst at low frequencies the interface reorients as a whole leading to a parallel orientation again [7].

These entanglements lead to reptation of the chains along the primitive path. In an ordered block copolymer melt the chains are stretched perpendicular to the interface [8],

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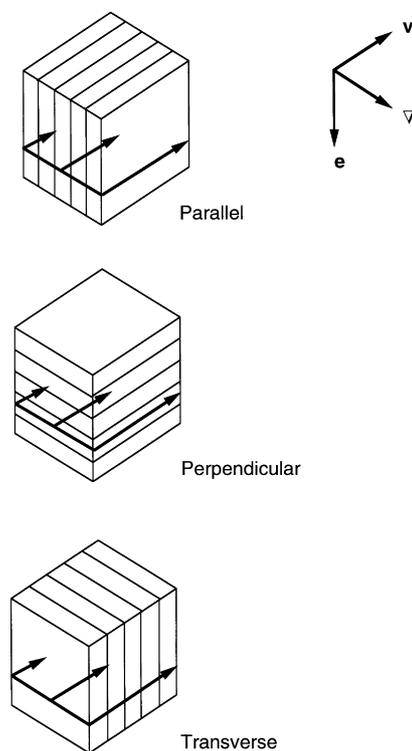


Fig. 1. Schematic representation of the three cases of lamellar orientation relative to the shear flow. The direction and relative magnitude of the shear flow are indicated by the solid arrows, and the axes of the shear direction v , the shear gradient ∇ and the vorticity axis e are also marked.

leading to preferential orientation of the tube in this direction. When the entangled diblock is subjected to shear, the primary path of the chains will thus be along the flow direction, resulting in a transverse lamellar morphology.

The evolution of microstructural orientation in block copolymers was studied in real time by Kornfield and coworkers using birefringence measurements on PS–PI [9] and PEP–PEE [10] diblocks sheared in situ. The birefringence was measured using laser light incident along the vorticity direction or velocity gradient direction in planar shear geometry, and this could be directly correlated to changes in the dynamic mechanical properties. Kornfield et al. observed that the flow process leading to the parallel alignment was associated with inhomogeneous deformation, such that ordered domains in the polymer were rocked irreversibly into the aligned structure. In contrast, the process that produces perpendicular orientation occurs under conditions in which the deformation was nearly homogeneous [9]. Recent work by this group has focused on alignment in a symmetric PS–PI diblock, using the same technique [11]. It was found that at high frequencies a parallel alignment was obtained, whereas at lower frequencies the perpendicular orientation resulted, in contrast to the results of Koppi et al. [2] on PEP–PEE diblocks. At high shear rates the parallel alignment of the lamellae were reasoned to grow from a transient bimodal texture, whilst at lower shear rates larger scale relaxations caused

rearrangements out of the shear plane, which resulted in perpendicular alignment of the lamellae [11]. The transverse alignment of lamellae to the shear direction, which is the least stable orientation, may be accessible for cases where the fluctuations arising from the applied deformation are fast enough to couple with the layered structure to produce alignment of the lamellae, but also slow enough not to be overcome by conformational distortion of the polymer chains [11].

A biaxial lamellar structure consisting of co-existing parallel and transverse orientations was observed using SAXS on a sheared PS–PEP diblock by Okamoto et al. [12], and in a PS–PI diblock by Zhang and Wiesner [3]. Polis and Winey [13] used TEM to investigate a biaxial morphology in a sheared PS–PEP sample, where kink bands were observed between parallel and transverse lamellae.

Much less work has been conducted on the alignment of the lamellar phase in diblock copolymer solutions. Balsara et al., working with concentrated solutions of PS–PI in dicetylphthalate, showed that oscillatory shear resulted in the lamellar planes becoming highly oriented parallel to the shear direction [14]. The orientation of the lamellae was deduced from small-angle neutron scattering (SANS) patterns, with the beam incident either radially or tangentially to a Couette shear cell [14]. By performing comparative oscillatory and steady state shearing studies they also demonstrated that, at temperatures close to the order–disorder transition temperature (ODT), oscillatory shear results in parallel orientation of the lamellae, and proposed that steady shear resulted in a coexistence of mutually orthogonal parallel and perpendicular states [15]. In a more recent work they showed that, under the application of reciprocating shear, the orientation of the lamellae flips from a well ordered perpendicular orientation to a poorly ordered parallel orientation, at a critical shear rate γ_c : $0.16 \text{ s}^{-1} < \gamma_c < 1.3 \text{ s}^{-1}$ [16]. The diblock solution then remained in the latter configuration irrespective of alterations in the applied shear rate, demonstrating that the poorly ordered (parallel) lamellar orientation was the more stable [16].

This study focuses on the effect of shear on the orientation of the lamellar phase formed in a concentrated block copolymer solution. The system studied is an EB diblock where E denotes the hydrophilic oxyethylene unit, OCH_2CH_2 and B denotes the hydrophobic oxybutylene unit $\text{OCH}_2\text{CH}(\text{C}_2\text{H}_5)$ in aqueous salt solution. The diblock copolymer solution is subjected to steady shear, and the alignment of the lamellae with respect to the shear direction which are exhibited by the diblock copolymer solutions is studied as a function of the applied shear rate.

2. Experimental

The material utilized in this work was the diblock $\text{E}_{18}\text{B}_{10}$, where the subscripts denote the number of repeats, in a

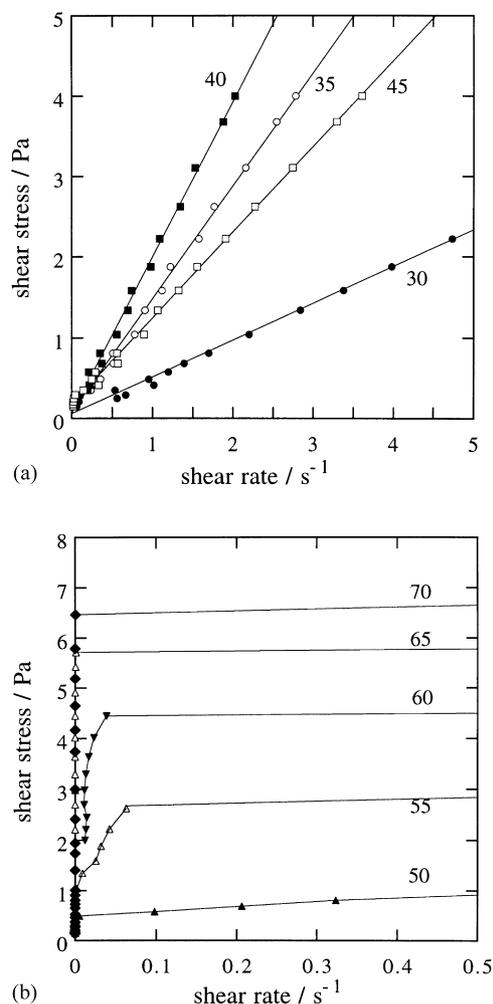


Fig. 2. Shear stress versus applied shear rate for a 35 wt.% E₁₈B₁₀ diblock copolymer in 0.2 mol dm⁻³ aqueous K₂SO₄ solution, measured in a Couette cell rheometer at temperatures as marked.

solution of 0.2 mol dm⁻³ aqueous K₂SO₄. The block copolymer was synthesized at the laboratories of the Dow Chemical Company in a manner previously described [17], and was used as received. Its composition has been variously described within the range from E₁₈B₉ to E₂₀B₁₀, possibly depending on batch, but more likely because of experimental uncertainty in its characterization. Its micellization behaviour and the properties of its micellar solutions, as revealed by surface tension and dynamic light scattering, have been reported [18,19]. Solutions were prepared by mixing 35 wt.% of copolymer in 0.2 mol dm⁻³ aqueous K₂SO₄ at 40°–50°C, followed by several days storage in a refrigerator.

Rheological characterization of the E₁₈B₁₀ copolymer solution is determined by measuring the yield stress of the solution as a function of an applied shear rate, using a Bohlin CS50 rheometer with Couette geometry. The stator is of 27 mm height and 24.5 mm diameter, and the rotor is of 29 mm height and 26.5 mm diameter, providing a gap of 1 mm. Approximately 2.5 cm³ sample material was added

to the Couette cell and measurements of shear stress and viscosity were made with the instrument in constant shear mode. Temperatures studied are between 30°C and 70°C and 5–10 min were allowed at every temperature for the temperature to reach equilibrium, before measurements were taken.

The continuous shear experiments, monitoring the orientation of the lamellae, were performed on the high brilliance beamline ID2 at the European Synchrotron Radiation Facility at Grenoble, France [20]. The X-ray beam, of wavelength $\lambda = 0.764 \text{ \AA}$, had a cross section of 0.2 mm diameter at the sample, and a two-dimensional gas filled detector with 512×512 pixels was employed to collect the scattered X-rays. The data were acquired using a specially constructed Couette cell constructed from aluminium, which has been described previously [21]. The gap between the stator and the rotor was 0.5 mm, and samples were studied with the application of continuous shear at shear rates between $\dot{\gamma} = 0.1$ and 500 s^{-1} .

The geometry of the Couette cell is such that either the ‘radial’ or the ‘tangential’ projections were probed. For the purposes of this work, the nomenclature ‘radial’ refers to cases where SAXS patterns are collected with the X-ray beam travelling normal to the plane containing the shear flow direction \mathbf{v} and the vorticity direction \mathbf{e} , (here $\mathbf{e} \equiv \nabla \times \mathbf{v}$). This is realized experimentally as the case where the X-ray beam passes through the centre of the Couette cell. Similarly the nomenclature ‘tangential’ refers to cases where SAXS patterns are collected with the X-ray beam travelling normal to the (∇, \mathbf{e}) plane. Experimentally this is realized when the X-ray beam passes between the stator and rotor at the edge of the cell.

3. Results and discussion

The diblock E₁₈B₁₀ has a rich phase behaviour [22], and we have used rheology and SAXS to map regions of ordered mesophase stability. Here we focus on a solution with a fixed concentration, 35 wt.% polymer, that forms a disordered micellar phase at low temperature and a lamellar phase at high temperature. The boundary between these phases was located using constant stress viscometry, whilst SAXS was used to identify the structures.

The shear stress of the E₁₈B₁₀ copolymer solution as a function of the applied shear rate in a cone and plate geometry is shown in Fig. 2. It can be seen from the figure that, for temperatures below 50°C, the rheological behaviour is Newtonian, characteristic of a liquid phase. At temperatures of 50°C and higher, the yield stress of the solution is finite, indicating the presence of structure. SAXS patterns from the solution at low temperatures contain a broad isotropic halo consistent with a liquid phase. There is some evidence for additional weak oscillations in the scattered intensity at higher angles, consistent with the form factor of micelles. Thus this phase is identified as a micellar solution. SAXS

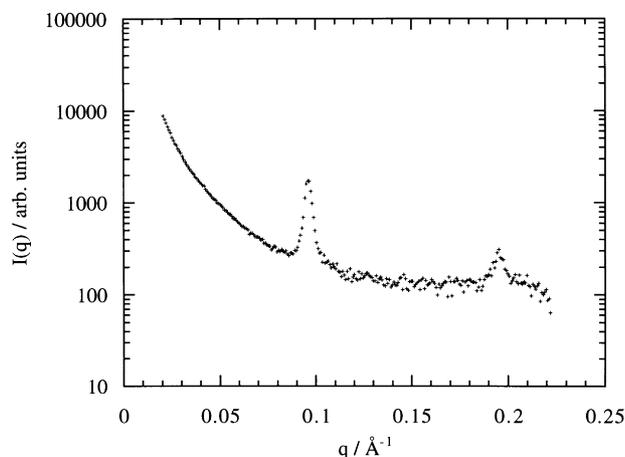


Fig. 3. Intensity profile obtained by radial integration of a two-dimensional SAXS pattern of the lamellar phase of a 35 wt.% $E_{18}B_{10}$ diblock copolymer in 0.2 mol dm^{-3} aqueous K_2SO_4 solution at 65°C .

patterns obtained at 65°C indicate a lamellar phase, with the relation between the first and second diffraction peaks being $q^* : 2q^*$, where q^* is used to define the position of the first order scattering peak. This information is shown in Fig. 3, where a two-dimensional SAXS pattern has been reduced to a one-dimensional form by a radial summing of the intensity distribution in order to enhance the signal to noise ratio. Thus the copolymer solution is shown to undergo a disorder–order transition (DOT) from a liquid phase to a high temperature lamellar phase, at around 50°C .

We now consider the orientation of the lamellar phase as a function of shear rate. Studies of the lamellar orientation of the $E_{18}B_{10}$ copolymer solution are performed at 65°C , 15°C above the DOT, at various shear rates, Azimuthal intensity profiles, obtained by integrating over a narrow band of reciprocal space centred on q^* , are extracted from typical SAXS patterns. Each of the SAXS patterns was collected during shear following a pre-shear treatment for 2 min to ensure a steady state condition. Here the deformation unit τ is the dimensionless quantity defined as: $\tau = \gamma t$, for a shear deformation of shear rate γ (s^{-1}) and duration time t (s). Balsara and co-workers discovered that lamellar phases of concentrated PS–PI diblock copolymers in solution exhibit transitions in the microstructure of the lamellar arrangements during shearing when sheared for less than 5000 deformation units, and thus conclude that initial lamellar configurations which are observed may well be transient states [15]. However some of the solutions studied in this work were deformed for 60 000 deformation units, and the lamellar alignment which was seen initially were maintained throughout that time.

Data are presented for both the radial and tangential aspects (Fig. 4) and in both cases the data are normalized to the static profile. The normalization process removes potential artefacts from the patterns, such as any alignment which might be imparted to the copolymer solution from the loading of the Couette stator.

For the case of the two lower applied shear rates: 1 and 10 s^{-1} , the radial aspect reveals two-fold anisotropy with equatorial maxima, whilst the tangential aspect reveals no discernible anisotropy in the scattering profile (Fig. 4). This suggests that the lamellar planes were oriented transverse to the shear direction (Fig. 1). For the case of the two higher applied shear rates: 100 and 500 s^{-1} , a clear transition is seen in the orientation of the lamellae. Both aspects show meridional maxima, (Fig. 4), indicating that the lamellae were aligned normal to the vorticity direction, i.e. in the perpendicular alignment (Fig. 1). In order to emphasize the anisotropy, meridional and equatorial profiles are extracted from the two-dimensional SAXS pattern obtained during shear at 500 s^{-1} , and shown in Fig. 5. Fig. 5 indicates that the meridional peak is three times more intense than the equatorial peak in the radial projection, whilst the meridional and equatorial peaks are of very similar intensity in the tangential projection. Thus the assignment of a preferential ordering of the lamellae, (in the perpendicular orientation), is confidently established.

The observation that the lamellae were oriented transverse to the shear direction at low shear rates, has not been witnessed previously in other diblock copolymer solutions. In addition, its observation is notable given that this is the least favoured orientation [11], although the combination of SAXS patterns in two orthogonal planes clearly indicates this orientation. This alignment arises because flow in this case involves transport of copolymer chains across the lamellar interface, i.e. into unfavoured domains where the hydrophobic block is brought into contact with the aqueous environment. The observation that the lamellae were oriented perpendicular to the vorticity direction at high shear rates is in agreement with the observations made by Koppi and co-workers for PEP–PEE block copolymer melts [2], but contrasts with the parallel orientation observed at high frequencies for PS–PI diblock melts [7,9]. In addition, the observation that two different orientation states can be accessed at the same temperature, and can be selected by an alteration in the applied shear rate is in accord with earlier results [2,7,9], although in these other cases transitions were observed between parallel and perpendicular orientations.

Our results also show that the perpendicular orientation of the lamellae is the condition reached above a critical shear rate, which for our system is in the range: $10 \text{ s}^{-1} < \gamma_c < 100 \text{ s}^{-1}$. Maring and Wiesner observed a critical shear rate for a transition from parallel to perpendicular orientation of the lamellar phase of a diblock melt subjected to oscillatory shear which was strain dependent [23]. At the highest strains, which provide the closest comparison to the continuous shear case employed here, the critical shear rate approached a value of $\gamma_c = 1 \text{ s}^{-1}$, although a further increase in shear rate resulted in a recovery of the parallel orientation at shear rates above 100 s^{-1} [23]. It remains possible, therefore, that a further increase in applied shear rate beyond that which was accessible on the $E_{18}B_{10}$ solution

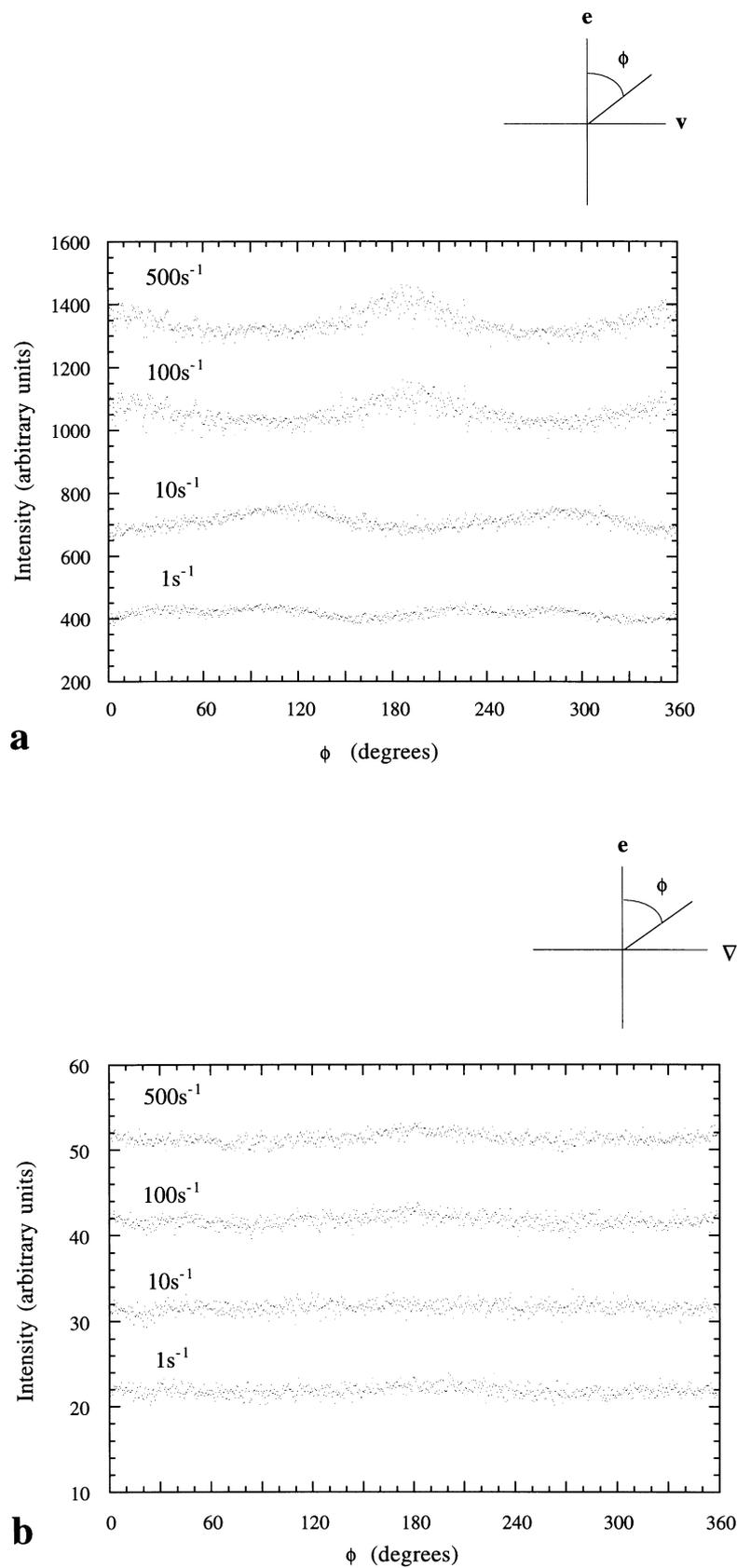


Fig. 4. Azimuthal profiles of the scattering intensity from an $E_{18}B_{10}$ diblock copolymer solution sheared in the lamellar phase at 65°C with shear rates as indicated; in the (a) radial and (b) tangential aspect. The intensity profiles have been shifted vertically for clarity.

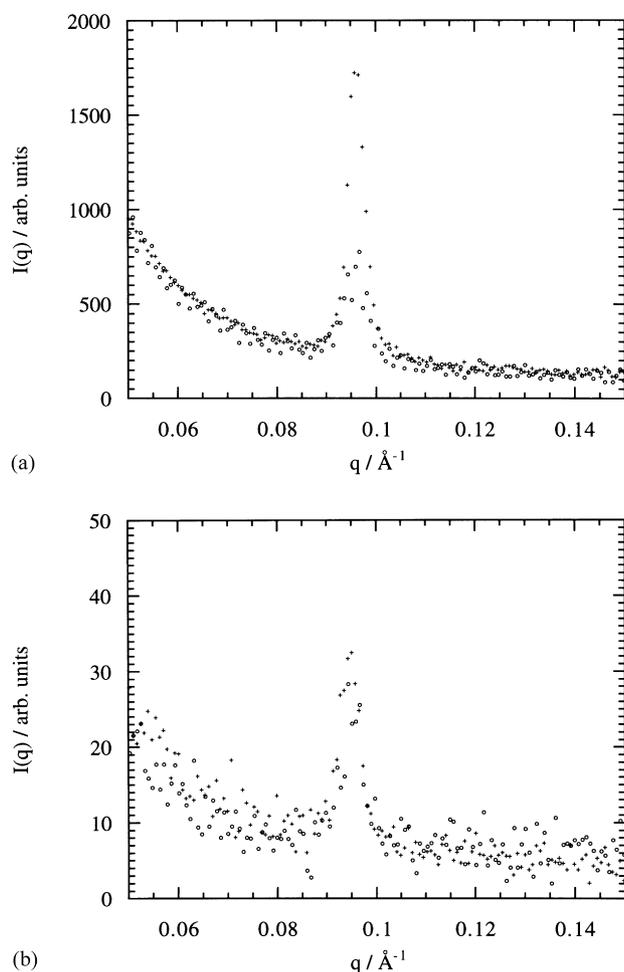


Fig. 5. Equatorial (o) and meridional (+) profiles extracted from SAXS patterns of an $E_{18}B_{10}$ diblock copolymer solution sheared in the lamellar phase at 65°C at a shear rate of 500 s^{-1} ; in the (a) radial and (b) tangential aspect.

studied here might produce a distinct lamellar orientation (parallel or perpendicular).

4. Conclusions

It has been shown that the application of shear results in macroscopically ordered samples of the lamellar phase of the diblock copolymer $E_{18}B_{10}$ in high concentration aqueous salt solution, 15°C above the disorder–order transition temperature. These macroscopic alignments are observed in situ during shear from the development of anisotropy in small-angle X-ray scattering (SAXS) patterns. The SAXS patterns reveal that the orientation of the lamellae with

respect to the shear direction can be selected by alteration of the rate of applied shear: lamellae are oriented transverse to the shear direction at low shear rates, and perpendicular to the vorticity direction at high shear rates. The transition between the two lamellar alignments occurs at a critical shear rate in the range: $10\text{ s}^{-1} < \dot{\gamma}_c < 100\text{ s}^{-1}$.

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