

Mesoscopic crystallography of shear-aligned soft materials

I. W. Hamley,^{a*} V. Castelletto,^a O. O. Mykhaylyk^a and A. J. Gleeson^b

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^aDepartment of Chemistry, University of Leeds, Leeds LS2 9JT, UK, and ^bSynchrotron Radiation Source, CLRC Daresbury Laboratory, Warrington WA4 4AD, UK. Correspondence e-mail: I.W.Hamley@chem.leeds.ac.uk

The development of a novel device for examining the three-dimensional structure of shear-aligned soft materials using small-angle X-ray scattering is reported. Following alignment *via* oscillatory shear, the shear plates are fixed together and the whole assembly mounted on a miniature goniometer placed within the oven of the rheometer. It is then possible to perform two-axis crystallography, rotating around the shear direction, and tilting with respect to this axis. Preliminary results are presented that highlight the information on aligned block copolymer nanostructures that can be accessed using the goniometer. Diffraction patterns obtained from a shear-aligned hexagonal close-packed micellar structure formed in an aqueous solution of an amphiphilic diblock are discussed, as well as those of the metastable hexagonal perforated lamellar structure formed in a diblock copolymer melt.

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1. Introduction

Soft materials such as polymer melts and gels, lyotropic liquid crystals and colloidal suspensions, are generally subjected to shear flow during processing. This flow often leads to orientation of the nano- or microstructures, and understanding the ultimate state of alignment and the pathway to it is presently the focus of much activity. Small-angle scattering of X-rays or neutrons is a powerful non-invasive technique to probe shear-induced orientation at the nanoscale.

The present paper describes a novel device that enables crystallographic studies of soft solids aligned by oscillatory shear. The sample is first subjected to large-amplitude oscillatory shear (LAOS) using a shear sandwich tool (Fig. 1*a*) within a Rheometrics RSA II rheometer, modified to allow simultaneous small-angle X-ray scattering (SAXS) experiments (Pople *et al.*, 1997; Hamley, Pople *et al.*, 1998). The X-rays are incident along the shear gradient ($\nabla\mathbf{v}$) direction so that scattering patterns in the (\mathbf{v} , \mathbf{e}) plane are obtained. The central oscillating tool is then detached from the actuator, and the whole assembly containing the shear-aligned sample is fixed together with a plate (Fig. 1*b*). This assembly is then placed on a mini-goniometer stage within the rheometer. The sample may be rotated around the shear direction (φ rotation, up to $\pm 60^\circ$, with reasonable transmission) with the possibility also to tilt (angle ω , $\pm 25^\circ$). In this way, the structure of shear-aligned 'crystals' can be examined in three dimensions. We have previously employed this technique in small-angle neutron scattering (SANS) studies of shear-induced alignment in a cubic micellar phase formed by an amphiphilic diblock copolymer (Hamley, Pople *et al.*, 1998) in a collaboration with researchers at Risø National Laboratory, who developed a system (also based on the Rheometrics RSA II rheometer) suitable for neutron scattering (Vigild *et al.*, 1998). At Risø, a shear cell mounted on a goniometer was used to probe the crystal structure of the bicontinuous gyroid structure in a diblock copolymer melt (Vigild, 1997). Because the characteristic length scale of the structures probed by small-angle scattering is typically 5–100 nm, we previously termed

this method 'mesoscopic crystallography' (Hamley, Mortensen *et al.*, 1998), although perhaps 'nanoscale crystallography' would be more appropriate nowadays.

Here, we describe the design of a shear cell/goniometer device for SAXS studies of soft materials. Representative preliminary results obtained for two ordered block copolymer structures (respectively face-centred cubic and hexagonal perforated layer) are included. These illustrate the insights into the shear-aligned structure that can only be provided when planes other than the (\mathbf{v} , \mathbf{e}) plane can be accessed.

2. Experimental

Small-angle X-ray scattering experiments were performed on station 16.1 at the Synchrotron Radiation Source, Daresbury Laboratory, UK. The wavelength λ was 1.41 Å. Data were collected on a two-dimensional gas-filled area detector (RAPID). The wavevector scale q ($= 4\pi \sin \theta / \lambda$, where θ is the scattering angle) was calibrated using a specimen of wet collagen (rat-tail tendon).

The modified Rheometrics RSA II rheometer is described in detail elsewhere (Pople *et al.*, 1997; Hamley, Pople *et al.*, 1998), and for convenience is illustrated in Fig. 2(*a*). The sample is subjected to oscillatory shear in a shear sandwich device (Fig. 1*a*) mounted within the rheometer oven (Fig. 2*a*). To enable the transmission of X-rays, the tools were made from polycarbonate. No peaks are observed in the small-angle region for this material. The transmission is inevitably reduced, by a factor of approximately two for each additional 1 mm of polycarbonate. Following shear, the central shear tool is detached from the actuator by unscrewing the L-shaped mount (Figs. 1*a* and 2*b*). The three plates in the shear sandwich are then fixed together *via* a fixing plate screwed into pre-drilled holes in the side of the polycarbonate tools (Fig. 2*c*). To enhance transmission, the fixing plate was made from polyimide film of thickness 0.5 mm. After fixing the plates, the assembly was removed from the rheometer. The actuator

post was removed and a miniature goniometer was mounted onto the transducer post. The shear cell assembly was then attached (inverted) onto a two-circle goniometer (Huber, custom built) *via* a grub screw. The tilt angle on the miniature cradle (Fig. 2c) must be set prior to closing the oven doors. The rotation angle φ can be set using the scale collar outside the oven.

3. Results

3.1. Twinned face-centered cubic structure

We have previously studied shear alignment of a close-packed structure formed in an aqueous gel of diblock $P_{94}E_{316}$ (Castelletto *et al.*, 2001). Here P denotes propylene oxide, E denotes ethylene oxide and the subscripts are numbers of repeats. This sample was mounted into the rheometer and prior to shear the diffraction pattern showed slight orientation due to compression of the sample when mounting into the shear sandwich. The first-order peak was located at $q^* = 0.0235 \text{ \AA}^{-1}$, corresponding to a cell parameter $a = 463 \text{ \AA}$ [in good agreement with the value reported previously (Castelletto *et al.*, 2001)]. LAOS was then applied. Fig. 3(a) shows the diffraction pattern obtained following shear ($T = 298 \text{ K}$, $\omega = 100 \text{ rad s}^{-1}$, $A = 45\%$) and shows essentially sixfold symmetry of reflections (higher orders were also observed, but are not shown for convenience). This sample has previously been shown to correspond to a (defective) face-centred cubic (f.c.c.) structure (Castelletto *et al.*, 2001). The shear tools were then detached from the rheometer and fixed on the goniometer as described above. The SAXS pattern obtained prior to rotation (*i.e.* $\varphi = 0^\circ$) is shown in Fig. 3(b). Some loss of orientation due to the manual handling of the sample is apparent; nevertheless, the main features are the same as those in Fig. 3(a). Rotation of the shear-aligned sample around the shear direction provides additional information on the symmetry of the structure. Fig. 3(c) shows the pattern obtained at a rotation angle $\varphi = (50 \pm 5)^\circ$. It shows four reflections at $1.15q^*$, close to the position expected for the 200-type reflections of an f.c.c. structure (space group $Fm\bar{3}m$). The angle selected is close to $\varphi = 54.7^\circ$, which corresponds to the angle between the 111 and 100 directions of a cubic structure. Therefore, these two diffraction patterns are consistent with a structure that is primarily cubic. The presence of sixfold symmetry along the 111 direction indicates that the structure does not consist solely of $ABCABC\dots$ stacked hexagonal close packed (h.c.p.) layers, but must contain some $ABAB\dots$ stacking [as discussed previously (Daniel *et al.*, 2000; Castelletto *et al.*, 2001)]. It should be noted that diffraction patterns with features intermediate between those shown in Fig. 3(a) and 3(b)

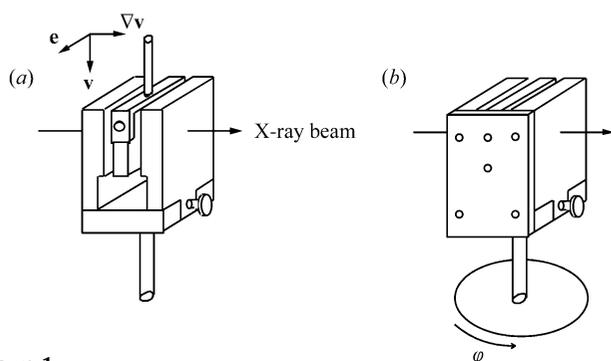


Figure 1
(a) Schematic of shear sandwich tools, made from polycarbonate to allow transmission of X-rays. (b) Following shear, the tools are inverted and placed on a miniature goniometer within the rheometer oven (see Fig. 2).

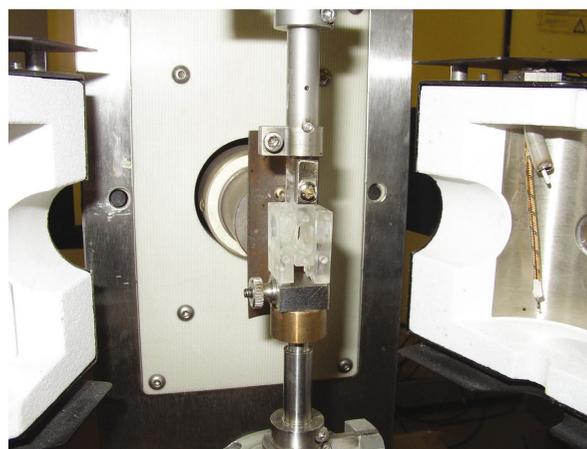
were obtained at intermediate angles, but these are not shown for reasons of clarity.

3.2. Hexagonal perforated layer structure

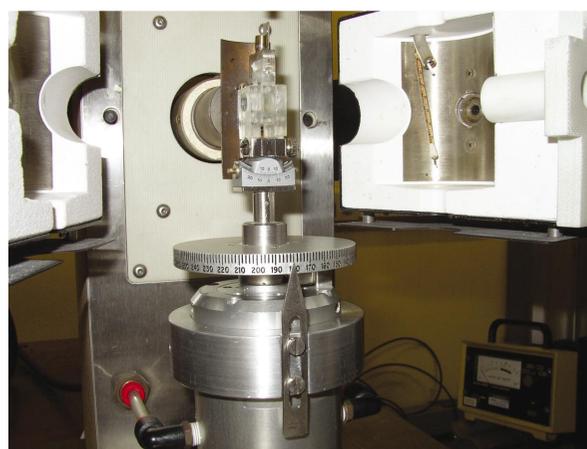
The hexagonal perforated layer (HPL) structure is known to be a non-equilibrium structure in diblock copolymer melts. However, it



(a)



(b)



(c)

Figure 2
(a) The Rheometrics RSA II rheometer *in situ* at the beamline, Synchrotron Radiation Source, Daresbury Laboratory, UK. (b) Detail of shear tools, prior to shear. (c) Inverted shear tool assembly mounted on the goniometer (the fixing plate is hidden behind the shear tools).

can be highly metastable, as illustrated by our prior work on PEP-PDMS diblocks where the growth of the equilibrium gyroid phase from the HPL phase can be extremely slow (hours or even days). In the present work, we study a blend very similar to one previously investigated (Vigild *et al.*, 1998), for which the HPL phase is found to be metastable at room temperature (where the lamellar phase is stable) (Vigild, 1997). The binary blend consists of two PEP-PDMS

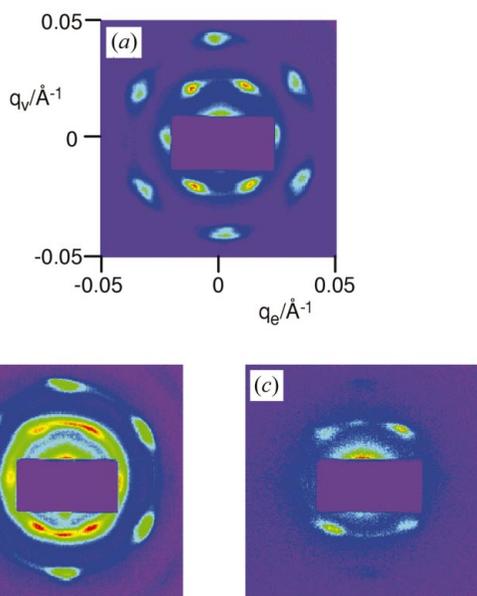


Figure 3
SAXS patterns obtained from a shear-aligned ($A = 45\%$, $\omega = 100 \text{ rad s}^{-1}$ for 5 min at $T = 298 \text{ K}$) sample of a 50 wt% gel of diblock $\text{P}_{94}\text{E}_{316}$ in water. (a) Pattern obtained following shear, prior to detachment of shear tools. (b) Pattern for sample mounted on the goniometer with a rotation angle (about the shear direction \mathbf{v}) $\varphi = 0^\circ$. (c) Pattern obtained for $\varphi = 50^\circ$.

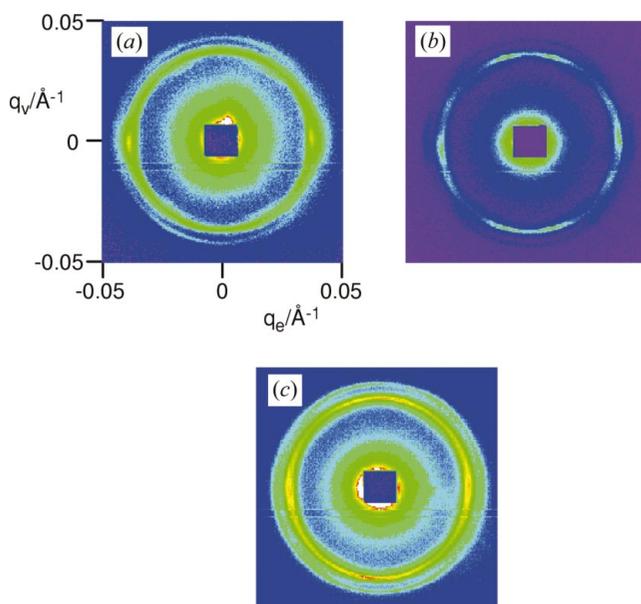


Figure 4
SAXS patterns obtained from a shear-aligned ($A = 80\%$, $\omega = 100 \text{ rad s}^{-1}$ for 10 min at $T = 333 \text{ K}$) sample of a blend of two PEP-PDMS diblocks with a volume fraction $f_{\text{PEP}} = 0.67$ (data obtained at $T = 303 \text{ K}$). (a) Pattern for the rotation angle (about the shear direction \mathbf{v}) $\varphi = 0^\circ$. (b) Pattern obtained for $\varphi = 60^\circ$. (c) Pattern upon returning to $\varphi = 0^\circ$.

diblocks [PEP = poly(ethylene propylene), PDMS = poly(dimethylsiloxane)], one with a volume fraction $f_{\text{PEP}} = 0.65$ and the other with $f_{\text{PEP}} = 0.70$. A 3:1 (by weight) mixture of these polymers has $f_{\text{PEP}} = 0.67$. In the ‘one component’ approximation (Matsen & Bates, 1995; Shi & Noolandi, 1995), we expect the phase behaviour of this blend of two closely matched diblocks to be equivalent to that of a single diblock of the same composition.

The PEP-PDMS diblock blend was subjected to LAOS ($A = 80\%$, $\omega = 100 \text{ rad s}^{-1}$) at $T = 333 \text{ K}$, corresponding to a temperature at which the HPL phase is highly metastable. Following this, the sample was cooled to 303 K , at which temperature the shear plates were fixed and mounted onto the goniometer stage. The sample was rotated from $\varphi = 0$ to 60° at various angles. Diffraction patterns corresponding to high-symmetry projections only are included in Fig. 4. Fig. 4(a) shows the pattern obtained following shear (at $\varphi = 0^\circ$). The pattern consists of two strong equatorial reflections, in addition to broad rings at the same value of q^* and at $1.1q^*$. Inside the first ring are four weak reflections ($\pm 57^\circ$ with respect to the equator) that arise from perforations within the lamellae. The origin of these reflections has been discussed in detail elsewhere (Hamley *et al.*, 1993, 1999; Förster *et al.*, 1994; Vigild *et al.*, 1998; Zhu *et al.*, 2003), and is not reiterated here. The pattern obtained upon rotation to 60° (shown in Fig. 4(b)), however, has not, to our knowledge, previously been reported. It contains ten reflections at q^* . A pattern with ten reflections at q^* in a shear-aligned diblock is often considered to be the signature of a gyroid structure (space group $Ia\bar{3}d$) (Förster *et al.*, 1994; Zhao *et al.*, 1996; Hamley, 1998; Vigild *et al.*, 1998; Wang & Lodge, 2002). However, most of the angles between the reflections in Fig. 4(b) are not consistent with allowed angles between 211 reflections (these are the first reflections for space group $Ia\bar{3}d$). Therefore, we discard the possibility that this pattern arises from a gyroid structure; rather it corresponds to a projection of a HPL structure. It has been shown elsewhere that the HPL structure corresponds to coexisting trigonal ($R\bar{3}m$) and hexagonal ($P6_3/mmc$) structures (with $ABCABC\dots$ and $ABAB\dots$ stacking of hexagonally perforated layers respectively) (Förster *et al.*, 1994; Vigild *et al.*, 1998; Zhu *et al.*, 2003). We therefore ascribe the pattern in Fig. 4(b) to such a structure. Further details of the indexation of the reflections will be provided elsewhere. Fig. 4(c) shows the pattern obtained upon rotation back to $\varphi = 0^\circ$. A pattern similar to the starting pattern is recovered, although the four weak reflections inside the inner ring appear to have disappeared. The ratio between the positions of the two diffraction rings is $1:1.15q^*$.

4. Conclusion

In summary, we have developed a novel device for crystallographic studies of soft materials, following alignment by large-amplitude oscillatory shear. The data presented from trial experiments are certainly preliminary, but we hope they illustrate the potential of the technique, which could also be used to study orientation in liquid-crystal polymers, biopolymer gels, *etc.*

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