# Effect of Shear on Diblock Copolymer Gels

**I.W. Hamley[1], J.A. Pople[1], J.P.A. Fairclough[2], A.J. Ryan[2], N.J. Terrill[2], C. Booth[3], G.-E. Yu[3] and O. Diat[4]**

1 School of Chemistry, University of Leeds (UK)
2 Department of Chemistry, University of Sheffield (UK)
3 Department of Chemistry, University of Manchester (UK)
4 ESRF, Experiments Division

*Low molecular weight block copolymers can behave as amphiphiles in solution, forming lyotropic liquid crystalline phases such as cubic micellar phases. The formation of such structures results in stiff transparent gels which have a number of technological applications for example in drug delivery.*

Of particular interest are block copolymers containing hydrophilic poly(oxyethylene) as well as a hydrophobic block such as poly(oxybutylene) or poly(oxypropylene) which are manufactured on a large scale because they behave as surfactants in aqueous solutions. Despite their industrial relevance, surprisingly little is known about phase formation in these systems, nor on the effect of shear on ordered structures which is relevant to processing. Small-angle x-ray scattering (SAXS) has been performed on the ID2 SAXS station to elucidate the effect of shear on the orientation of cubic micellar phases formed by a poly(oxyethylene)-poly(oxybutylene) diblock copolymer in aqueous solution [1,2]. Macroscopic orientation of samples was achieved by shearing in the Couette cell available on ID2 using steady shear. By translation of the Couette cell it was possible to access two orthogonal planes with either the shear direction (**v**) or shear gradient direction (∇**v**) horizontal and the vorticity direction (**e** = ∇**v** x **v**) vertical. Experiments were conducted on the diblock $E_{40}B_{10}$ (here E = oxyethylene, B = oxybutylene and the subscripts denote the number of repeats) in 0.2 M $K_2SO_4$. A body-centred cubic phase observed for gels with concentrations greater than 30 wt% copolymer was found to orient into a polydomain structure, with the close-packed {110} planes both parallel and perpendicular to the shear plane [1-3]. This is indicated by the SAXS patterns in Figure 1. For gels with 30 wt% copolymer or less, an fcc phase was observed, and this was also observed on heating the more concentrated gels that formed a bcc phase at room temperature [1-3]. The hard gel fcc phase could be oriented to form a highly twinned structure (as shown by the SAXS patterns in Figure 2), with a significant deviation from the ABCABC… stacking sequence of the ideal structure due to random stacking sequences resulting from the slip of {111} hexagonal close-packed planes. For the lower concentration solutions, a transition from hard to soft fcc gels at increasing temperatures was found to be characterized by a change in the susceptibility of the sample to macroscopic shear orientation, as probed using SAXS [2]. The hard gel could be oriented by shear into a twinned fcc structure, whereas the soft gel comprised an fcc phase with a small grain size, which could not be sheared to form a macroscopically oriented domain. Shear only homogenized the sample, producing a powder SAXS pattern [2]. ■

## References

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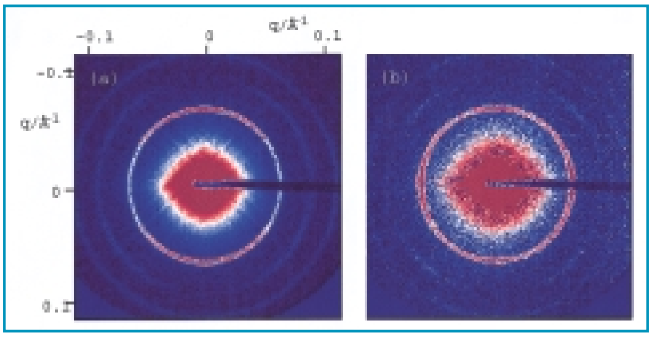
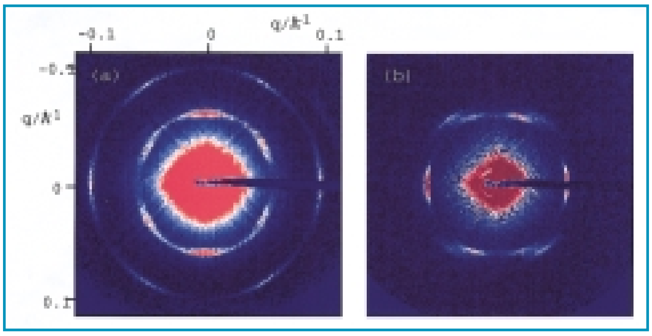
*Fig. 1: SAXS patterns for a 38 wt% solution of $E_{40}B_{10}$ in the bcc phase at 25 °C.*




*(a) ($q_v$, $q_e$) plane, during shear at $\dot{\gamma}$ = 8 $s^{-1}$, (b) $q_\nabla$, $q_e$) plane during shear at $\dot{\gamma}$ = 8 $s^{-1}$. The vorticity direction is vertical.*

*Fig. 2: SAXS patterns for a 38 wt% solution of $E_{40}B_{10}$ in the fcc phase at 52 °C.*




*(a) ($q_v$, $q_e$) plane, during shear at $\dot{\gamma}$ = 0.8 $s^{-1}$, (b) $q_\nabla$, $q_e$) plane during shear at $\dot{\gamma}$ = 0.8 $s^{-1}$. The vorticity direction is vertical.*