Chapter 53 – **SANS UNDER SHEAR**

SANS is useful for investigating structures under shear. The orientation of layered structures can be monitored by SANS using shear cells. Here, a couple of projects are described using in-situ shear cells. In-situ shear cells include the Couette type and the plate-plate geometry type.

1. SHEARED DISCOTIC LIQUID CRYSTAL MICELLES

A lyotropic mixture of cesium-perfluoro-octanoate (CsPFO) in water (55 % mass fraction) was investigated using a Couette shear cell (Mang et al, 1994; Hammouda et al, 1995). This mixture forms discotic liquid crystal micelles with a characteristic smectic-to-nematic transition temperature of 47 ^{o}C and a nematic-to-isotropic transition temperature of 52 ^{o}C.

The in-situ Couette shear cell consists of a cylindrical stator and rotor pair made out of quartz and separated by a 0.5 mm gap. The rotor diameter is 6 cm so that the sheared sample volume is around 12 ml. Its computer controlled rotation can be steady (for simple shear) or reciprocating (for oscillatory shear). Shear can be controlled up to a shear rate (or shear frequency) of 6000 Hz (note that 1 Hz corresponds to 1 rotation per second). Sample heating was performed using circulating fluid through the stator. The shear cell has two measurement configurations: one radial and one tangential. The radial configuration uses standard beam geometry with a 1.27 cm circular sample aperture diameter whereas the tangential configuration uses a vertical beam defining slit 0.5 mm in width. The oscillatory mode of operation uses 200 % strain, i.e., it oscillates by about 1 mm in each direction.

The SANS spectrum for the discotic micelles is characterized by two peaks: one at Q = 0.113 Å^{-1} and one at Q = 0.146 Å^{-1}. The first one represents the center-to-center inter-distance for micelles that lie planar in an edge-to-edge configuration while the second one corresponds to the face-to-face inter-distance for stacked disks. SANS measurements with the Couette shear cell were performed in the smectic phase at 45 ^{o}C, in the nematic phase at 49.7 ^{o}C and in the isotropic phase at 54 ^{o}C. Monitoring of the two peaks in the radial and tangential configurations gave clues as to the orientation of the discotic structures.

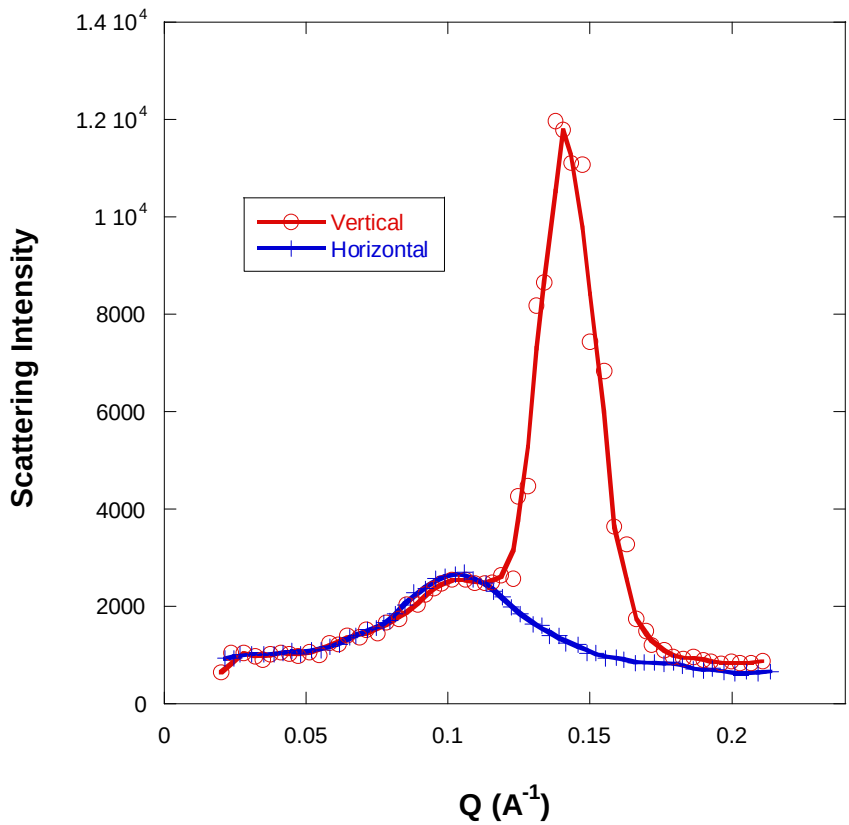

Figure 1: The two SANS peaks characterizing the discotic liquid crystal micelles structure. Vertical and horizontal sector cuts through the anisotropic SANS data are shown.

The sheared discotic micelles orient mostly parallel to the moving shear cell (rotor) walls. This is referred to as the "C alignment" type.

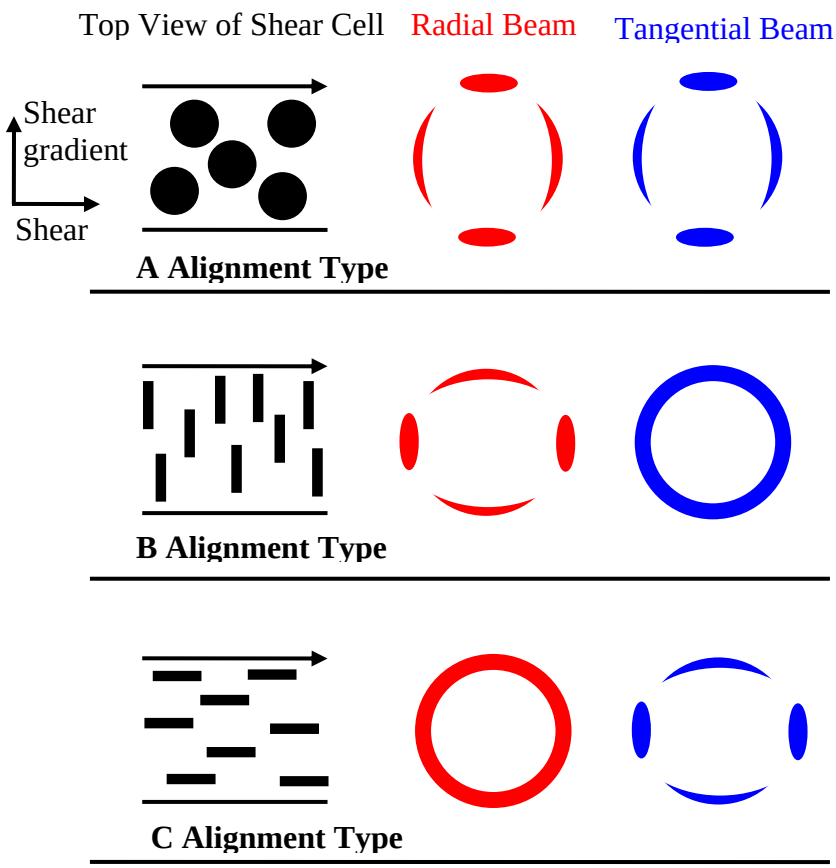

Figure 2: The three types of possible alignments as viewed using the radial and tangential configurations.

Flipping of the discotic structures occurred from the C type alignment observed in the nematic phase to the A type alignment observed in the smectic phase. The flipping transition has been observed with oscillatory shear either by varying temperature or shear rate. The flipping was not complete so that mixtures of A and C alignment types were often mixed.

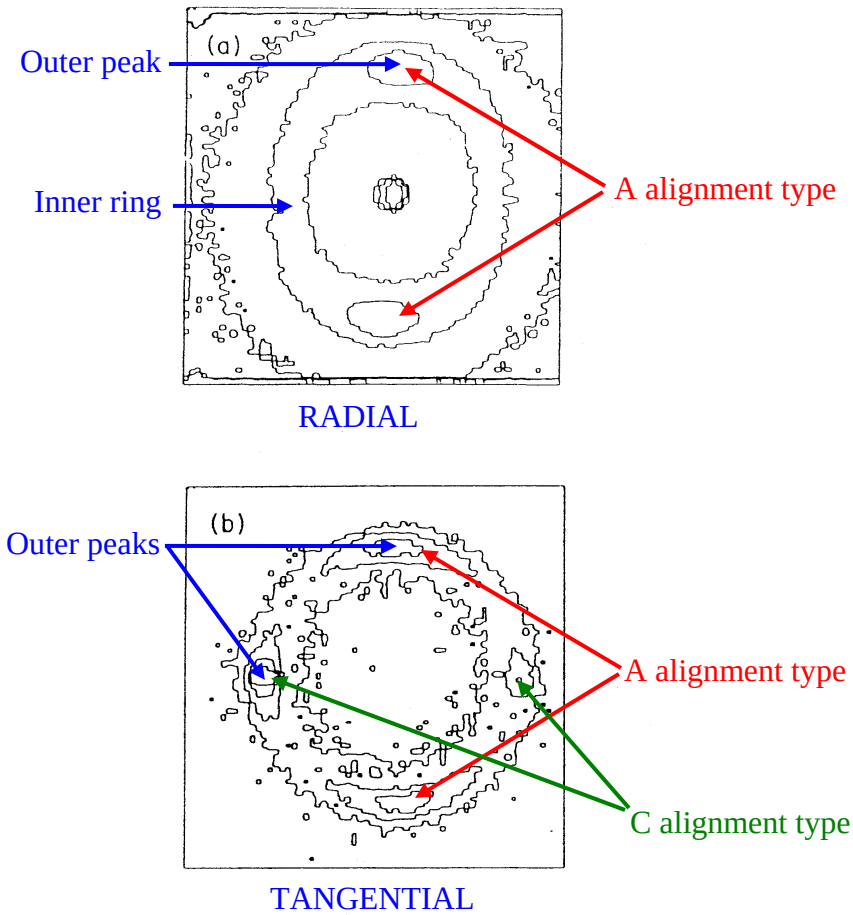

Figure 3: Iso-intensity contour plots for an oscillatory shear rate of 5835 s^{-1} at a temperature of 49.7 ^{o}C (i.e., in the nematic phase) for radial (top) and tangential (bottom) beam geometries. The top contour plot shows an inner scattering ring and two outer scattering peaks in the vertical direction pointing to the A alignment type. The bottom contour plot shows four outer scattering peaks in the vertical and horizontal directions pointing to a mixture of A and C alignment types.

When oscillatory shear is used, shear-induced shifts of the phase transition temperatures were observed. These are interpreted as shear-induced damping of critical fluctuations that become stronger close to phase boundary lines. Moreover, interesting competing "bulk" and "wall" effects have also been observed. These effects were seen by changing the shear cell sample gap (from 0.5 mm to 1 mm).

2. SHEARED COPOLYMER LAMELLAE

Diblock copolymers form lamellar, cylindrical and spherical morphologies. Lamellar morphologies are amenable to investigations under shear. A polystyrene-polyisoprene (SI) diblock copolymer in concentrated DOP solution was investigated under Couette shear (Balsara-Hammouda, 1994; Balsara et al, 1994). The diblock molecular weights

were M_w = 11,000 g/mol for the styrene block and M_w = 17,000 g/mol for the isoprene block. This corresponds to a lamellar morphology. DOP solvent was added (65 % polymer fraction) in order to lower the order-disorder temperature (ODT) to an easily reachable value of 38 ^oC. Scattering from the SI diblock is characterized by a peak at Q = 0.032 $Å^{-1}$. Monitoring of this peak in the vertical and horizontal directions with radial or tangential beam configurations provides helpful clues to determine the lamellar orientation in each case.

The diblock thermal history was "erased" in each case by heating the sample above the ODT. The temperature was lowered before starting the shear. Some of the observations follow. Couette shear can orient the diblock lamellae even above the ODT as shown on an azimuthally averaged SANS data. This is due to a shear-induced shift of the phase boundary.

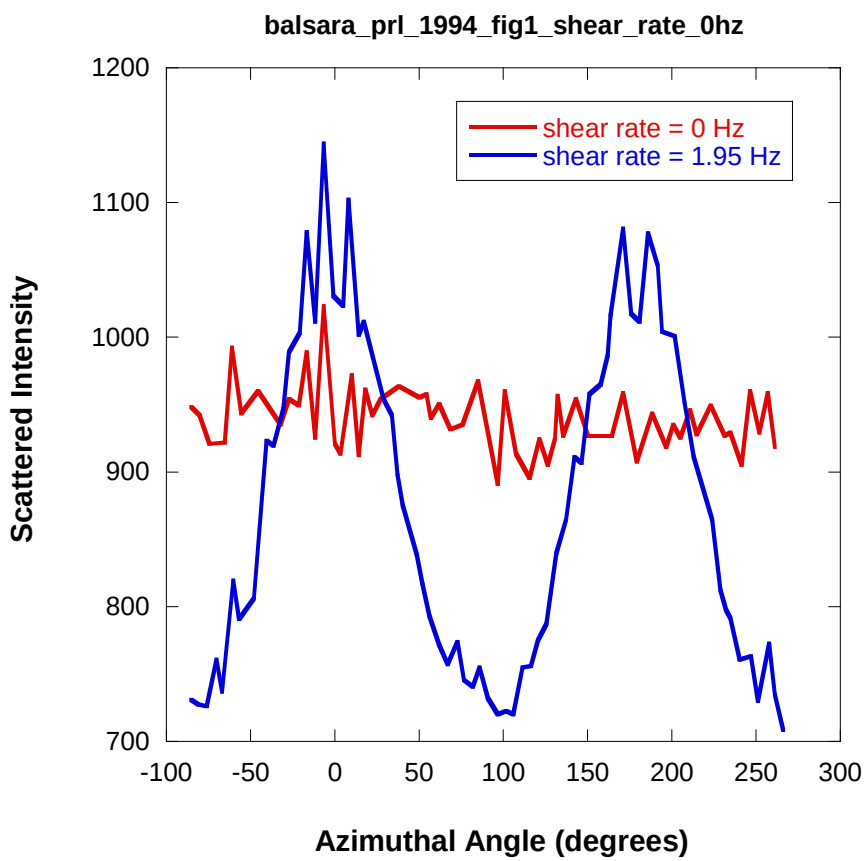

Figure 4: Effect of shear on azimuthally averaged SANS profiles obtained at 43 ^oC, i.e., above the quiescent ODT. The zero degree orientation is along the vertical axis.

The shear-induced orientation occurs above a critical shear rate $\dot{\gamma}_c$. The lamellar orientation is quantified through an anisotropy ratio ρ (ratio of the intensities in the vertical and horizontal directions). This ratio is seen to follow a universal behavior when plotted *vs* the scaled Couette shear rate $\dot{\gamma}/\dot{\gamma}_c$. Curves corresponding to different

temperatures fall on a same master curve represented by $\rho \sim (\dot{\gamma}/\dot{\gamma}_c)^{0.19}$. This is reminiscent of the time-temperature superposition principle for polymer melts in the rubbery region.

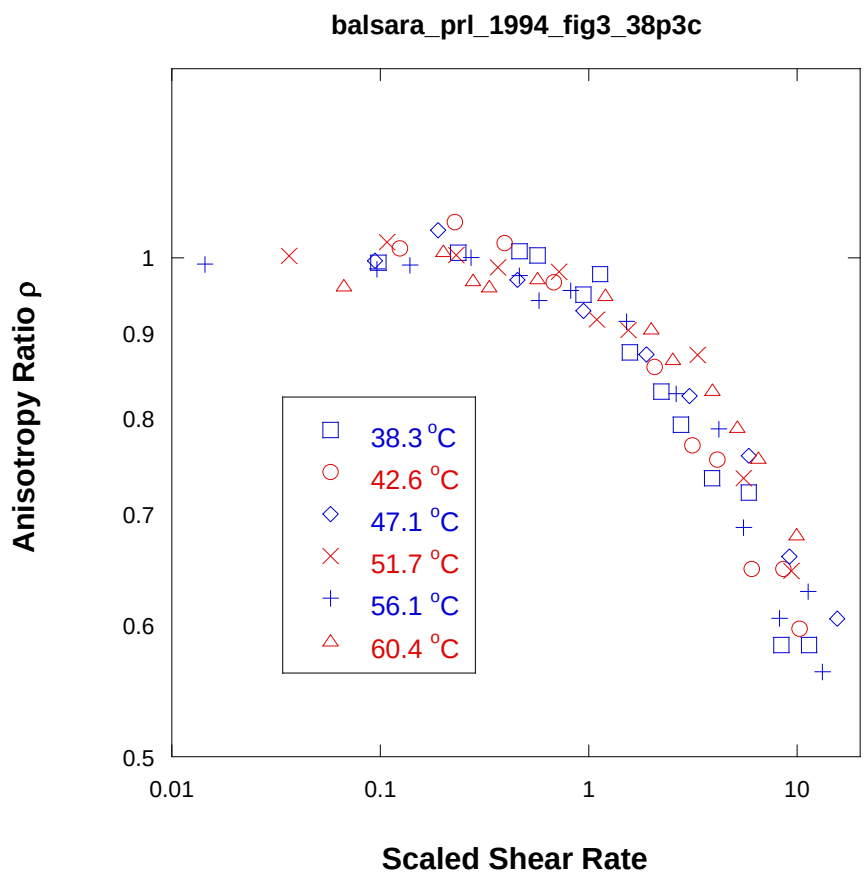

Figure 5: Master curve for the dependence of the peak anisotropy ρ with increasing scaled shear rate $\dot{\gamma}/\dot{\gamma}_c$ for various temperatures.

A 3D map of the SANS data under shear with the radial and tangential beam geometries leads to the following conclusions. The lamellar morphology is not perfect and contains lamellar "crumples" or "ripples" that are seen in the radial geometry (vertical peaks). The much higher intensity horizontal peaks in the tangential geometry show that the lamellae themselves are oriented mostly parallel to the shear cell walls (C type alignment).

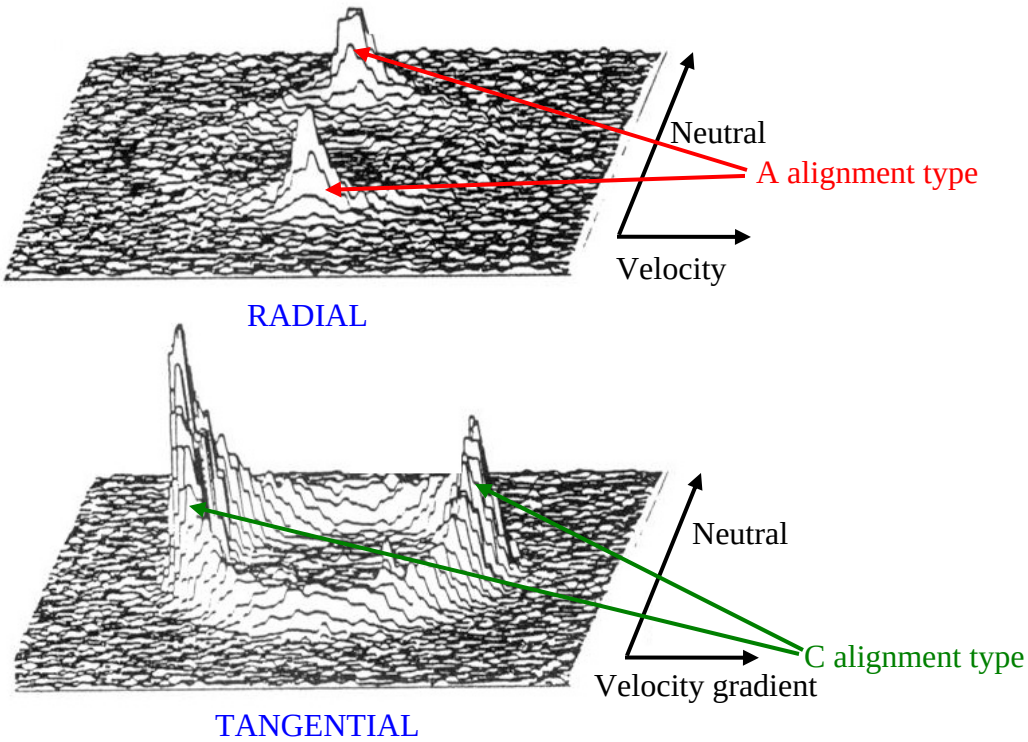

Figure 6: SANS iso-intensity contour plots obtained at ambient temperature (25 ^{o}C) and for a simple shear rate of 0.2 s^{-1} for the radial configuration (top) and tangential configuration (bottom). Note that the scattering volume is not uniform for the tangential configuration resulting in non-uniform peak heights.

Oscillatory shear produces lamellar alignment of the C type. Steady shear on the other hand produces lamellar alignment of the C type at high shear rates and of the A type at low shear rates. This is the "flipping" transition discussed before. The kinetics of lamellar flipping are characterized by time scales taking up to 90 minutes (Wang et al, 1999).

3. PLURONICS UNDER SHEAR

Pluronics are triblock copolymers of the type PEO-PPO-PEO containing poly(ethylene oxide) and poly(propylene oxide) blocks. They form micelles in water. P85 Pluronic forms spherical micelles in d-water in the mass fraction range of 25 % or 30 % (used here) and for temperatures above 20 ^{o}C. SANS investigations have been performed using SANS and the Couette shear cell. Interesting shear-induced texture of the packed spheres structure was observed (Slawecki et al, 1998). For example, a novel shear-induced structure with 2D hexagonal symmetry was observed. The unit cell of this "crystalline" structure was determined to be characterized by a = b=133 Å and c = 209 Å. This structure changes upon shear cessation.

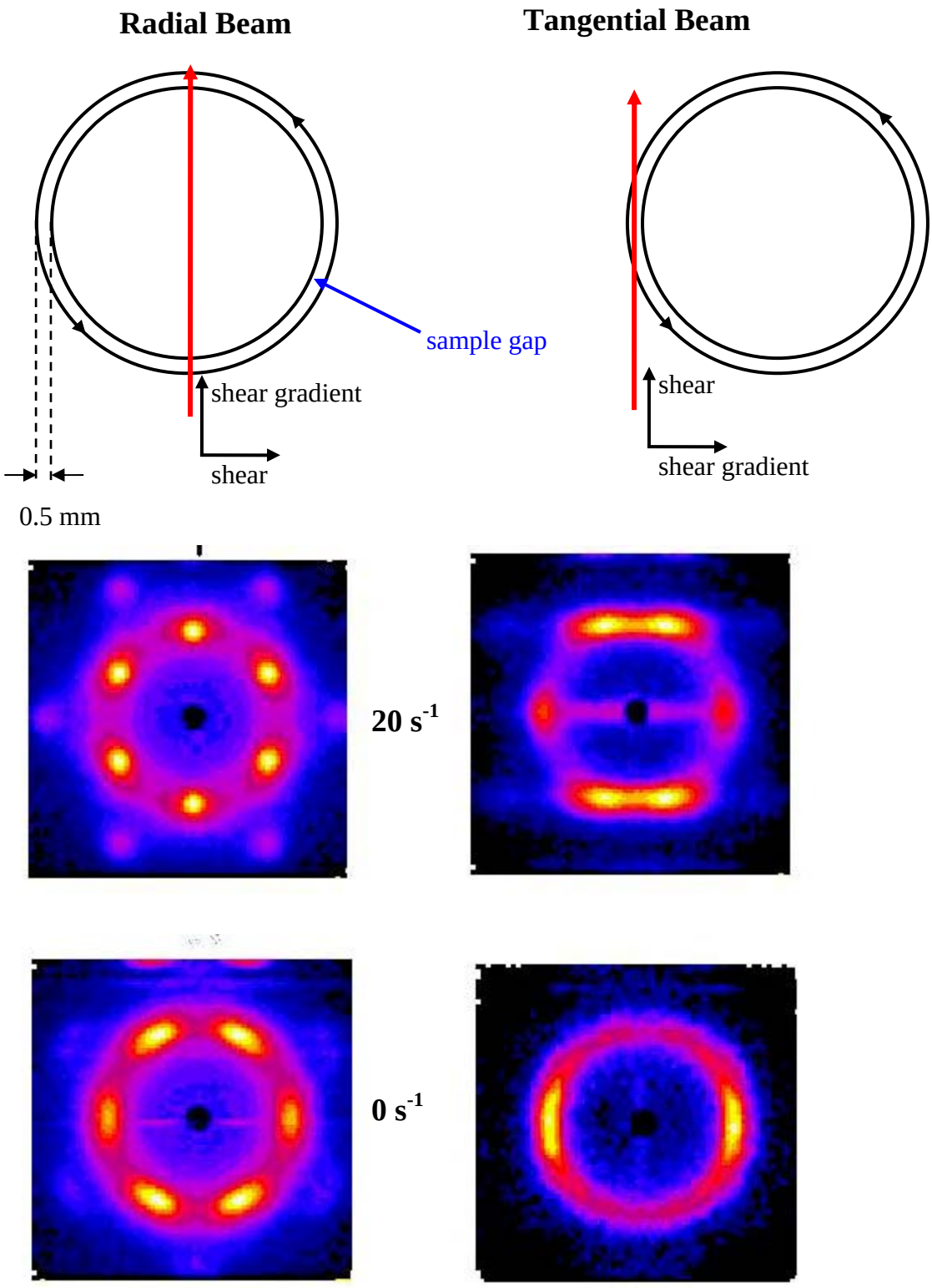
Radial Beam
Tangential Beam
sample gap
shear gradient
shear
0.5 mm
shear
shear gradient
20 s-1
0 s-1

Figure 7: SANS patterns from 25 % P85 in d-water under steady shear (20 s^{-1}) and after shear cessation. The left and right sides are for the radial and tangential beam geometries respectively. The schematics on the top show the Couette shear cell flow geometry.

4. MIXED COPOLYMER MORPHOLOGIES UNDER SHEAR

Individual lamellar and spherical copolymer morphologies have been investigated extensively under shear. A question comes to mind: what morphologies would be obtained when mixing samples with lamellar and spherical morphologies together? The answer to this question is addressed here.

The plate-plate shear cell is well suited for SANS investigations of sheared copolymers. It consists of sandwiching the copolymer sample in-between a sliding plate and a fixed one. The shear rate (or frequency) and the strain (or travel distance) are controlled. Note the three characteristic directions: shear, shear gradient and neutral.

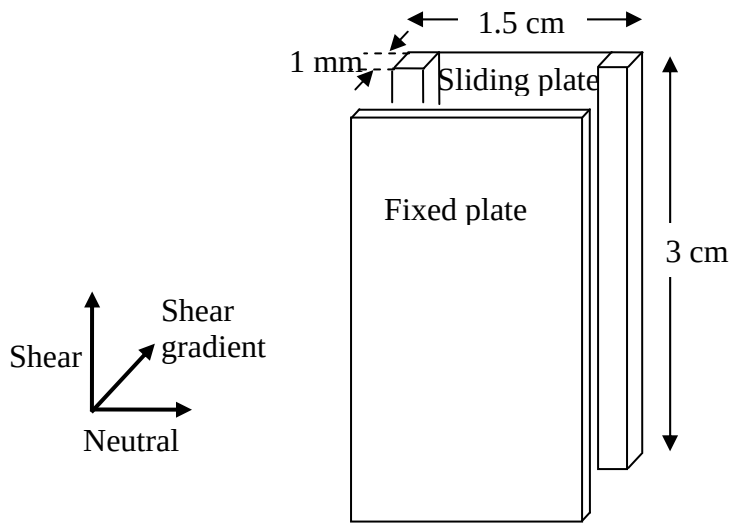

Figure 8: The plate-plate shear cell used for copolymers.

Asymmetric copolymer samples characterized by lamellar and spherical morphologies were homogeneously mixed and then investigated by SANS with in-situ plate-plate reciprocating shear. Two separate copolymers were measured (1) block copolymers of polystyrene and poly(ethylene-butene-1) (Krishnamoorti et al, 2000) and (2) block copolymers of polystyrene and polyisoprene (PS-PI) (Krishnamoorti et al, 2000).

Shearing at various temperatures (below the ODT) helps orient the sample morphology yielding scattering peaks in the horizontal and vertical directions. Two geometries were used (1) with a circular neutron beam along the shear gradient direction or (2) with a (vertical) slit-defined neutron beam along the neutral direction. Note that lamellae are characterized by a series of reflections at Q*, 2Q*, 3Q* where Q* is the first reflection.

Cylinders are characterized by Q*, $\sqrt{3}$ Q*, $\sqrt{4}$ Q* while spheres are characterized by Q*, $\sqrt{2}$ Q*, $\sqrt{3}$ Q*. Monitoring the first couple of peaks gives clues as to the sample structure.

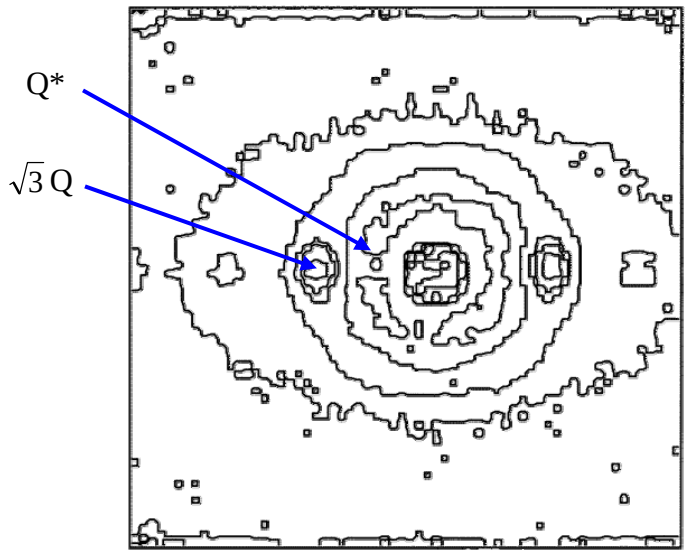

Figure 9: Shear aligned copolymer sample with cylindrical morphology characterized by a hexagonally close packed structure for cylinders aligned vertically with peaks at Q*, $\sqrt{3}Q*$, etc. The neutron beam is parallel to the shear gradient direction.

This technique yields a wide range or possible morphologies obtained by mixing lamellae and spheres. These include spherical, lamellar and cylindrical morphologies among others. Temperatures above the order-to-disorder temperature (ODT) correspond to the disordered phase whereas those below the ODT correspond to ordered phases. These SANS results were verified using rheology. Simple ideal mixing predictions are far from what was observed experimentally. Two copolymers characterized by different morphologies seem to follow non-ideal mixing behavior.

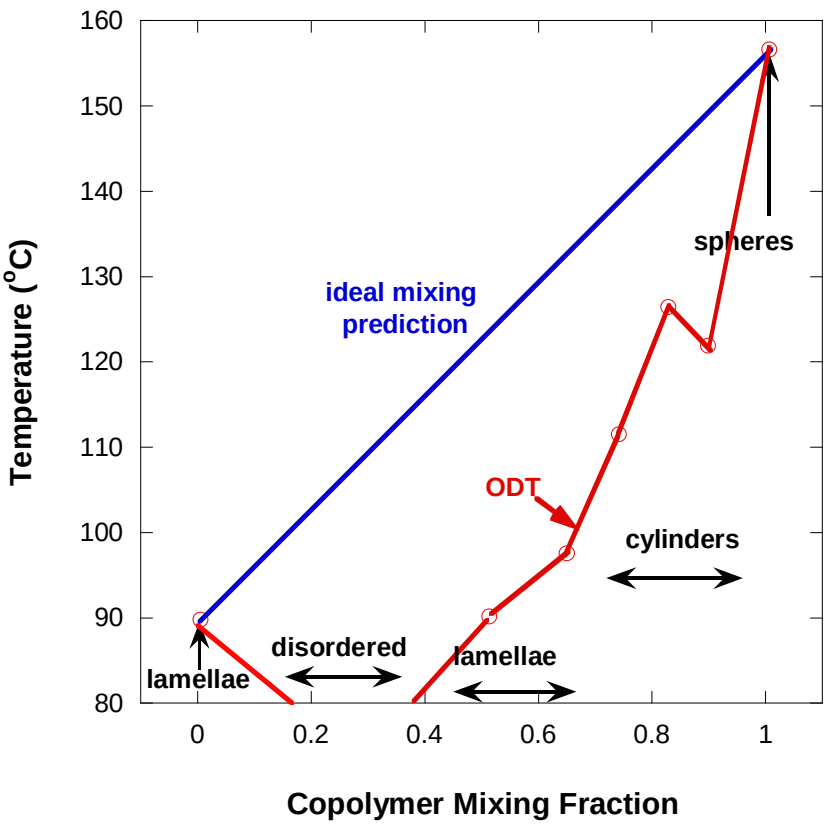

Figure 10: Different morphologies obtained by mixing PS-PI copolymer samples corresponding to lamellar and spherical morphologies at various fractions. The order-to-disorder temperature is plotted. Non-ideal mixing behavior is observed.

5. COMMENTS

Our focus here was on demonstrating the richness of possibilities afforded by the use of SANS with in-situ shear. We have described the effect of Couette and plate-plate shear on liquid crystal micelles and copolymer systems. Shear is useful for the investigation of various morphologies including lamellar, cylindrical and spherical. It is noted that the projects described here made use of in-situ shear cells with no regard to stress measurements; these are not rheometers. Rheometers have recently been adapted for SANS geometry.

REFERENCES

J. Mang, S. Kumar and B. Hammouda, "Discotic Micellar Nematic and Lamellar Phases under Shear Flow", Europhysics Lett. 28, 489-494 (1994)

B. Hammouda, J. Mang and S. Kumar, "Shear-Induced Orientational Effects in Discotic Liquid Crystal Micelles", PRE 51, 6282-6285 (1995)

N.P. Balsara and B. Hammouda, "Shear Effects on Solvated Block Copolymer Lamellae: PS-PI in DOP", PRL 72, 360-364 (1994)

N.P. Balsara, B. Hammouda, P.K. Kesani, S.V. Jonnalagadda and G.C. Straty, "In-Situ Small-Angle Neutron Scattering from a Block Copolymer Solution under Shear", Macromolecules 27, 2566-2573 (1994)

H. Wang, M.C. Newstein, A. Krishnan, N.P. Balsara, B.A. Garetz, B. Hammouda and R. Krishnamoorti, "Ordering Kinetics and Alignment of Block Copolymer Lamellae under Shear Flow", Macromolecules 32, 3695-3711 (1999)

T.M. Slawecki, C.J. Glinka and B. Hammouda, "Shear-Induced Micellar Crystal Structures in an Aqueous Triblock Copolymer Solution", PRE 58, R4084-R4087 (1998)

R. Krishnamoorti, A.S. Silva, M.A. Modi and B. Hammouda, "SANS Study of a Cylinder-to-Sphere Order-to-Order Transition in Block Copolymers", Macromolecules 33, 3803-3809 (2000).

R. Krishnamoorti and B. Hammouda, "Mixed Copolymer Morphologies under Shear", Unpublished Results (2000).

QUESTIONS

1. What is the difference between a shear rate and a shear frequency? How about a rotation frequency and an angular rotation frequency?
2. What are the various types of shear cells? Which ones were used here?
3. What is the most common orientation of layered (lamellar) structure under Couette shear?
4. Define the three main axes used with shear geometry.
5. Define the three (called A, B, and C) types of shear alignment.
6. Describe the "flipping" transition. What shear alignment types does it involve?
7. How much travel is required to shear a 0.5 mm thick sample to a strain of 200 %?

ANSWERS

1. The shear rate and shear frequency are the same thing. This is the number of rotations per second (given in units of Hz). The rotation frequency ν (units of Hz) is related to the angular rotation frequency ω (units of rad/s) as $\omega = 2\pi\nu$.
2. Shear cells include the Couette type, the Poiseuille type, the plate-plate type and the cone-plate type among others. The Couette and the plate-plate were used here.
3. Layered (lamellar) structures tend to orient parallel to the moving shear cell walls under Couette flow.

4. The three main axes used in shear geometry are: the shear direction, the shear gradient direction and the neutral (also called the vorticity) direction.
5. The three types of shear alignment are described in Figure 2 in the text.
6. The flipping “transition” corresponds to a transition from the C alignment type to the A alignment type.
7. 1 mm of travel is required in order to shear a 0.5 mm thick sample to a strain of 200 %.