ESRF	**Experiment title:** Grazing-incidence small-angle scattering investigation of self-assembling molecular systems	**Experiment number:** 28 01 774
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Report:

Complex nanostructures can be formed by T-shaped molecules with three incompatible segments. These molecules have a rod-like biphenyl or terphenyl core, to which a polar group is attached at each end, and a long hydrophobic chain in a lateral position ("bolaamphiphiles"). The interactions between the aromatic backbone, the polar endgroups and the hydrophobic sidechains lead to complex structures which are sensitive to temperature and to small changes in chemical compositions (Fig. 1) [1]. Alternatively, an aliphatic chain is attached at each end and a polar (oligo-oxyethylene) chain is attached laterally ("facial amphiphiles") [2]. XRD studies have revealed a number of unorthodox liquid crystal phases with 2-d and 3-d order [2-5]. Among these are novel columnar honeycomb-type phases. The rod-like groups provide the walls of the honeycomb channels, which are filled by the lateral chains. The channels have different polygonal cross-sections, ranging from triangular to hexagonal, the side of the polygon being the length of one molecule.

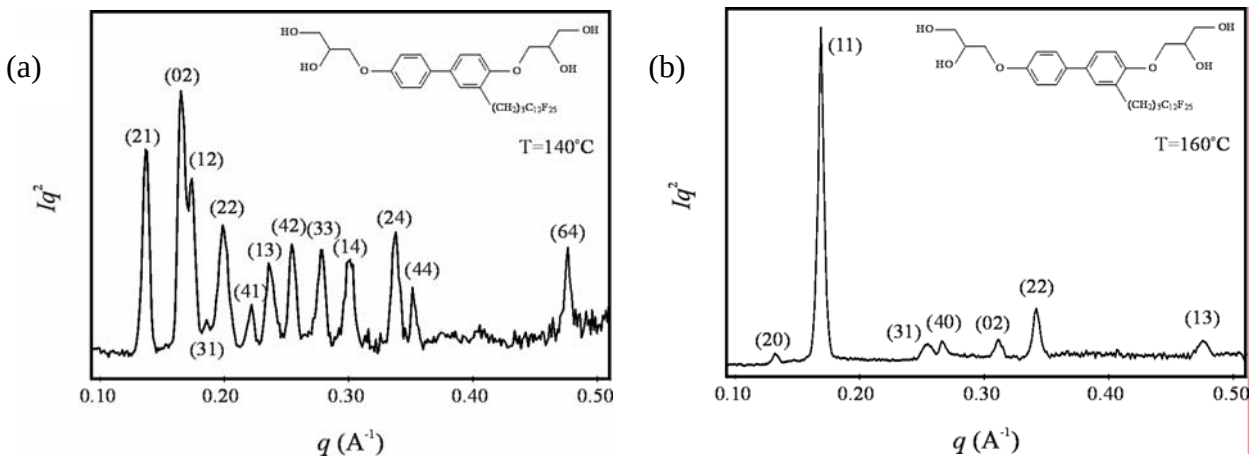
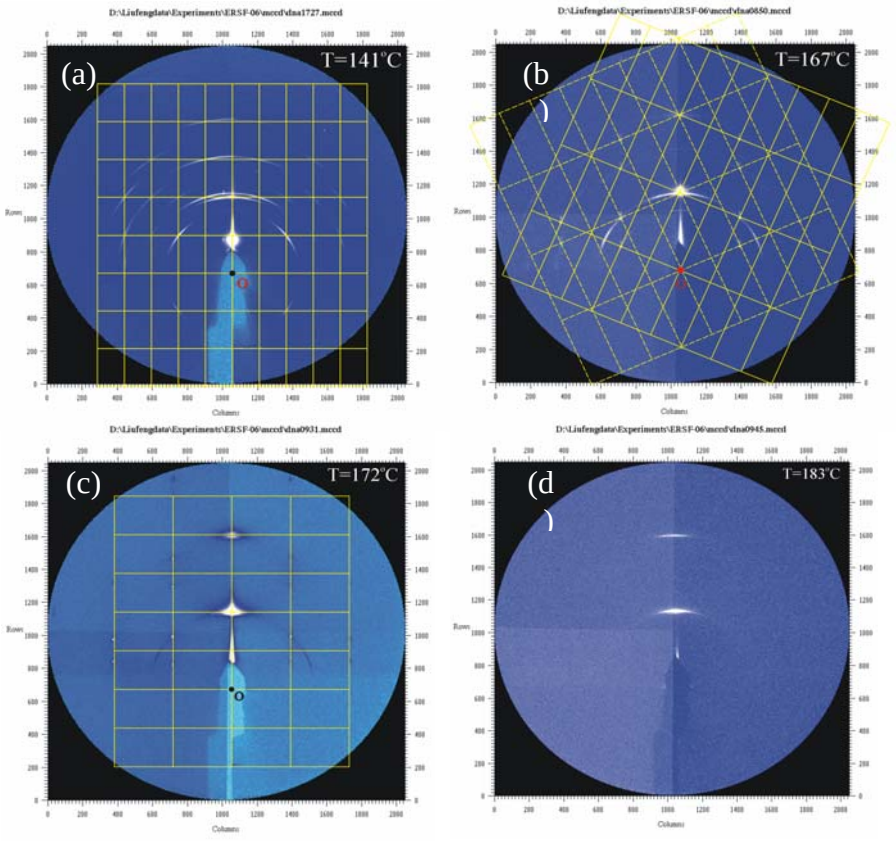


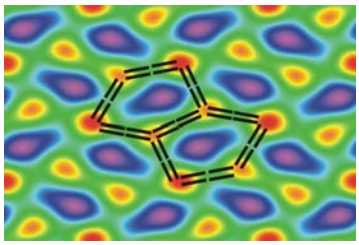
Figure 1 (a) SAXS bulk powder diffraction pattern, recorded at SRS, of the "giant pentagon" (*p2gg*) phase recorded at 140ºC; (b) SAXS diffraction pattern of the "giant hexagon" (*c2mm*) phase recorded at 160ºC

Grazing-incidence SAXS (GISAXS) experiments were carried out on this compound, deposited as a thin film on a silicon surface, to investigate the effect of the surface on the formation and structure of the liquid crystalline phases. The thin films were prepared by melting the compounds on silicon substrate and applying pressure to form films a few micrometers in thickness. A photon energy of 9 keV was employed and the sample was mounted on a customised heater stage in a helium-filled chamber. The MAR detector was mounted at the back wall of the hutch and a helium-filled beampipe monted on the detector arm. GI-SAXS images were then obtained during *in-situ* heating, both as a time-series at fixed incident angle α, with occasional finely-spaced scans of α to investigate the depth-dependence of the scattering. The GI-SAXS results show liquid crystalline phase transitions at temperatures consistent with the bulk SAXS data (fig. 2). Three additional results arise from the GI-SAXS images:

1. The effect of the surface in determining the alignment of the supramolecular structure: there is a well-defined direction normal to the surface normal.
2. The uniaxial alignment caused by the presence of the silicon surface has resolved peaks which could not be resolved in the bulk powder SAXS, giving unequivocal determination of peak intensities. This has also enabled us to identify a new phase that could not be detected in the bulk SAXS data (fig 2c).
3. Depth-resolved scans, where the GISAXS intensity distribution is measured as a function of α, show depth-dependent ordering around 140-150°C, in which three different kinds of order where the free surface is polycrystalline, the material close to the buried interface is one liquid crystalline phase and the material in between the two interfaces displays a different ordered state. This effect is currently being analysed and will be investigated further in the next scheduled experiment in May 2007.

From the reconstructed electron density maps of these phases based on the diffraction patterns of GISAXS, the existence of giant pentagon and giant hexagon has been verified. Good agreement between the electron density map and previously proposed molecular models [1], has also been achieved. The resulting electron density for the giant pentagon and lamellar phases are shown in Fig 2 (e,f).





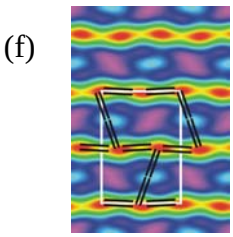


Fig. 2 GISAXS images for the bolaamphiphile shown in Fig 1 at (a) 141°C, p2gg 'giant pentagon' phase, *a*=11.6nm *b*=7.8nm (b) 167°C, *c2mm* 'giant hexagon' phase *a*=9.6nm *b*=4.1nm (c) 172°C, new *p2gg* phase *a*=5.2nm *b*=7.5nm (d) 183°C, lamellar phase, *a*=3.8nm. Calculated electron density maps for (e) the giant pentagon phase (f) the lamellar phase. The molecular backbone is shown in black.

References

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