GISAXS study of the complex self-assembly of X-shaped molecules and block copolymers

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The aim of the experiments carried out at BL40B2 was to study the complex self-assembly of soft matter systems which consist of multiple blocks and involve micro-phase separation between incompatible but covalently bonded blocks. These include relatively small liquid-crystal-forming molecules, with typical self-assembled asymmetric units on the scale of several nanometers, as well as multi-block copolymers, with typical scale of several tens to hundreds of nanometers. The study of these systems holds the key to the fabrication of nano-objects via controlled self-assembly, with potential applications in optical, electronic and medical fields.

Key word: self-assembly, multi-block, liquid crystals, GISAXS

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During the experimental session, a tri-block copolymer, polystyrene-block-polybutadiene –block-poly (methyl methacrylate), was firstly studied. An unusual double-helical structure, composed of polybutadiene microdomains surrounding polystyrene columns, has been discovered by our collaborators using transmission electron microtomography [1]. Grazing-Incidence Small Angle X-ray Scattering (GISAXS) experiments were carried out on oriented thin films of the compound, in order to further investigate the 3-dimensional arrangement of these helical columns. As the scale of the self-assembled structure is several tens of nanometers, a long camera length of ~3.5 meters was used. Hexagonal packing of the columns was typically observed, in line with previous studies with electron microscopy and microtomography. With the help of GISAXS, however, more details on the nature and degree of ordering, e.g. correlation in position and helicity between neighbouring columns, can be retrieved. An example of such GISAXS patterns, obtained on a particularly well oriented film, is shown in Figure 1. Here, in addition to the 2-d

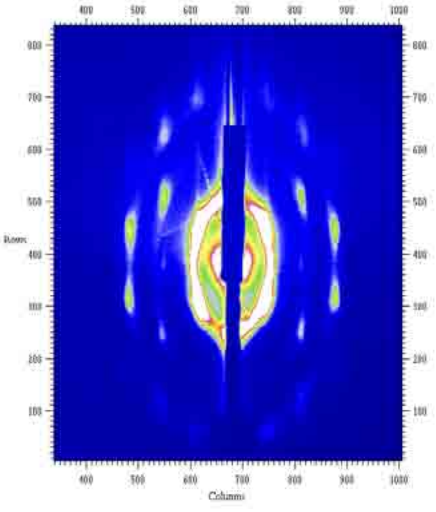
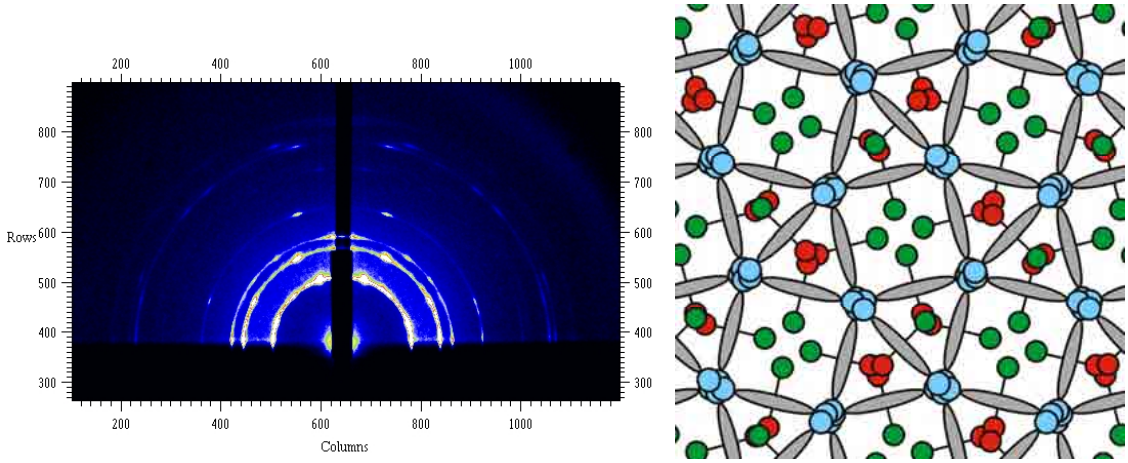


Figure 1. GISAXS diffraction pattern from a well oriented thin film of the triblock PS-PB-PMMA copolymer.



(a) (b)

Figure 2. a) GISAXS diffraction pattern of an X-shaped molecule. b) Schematic drawing of the molecular arrangement in the phase observed in a, based on the

hexagonal reflections on the equator, a number of nonequatorial diffraction peaks were observed. These can be indexed on a centered rectangular lattice. Data analysis is underway in order to solve its exact structure.

The second group of GISAXS experiments were carried out on X-shaped molecules, which consist of an aromatic core terminated by diol groups at each end, with two incompatible side chains attached at opposite sides of the core [2]. Typically these compounds form honeycomb structures, consisting of columns with polygonal shaped cross sections. The walls of the nano-columns are formed by the rigid aromatic core, connected to each other via hydrogen bonds at the edges of the columns. The incompatibility between the two side chains may lead to further segaration of them into neighbouring columns, resulting in complex “multi-colour” tilings and sometime frustrated structures for certain lattices. Again, oriented films were prepared for the study of the complex self-assembled phases by GISAXS. As the size of the columns is several nanometers, a shorter camera length, ~1.0 m, was used for these samples. An example GISAXS pattern of one of such phases, consisting of a combination of square and triangular columns (with different “colours”), is shown in Figure 2.

In summary, GISAXS is found to be an extremely useful technique in determining complex nanostructures at different scales: from several to hundreds of nanometers. Several research papers, on block copolymers and X-shaped molecules studied in this experimental session, are in preparation.

References

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