GISAXS in the study of supramolecular and hybrid liquid crystals

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Abstract

The use of grazing incidence small and intermediate angle X-ray scattering in the study of structure and alignment of thermotropic liquid crystals is illustrated on selected examples. These include columnar LC phases of a star-shaped mesogen, several honeycomb phases of T-shaped and X-shaped bolaamphiphilic LCs, and gold nanoparticles coated with mesogenic ligands. Sharp Bragg reflections from systems with 2-d and 3-d periodicities are obtained through annealing. Due to nearly perfect surface alignment in most cases, indexing of complex diffraction patterns is facilitated. Honeycomb cells with deformed hexagonal cross-sections, as well as kagome lattice, are shown. The tilt of the reciprocal lattice is shown to help establish the correct structure in the case of the stretched hexagonal honeycombs and the rhombohedral arrays of ordered strings of gold nanoparticles.

Grazing incidence small angle x-ray scattering has become an indispensable technique in the study of surfaces and interfaces ([1,2,3] and references therein), systems which include semiconductor multilayers, metallic nanoparticles, quantum dots, mesoporous films [4,5,6,7,8], lipids and surfactants [9,10,11,12], and block copolymers [13,14,15,16,17]. There are only a few studies of liquid crystalline systems using GISAXS though: spin coated and LB films of phthalocyanines [18], liquid crystalline side chain block copolymers [19], discotic supramolecules in thin films [20,21], dendrimers in thin films [22], self-assembly of block copolymer-based supramolecules in thin films [23] and surface micelles of surfactant [24].

Here we will illustrate the usefulness of grazing incidence small and intermediate angle diffraction in investigations of surface aligned periodic thermotropic LC structures, as well as LC-coated metal nanoparticles, on examples from our recent practice.

Columnar liquid crystals

In the study of columnar LCs a surface alignment technique for recording 2d X-ray diffraction patterns has been introduced by G. Pelzl [25], whereby a LC droplet on a glass surface is irradiated with a beam close to parallel to the slide. The alignment occurs at the LC-air interface and due to its convex curvature the transmitted beam is likely to hit areas under Bragg condition. Even better alignment is obtained in thin films either spin-coated from solution or melt spread on surfaces such as Si (111). This way true grazing incidence diffraction experiments can be carried out. The most useful q range for liquid crystals is ca. 0.3 to 5 nm⁻¹, i.e. small to intermediate scattering angles. Here both ranges are referred to as GISAXS. In the GISAXS experiments described below typical x-ray wavelength used is 1.0 Å with beam size 200 µm x 50 µm on the sample and sample to detector distance of ~75 cm.
Classic columnar LCs are formed by discotic molecules [26]. However, other molecular architectures can also give rise to columnar phases through self-assembly. Here we give the example of a star-shaped compound (compound 1) [27]

![Compound 1](image1)

kindly donated by Prof. M. Lehmann of TU Chemnitz, Germany, which forms a hexagonal columnar phase with a lattice parameter 3.5 nm. Figure 1 shows the GISAXS pattern of compound 1 spin-coated on silicon. The pattern shows a hexagonal array of sharp Bragg spots. The columnar LC has planar orientation, with high in-plane alignment of the columns (normal to $z$) but random orientation in the surface $x,y$ plane. Thus the reciprocal lattice is 2-dimensional and, apart from the meridional reflections, all others arise when the columns are parallel to the incident beam and the reciprocal $x*y*$ plane crosses the Ewald sphere. For all columns the [10] direction coincides with the $z$-axis. There is virtually no azimuthal spread of the higher order reflections, and the value of the order parameter is therefore exactly $-\frac{1}{2}$. The diffuse wide-angle scattering halo centered around $q = 14$ nm$^{-1}$ confirms the liquid crystal nature of the phase.

![GISAXS-GIWAXS pattern](image2)

Figure 1. GISAXS-GIWAXS pattern of the columnar LC phase of the star-shaped compound 1 on Si (111) surface. Due to the large detector size (Pilatus-2M, Dectris) $q$-range 0.2 - 14 nm$^{-1}$ is covered with high resolution. Linear intensity scale. Recorded at beamline I16, Diamond Light Source.

**Liquid crystal honeycombs**
Among the more recently introduced molecular architectures forming liquid crystal phases are polyphilic LC compounds that have a polar H-bonding group at each end, and one or two flexible chains attached laterally to the aromatic rod [28,29]. These molecules combine three or four types of incompatible units which results in a wide range of novel and sometimes highly complex self-assembled patterns with 2-d or 3-d mesoscopic order [30]. The most common class of such structures are honeycomb columnar phases, where the rod-like mesogens form the walls and the side chains fill the cells. The polygonal cross-section of the cells ranges from triangular, via square and pentagonal to hexagonal and extended hexagonal.

Figure 2 shows a GISAXS pattern of compound 2, which forms a honeycomb phase of hexagonal symmetry between 86°C and 116°C.

Here the incidence angle $\alpha_i$ is comparatively high (2°) since higher diffraction orders were targeted, taking advantage of the Bragg-Brentano geometry. Intensities from powder diffraction were used for the reconstruction of the electron density map [31]. This is shown in Figure 3b, along with a snapshot of molecular dynamics simulation based on the experimental unit cell parameters (Figure 3c).
In spite of the hexagonal reciprocal lattice, the structure of the LC phase is not a simple hexagonal honeycomb, but rather one based on the kagome lattice or trihexagonal tiling (Figure 3a). Thus there is one hexagonal and two triangular channels per unit cell, the former containing the alkyl, and the latter the partially perfluorinated alkyl chains. In this way these two incompatible chains are fully separated.

Figure 3. a) Kagome lattice. b) Electron density map calculated from powder diffraction pattern [31]; the schematics of rod-like aromatic cores of eight molecules are overlaid (black lines) with their terminal glycerol groups (white ellipses); one of the cores has its two lateral chains drawn. c) Snapshot of a molecular dynamics simulation (box equal to experimental unit cell with \( c = 0.45 \) nm, with periodic boundary conditions. Colour coding: red = alkyl chains, purple = fluoroalkyl chains, green aromatic cores and glycerol units. View down the column axis [31].

The following example illustrates the way GISAXS may be used to test a particular structural model. Compounds 3 and 4 both form rectangular columnar phases, plane group \( c2mm \). Based on electron density maps reconstructed from powder diffraction intensities [32], on consideration of molecular dimensions and on comparisons with the phase structures of homologous compounds [33], it was suggested that both compounds form honeycombs with stretched hexagons as basic tiling units. In compound 3 the circumference of the hexagon is made up of 10 molecules, four sides consisting of two molecules end-to-end and the remaining two sides of only one molecule each – see Figure 5a [32]. In compound 4 the hexagons contain only 8 molecules in circumference: two molecules in two of the sides and one in each of the four remaining sides (Figure 5b) [33]. The difference between these two structures is due to the smaller volume of the side chain in 4 compared to that in 3. Homologous compounds with still smaller side chains display honeycombs with regular hexagons, or else with pentagons, squares or triangles as elementary tiles [30,34].
Figure 4 shows the GISAXS patterns of compounds 3 and 4 on Si surface. The rectangular reciprocal $x^*y^*$ nets again show that the honeycombs lie with their channels parallel with the substrate surface. However, while in Figure 4a one of the unit cell axes is parallel to the surface, in Figure 4b the lattice is tilted with the lattice plane [11] parallel to the surface instead. Figure 4b is therefore effectively a fibre pattern with [110] the fibre axis. This observation is perfectly in line with the structural model proposed for these two phases, as seen in Figure 5. The orientation of the honeycombs is such that the closely spaced edges rest on the substrate surface, causing minimum distortion to the bottom layer of the honeycomb.

![Figure 4. GISAXS patterns of rectangular columnar c2mm phases in a) compound 3 at 60°C and b) compound 4 at 115 °C. The tilt of the reciprocal lattice in b) is explained in Figure 5b.](image)

Figure 5. Schematic structures of the stretched hexagonal honeycomb phases resting on the substrate surface. a) Compound 3 (hexagons with 10 molecules in
circumference), b) compound 4 (hexagons with 8 molecules in circumference). Compare with Figure 4.

**LC-coated gold nanoparticles**

While metal nanoparticles deposited on flat substrates normally give more or less diffuse low-angle scattering at grazing incidence [35,36], more recently ordered monolayer and multilayer superlattices of nanoparticle systems have been achieved by various film preparation techniques, and GISAXS has been instrumental in examining them [37,38,39,40,41,42]. In a different approach, nanoparticles that are coated with mesogenic ligands and annealed have been found to order in the bulk so as to give sharp Bragg reflections of the superlattice [43,44]. As with the examples given above, surface alignment may again be an effective aid in determining the structure of such superlattices. Two examples of such LC-capped 2 nm gold nanoparticles are shown in Figure 6a, the difference between being only in the length of the thioalkyl co-ligand [45]. The material exhibit Schlieren texture between crossed polarizers (Figure 6b), indicating that the mesogens maintain long-range nematic-like orientational order. The GISAXS pattern of a spin-coated and annealed film on Si (111) substrate is shown in Figure 6c for sample **AuL4C12** that has the longer co-ligand chains. Indexing revealed a rhombohedral superlattice of Au nanoparticles, with $a = 8.0$ nm and $c = 3.5$ nm. The nanoparticles form strings, the three stings passing through a unit cell being displaced by $c/3$ with respect to each other – see Figure 6d. The strings are tilted relative to the surface normal as this allows the densely packed (111) plane of the superlattice to lie on the Si substrate.
Figure 6. a) Schematic structure of the gold nanoparticles coated with a rod-like mesogen laterally attached via an alkylthiol spacer; dodecylthiol (compound AuL4C12) or hexylthiol (compound AuL4C6) were used as co-ligands, or surface diluents. b) Micrograph of AuL4C12 between crossed polarizers at room temperature showing threaded nematic texture; bar = 10 μm. c) GISAXS pattern of a thin layer of AuL4C12; the white circles overlaid on the right-hand half of the diffraction pattern indicate the positions of diffraction peaks as calculated from the best-fit unit cell parameters. d) Nanoparticle array in the R̅3m phase resting on the densely packed \((1 \overline{1} 1)\) plane, as in the thin films recorded by GISAXS; the c-axis is tilted by 27° to the substrate normal. After ref. 44 (with permission of VCH-Wiley).

In comparison, the system AuL4C6, having shorter co-ligands, forms a superlattice with nanoparticles virtually touching each other within a string, while the distance between the hexagonally arranged strings is nearly the same as in AuL4C12. Here the strings stand normal to the substrate, as there are no well developed crystallographic planes with \(I > 0\).

Conclusions

As illustrated by the above examples, GISAXS is a very useful technique for studying alignment and structure of complex self-assembled liquid crystals and supramolecular systems, as well as their composites with nanoparticles. When liquid crystalline alignment is required to create e.g. molecular wires on nanopatterned surfaces, angle resolved GISAXS patterns as a function of the rotation around the surface normal can also yield important information [46]. Another area of application of GISAXS is the study of liquid crystal infiltrated into nanoporous ceramics, such as nanoporous silica or anodic alumina. Depth profiling by varying the incidence angle can also be applied in order to study surface phase transitions. A related subject is the study of alignment layers acting as substrate for controlling the orientation and pretilt in LC devices. With increasing availability of dedicated synchrotron and off-line facilities, it is expected that in forthcoming years the application of GISAXS in research related to thermotropic LCs and supramolecular self-assemblies will undergo considerable expansion.

This work was supported by EPSRC and DFG through the NSF EUROCORES programme SONS-2, Project SCALES. It was also supported by the European Union Collaborative Project NANOGOLD (FP7-NMP-2008-SMALL-2), as well as by the WCU program through the National Research Foundation of Korea funded by the Ministry of Education, Science and Technology (R31-10013). We thank Drs. D. Mannix, S. Brown and P. Thompson for technical help at the BM28 XMaS beamline, ESRF, as well as Drs. S. Collins and A. Bombardi at I16, Diamond Light Source.

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