



	<b>Experiment title:</b> SMECTIC ORDERING IN POLYMER-DISPERSED LIQUID CRYSTALS PROBED BY X-RAY MICRODIFFRACTION	<b>Experiment number:</b> SC-1570
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**Report:**

Polymer Dispersed Liquid Crystals (PDLCs) are composite materials consisting of droplets of low molar mass liquid crystals (LCs), randomly dispersed in a polymeric matrix. Liquid crystal droplet sizes are typically in the range 0.1  $\mu\text{m}$  - 10  $\mu\text{m}$ , where droplets of 1-5  $\mu\text{m}$  are the most common. PDLCs exhibit unique linear and non-linear optical properties<sup>1-2</sup> which are expected to boost the LC technology in the near future. Beyond the scope of applications, the interest in PDLCs has considerably stimulated fundamental research, concerning the phase separation and polymerization process, the optical properties, and especially the effects which are due to the confinement of LCs to small cavities<sup>3</sup>. In this case, a variety of unusual effects are introduced due to the large surface-to volume ratio, the most observable being changes in the nature of the phase transitions and the specific director configuration inside the cavity. When the droplet sizes are of the order of a few microns, the critical interplay between the ordering interactions at the boundary surface and the strong elastic deformation energies inside the volume results in a rich variety of director configurations<sup>1</sup>. External fields and temperature changes can be used to induce transitions from one configuration to another, and these transitions can be used to obtain a measure of the surface anchoring strength.

The aim of the proposed experiment was to understand the details of the LC director configuration within single  $\mu\text{m}$ -sized droplets of PDLCs by X-ray diffraction using a micro-focused X-ray beam ( $\mu$ -XRD). This experimental technique provides a unique tool to study the dependence of LC ordering on the droplet shape and size as well as on the nature of the polymer matrix. In previous experiments, we have probed the nematic ordering and director configuration within single  $\mu\text{m}$ -sized droplets [4]. The aim of the present

experiment was to demonstrate the effectiveness of X-ray microdiffraction ( $\mu$ -XRD) as a new experimental tool to probe the smectic LC ordering and director-field configuration within single droplets of PDLCs. To this purpose a micro-focused X-ray beam was used in transmission geometry and diffraction patterns from single droplets of an ultrathin-layer PDLC sample were collected and analyzed. As very distinctive patterns can be observed corresponding to different configurations, this technique provides a unique tool to investigate the dependence of both LC ordering and director configuration on the droplet shape and size. The samples were studied as polymeric films (from 5  $\mu\text{m}$  to 20  $\mu\text{m}$  thickness) containing the LC droplets, supported by an electron microscopy copper grid. The LC droplets confined in the polymeric materials consisted of the commercial 8CB LC that exhibits the mesophase sequence  $K \rightarrow \text{SmA} \rightarrow \text{N} \rightarrow \text{I}$  with transition temperatures:  $T_{KA}=295$  K,  $T_{AN}=307$  K,  $T_{NI}=314$  K. Scanning Electron Microscopy (SEM) analysis of a section of the investigated sample revealed a distribution of spherical droplet sizes with an average droplet diameter of  $2.6 \pm 0.5$   $\mu\text{m}$ . The diffraction experiments were carried out using the SAXS/WAXS scanning microdiffraction setup of the ID13 microfocus beamline. A monochromatic beam with  $\lambda=0.9755$   $\text{\AA}$  and of 0.8  $\mu\text{m}$  (horizontal) and 0.6  $\mu\text{m}$  (vertical) dimensions was used. The 2D diffraction patterns were recorded using a MAR CCD detector. The  $\mu$ -XRD patterns were collected in the temperature range between  $T=263$  K and 340 K. Because of radiation damage, it was not possible to study the thermotropic phase behavior within a single droplet. Therefore, we mapped a 2D region of the sample ( $200\mu\text{m} \times 50\mu\text{m}$ ) by moving in sequence horizontally and vertically the sample relative to the incident beam, in steps of 2  $\mu\text{m}$ , while linearly varying the temperature (from 340 K at starting point to 263 at final point) in order to get correspondence between sample position and temperature. These measurements give information of the effects of an “average” droplet dimension on the LC confinement and the related ordering mesophasic behavior. The results (an example is reported in fig. 1) have shown great differences between the mesomorphic behavior of these samples compared with that of bulk samples, both for transition temperatures and LC ordering.

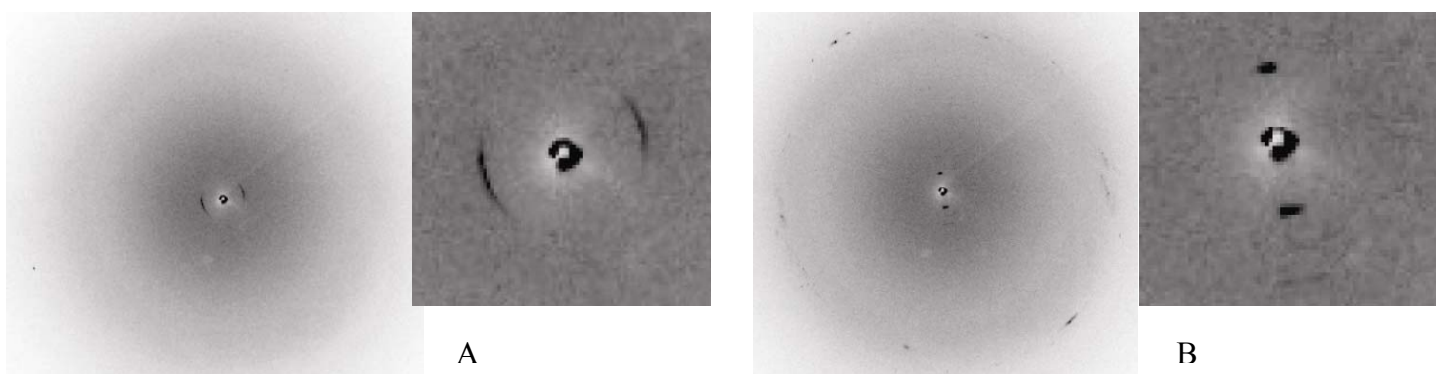


Fig1 Wide-angle and (inset) low-angle region of the  $\mu$ -XRD patterns acquired inside a smectic droplet of 8CB in a PDLC sample at 286.3 K (A) and in a nematic droplet of 8CB at 306.3 K (B).

However, based solely on the present data we can not discriminate the effects on the mesomorphic behavior of a possible contamination of the droplet-confined LC by small amounts of the unreacted starting monomer. Accordingly the XRD data, which are presently under elaboration, will be complemented with a series of DSC measurements on bulk LC+monomer mixture samples prepared at different weight relative ratios of the monomer (between 0.1% and 5%).

## REFERENCES

- [1] P. S. Drzaic, *Liquid Crystal Dispersions* (World Scientific, Singapore, 1995).
- [2] F. Simoni and O. Francescangeli, *Intern. J. Polymeric Mater.* **45**, 381 (2000).
- [3] G. P. Crawford and S. Zumer, in *Liquid Crystals in Complex Geometries*, edited by G.P. Crawford and S. Zumer (Taylor & Francis, London, 1995), Chap. 1, and refs.
- [4] O. Francescangeli *et al.*, *Euromphysics Letters* **59**, 218 (2002).