ESRF	**Experiment title: X-RAY MICRODIFFRACTION STUDY OF ORDERING AND DIRECTOR-FIELD CONFIGURATION IN POLYMER-DISPERSED LIQUID CRYSTALS**	**Experiment number**: SC-837
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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 μm - 10 μm, where droplets of 1 - 5 μm are the most common. PDLCs exhibit unique linear and non-linear optical properties [1-3] which are expected to boost the LC technology in the near future (new displays and light shutters, storage devices and nonlinear optical elements). 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 [4]. 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 [1]. 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 understandand the details of the nematic director configuration within single droplets of PDLCs by X-ray diffraction using a micro-focused X-ray beam (μ-XRD). The primary experimental tools used so far to determine the director field configuration within LC droplets have been optical polarizing microscopy and magnetic resonance spectroscopy. The former is limited to droplet sizes greater than a few microns whereas for NMR investigations, specially deuterated nematic probe molecules must be used and, for the calculation of lineshapes, it is necessary to postulate a nematic configuration for all cavities within the sample and then average the local director orientation both within each cavity as well as over all cavities.

μ-XRD in principle 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. The aim of the present paper was to demonstrate the effectiveness of X-ray microdiffraction (μ-XRD) as a new experimental tool to probe 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 analysed. 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 prepared via thermally-initiated *Polymerization Induced Phase Separation* (PIPS) starting from a mixture of the epoxy resins EPON815 (by Shell, 25.4 % in weight) and MK107 (by Wilmington, 7.1 %) with the hardener Capcure 3-800 (by Miller Stephenson, 32.5 %) and the nematic LC E7 (by Merck, 35%; T_{KN}=263 K, T_{NI}=334 K). This mixture is known to form LC droplets with the *bipolar* configuration. A similar mixture with the smectogenic LC 8CB (T_{KA}=295 K, T_{AN}=307 K, T_{NI}=314 K) replacing E7 was also prepared ro get samples with smectic LC droplets. Ultra-thin films of the PDLC samples were sliced out by means of a liquid nitrogen-refrigerated microtome. The thickness of the film (≈5 μm) was chosen to be comparable with the droplet size in order to reduce the probability for the probing X-ray beam to cross more than one droplet. Scanning Electron Microscopy (SEM) analysis of a section of the investigated sample revealed a narrow distribution of spherical droplet sizes with an average droplet diameter of 2.0±0.1 μm for PDLC samples with E7. Slightly larger values were found for samples with 8CB. The diffraction experiments were carried out using the SAXS/WAXS scanning microdiffraction setup of ID13 microfocus beamline. A monochromatic beam (λ=0.784 Å or λ=1.109 Å) of 2 μm diameter (2 μrad divergence) produced by a tapered glass capillary X-ray optics was used. The PDLC-film sample (S) was supported by an electron-microscopy copper grid which was mounted on a high-resolution (<1 μm) translation stage. A CCD microscope was used to select areas of interest on the sample. The data were collected at room temperature (T=297 K) for samples with E7 and at different temperatures between room temperature and 340 K for the samples containing the 8CB LC. Two-dimensional (2D) diffraction patterns were recorded using a 130mm MarCCD detector (D; pixel size 64.45 μm). The S-D distance was 109.08 mm The resolution in the scattering angle was $\Delta(2\theta)=3\cdot10^{-2}$ deg. The selected region was mapped in steps of 2 μm in both horizontal and vertical directions. Different areas of the sample were investigated. As the polymer matrix is amorphous and isotropic (at least on the micrometer length scale) whereas bipolar droplets possess LC ordering and anisotropic director configuration, we could discriminate between the scattering from a droplet and that from the polymer binder in all cases except when the droplet axis was parallel to the incident beam.

Figure 1 reports a representative example of the μ-XRD pattern of a single nematic (E7) LC droplet. This pattern was obtained from the measured one after subtracting the contribution of the isotropic background due to the polymeric matrix surrounding the selected droplet (inset of fig. 1). The diameter of this droplet was estimated to be less than 2 μm because no LC contribution to the scattered intensity was observed in the nearest neighbours sampling points. The anisotropy of the pattern is associated with a director-field configuration possessing cylindrical symmetry and is similar to the typical diffraction patterns observed for axially-oriented nematics. Other examples of μ-XRD patterns of single spherical droplets are reported in fig.2 where different orientations of the droplet axis are shown. The weak scattering signal in (C) is due to a submicrometer droplet; measurements of relative intensity allowed us to estimated a radius R≤0.3 μm. The pattern of fig.2(D) was taken after submitting the sample to a thermal cycle through the clearing point in order to eliminate possible effects of the slicing process on the LC orientation. The dominant feature of the scattering (fig. 1) for $\mathbf{q} \parallel \mathbf{N}$ ($q = 4\pi \sin\theta / \lambda$) is the pair of small-angle diffuse peaks centered at q=0.218 Å^{-1} arising from longitudinal correlations in the molecular arrangement and corresponding to a spacing $d = 2\pi / q = 28.8$ Å . The two wide-angle diffuse crescents centered on the equatorial line ($\mathbf{q} \perp \mathbf{N}$) at $q \cong$ 1.4 Å^{-1} are associated to the short-range liquid-like positional order of the molecules and correspond to an average molecular distance d≅4.5 Å . However, differently from what observed for perfect axially-aligned samples, distinct arc-shaped profiles of both meridional and equatorial reflections are clearly evident in the diffraction pattern, indicating a distribution of angular orientations of the coherently scattering domains relative to the average **N**. Such a distribution reflects the curvature of the nematic director-field lines inside the bipolar droplet. By analyzing the azimuthal intensity profile of the wide-angle diffuse crescents we have obtained the distribution function of the nematic director in the droplet and determined the droplet order parameter S_D [5]. The obtained value of S_D is in excellent agreement with theoretical calculations. This represents the first experimental determination of such quantities that are of great importance in the characterization of the electrooptical behavior of PDLCs.

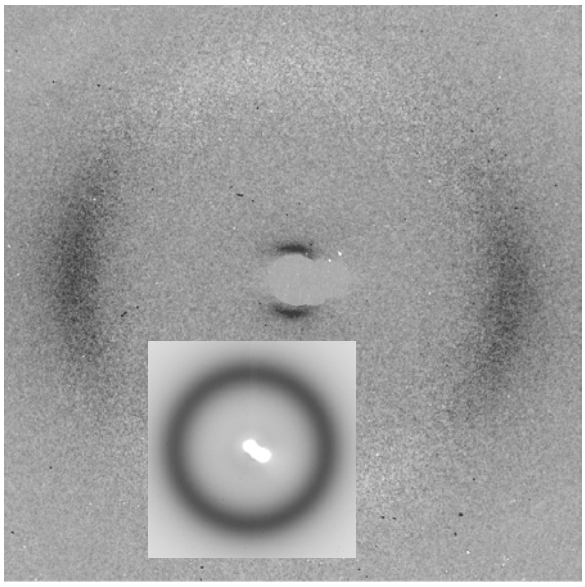

Fig.1 XRD pattern (λ=0.784 Å) of a single nematic spherical droplet of a 5 mm-thick PDLC film measured with microfocused (2μm x 2μm) beam. The droplet radius is R≤1 μm. The inset shows the μ-XRD pattern of the polymer matrix surrounding the LC droplet.

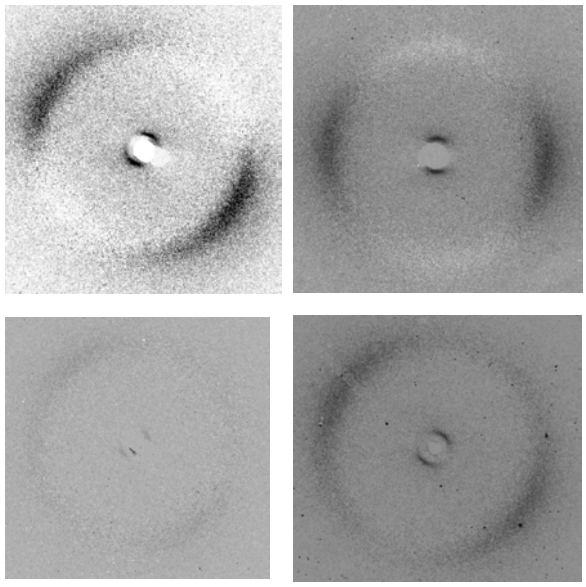

Fig.2 Examples of XRD patterns of single nematic droplets showing different orientations of the droplet axis. In all cases the droplet radius is less than 1 μm. (A-C): λ=0.784 Å; (D): λ=1.1.09 Å. The pattern in (D) was taken after submitting the sample to a thermal cycle.

Examples of μ-XRD patterns of single smectic LC droplets (in PDLC samples with 8CB) are shown in figures 3 and 4. In particular, figure 4 clearly evidences the continuous rotation of the average orientation axis inside a large droplet. Work is still in progress for what concernes the complete interpretation of the μ-XRD data in smectic LC droplets.

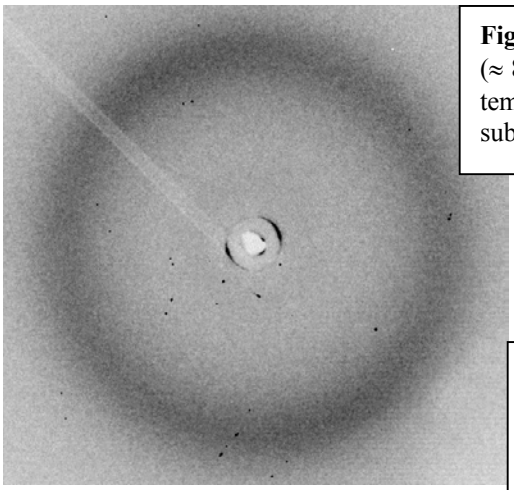

Fig.3 μ-XRD pattern (2μm x 2μm beamsize) from a single spherical droplet (≈ 8 μm diameter) of a PDLC film made with 8CB liquid crystal in its room temperature smectic phase (λ=1.1.09 Å). The pattern is before background subtraction for the amorphous polymeric matrix contribution

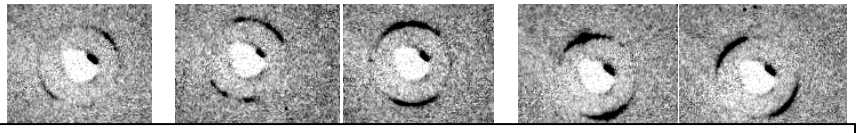

Fig.4 Sequence of μ-XRD patterns of the smectic phase of the confined 8CB liquid crystal in its smectic phase, taken within the same large droplet of a PDLC thin layer film on moving the sample relative to the beam horizontaly with steps of 2 μm.

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