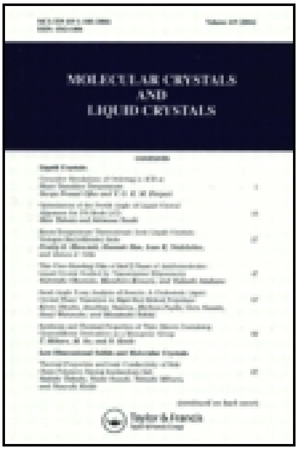

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X-ray Microdiffraction Study of the Liquid Crystal Ordering in Confined Geometries

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X-RAY MICRODIFFRACTION STUDY OF THE LIQUID CRYSTAL ORDERING IN CONFINED GEOMETRIES

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We report the results of recent experiments where for the first time X-ray microdiffraction has been used to probe liquid crystal ordering and nematic director-field configuration in single micron-sized droplets of polymer-dispersed liquid crystals. The pattern of the bipolar configuration has been detected in a droplet with radius $R \leq 1$ μm and the main quantities characterizing the orientational and short-range positional order of the confined nematic have been determined. We report a detailed description of the procedure followed to determine the distribution function of the nematic director in the droplet and the droplet order parameter from the azimuthal intensity profile of the diffraction pattern.

Keywords: confined geometries; director-field configuration; polymer-dispersed liquid crystals; x-ray microdiffraction

INTRODUCTION

Studies on the influence of confinement by restricted geometries on physical properties of the materials are particularly important for liquid crystals (LCs) since their relatively weak orientational and translational order is strongly influenced by the presence of confining surfaces. In addition, because of the existence of long-range correlations near a phase transition and the presence of different order phase transitions, LCs are a unique and rich system to test in confined geometries. Independent on the method used to constrain LCs, these systems have an underlying common theme: a symmetry-breaking, non-planar confinement imposed by the surrounding matrix. Their composite nature deeply affects the ordering of the LC molecules and their susceptibility to external fields, making them ideal for a host of new electro-optic applications. For these reasons, confined LC systems have received a great deal of interest in recent years [1] and, among these, polymer-dispersed liquid crystals (PDLCs) play a unique role [2].

PDLCs are composite materials consisting of spherical droplets of low molar mass LCs, randomly dispersed in a solid polymeric binder [3]. A fundamental aspect in the study of PDLCs is identification of the nematic director-field configuration inside the droplets. In fact, the operation of PDLC-based devices depends on the type of director configuration and its response to an applied field. When the droplet sizes are lower than a few microns, the large elastic distortion energies imposed by the cavity curvature strongly compete with the molecular anchoring energies, which results in a rich variety of stable director configurations. The expected director configuration of a nematic LC in a spherical droplet has been calculated and microscopically verified in large droplets by several workers. Depending on the characteristics of the surface anchoring and the bulk elastic properties of the LC, different configurations can be adopted by the nematic director in spherical droplets, the most common being the bipolar, the axial and the radial [2,3]. The primary experimental tools used so far to determine the director-field configuration inside the LC droplets have been optical polarizing microscopy and magnetic resonance spectroscopy. The former is particularly easy to perform, however is limited to droplet sizes grater than a few microns. On the other hand, NMR methods [4] are powerful means to probe systems which are not amenable to optical microscopy. However, several factors must be taken into account in order to apply ^{2}HNMR to LC systems, which add complexity to this technique. In particular, specially-deuterated nematic probe molecules must be used and, for 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. In addition, the surface competes with the field of the NMR magnet in aligning the directors inside a droplet and this requires droplets with a diameter $d < 1\ \mu\text{m}$ in order to prevent significant distortion of the director configuration by the magnetic field [4].

Very recently, we have demonstrated the possibility of using X-ray microdiffraction (μ-XRD) as a new experimental tool to probe LC ordering and director-field configuration within *single* droplets of PDLCs [5]. In particular, we carried out a pioneering experiment in which a micro-focused synchrotron X-ray beam was used to obtain diffraction patterns from single µm-sized droplets of an ultrathin-layer PDLC sample. This technique reveals to be unique in its application to dispersed mesophases in that it allows to probe the local LC ordering on the µm-length scale. In addition, the possibility of focusing measurements on single droplets eliminates the problems connected with averaging typical of other techniques. In this paper we review the direct observation of the bipolar director-field configuration in single μm-sized droplets of PDLC by μ-XRD and provide a description of the calculations made to determine the orientational distribution function of the nematic director inside the droplet and the droplet order parameter, which represents the first experimental determination of such important quantities.

EXPERIMENTAL

The samples were prepared [5] via thermally-initiated Polymerization Induced Phase Separation (PIPS) starting from a mixture of the commercial epoxy resins EPON815 (25.4% in weight) and MK107 (7.1%) with the hardener Capcure 3-800 (32.5%) and the nematic LC E7 (35%; $T_{KN} = 263\,K$, $T_{NI} = 334\,K$). This mixture forms droplets with the *bipolar* configuration [1–3]: the director-field has cylindrical symmetry with the symmetry axis defined by two surface-point defects lying at opposite ends of the droplet surface. Ultra-thin films of the PDLC samples were sliced out by means of a liquid nitrogen-refrigerated microtome. The thickness of the film was 5 μm. Scanning Electron Microscopy (SEM) analysis of a section of the investigated sample (Fig. 1) showed a narrow distribution of spherical droplet sizes with an average droplet diameter of 2.0 ± 0.1 μm.

The diffraction experiments were carried out [5] using the SAXS/WAXS scanning microdiffraction setup of the ID13 microfocus beamline at the

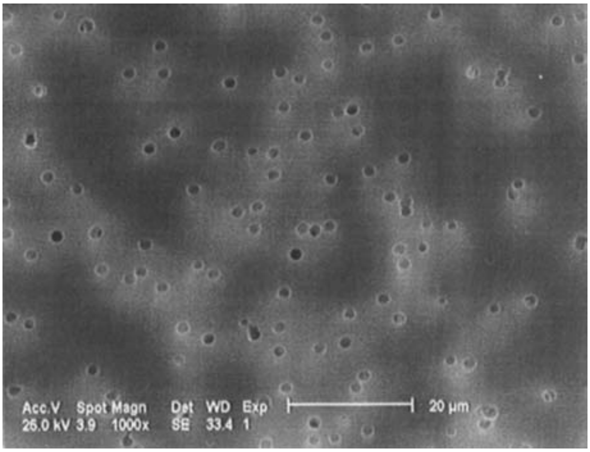

FIGURE 1 SEM micrograph of a section of the investigated PDLC sample.

ESRF (Grenoble, France). A monochromatic beam ($\lambda = 1.109\,\text{Å}$) of 2 μm diameter (2 μrad divergence) produced by a tapered glass capillary X-ray optics was used. The PDLC-film sample was supported by a copper grid mounted on a high-resolution (<1 μm) translation stage. Two-dimensional diffraction patterns were recorded using a 130 mm MarCCD detector. The selected region of the sample was mapped in steps of 2 μm in both horizontal and vertical directions.

RESULTS AND DISCUSSION

As the polymeric binder is amorphous and isotropic [5] whereas bipolar droplets exhibit LC ordering and anisotropic director configuration, it is possible to discriminate the scattering of the droplet from that of the polymer matrix. In fact, the diffraction pattern of the bipolar LC droplets is anisotropic (except when the droplet axis is parallel to the incident beam) and is featured by a weak small-angle diffuse peak characteristic of the short-range nematic positional order whereas the polymer gives rise to an isotropic pattern without any signal in the small-angle region. Figure 2 shows a representative example of the μ-XRD pattern recorder when the primary X-ray beam intercepts a droplet (A) and when it does not (B).

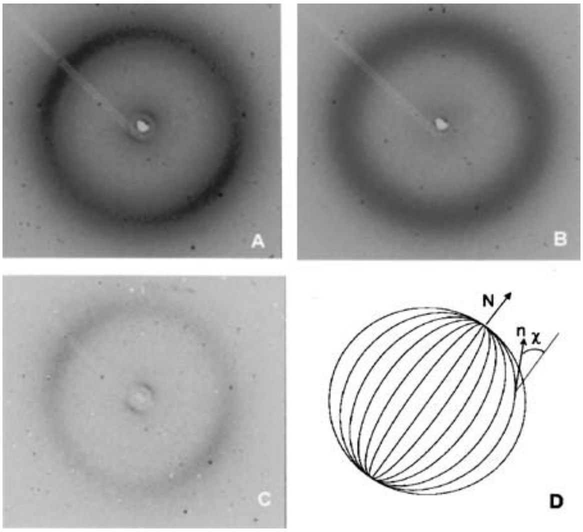

FIGURE 2 (A) μ-XRD pattern recorded when the primary beam intercepts a LC droplet. (B) μ-XRD pattern of the polymer binder. (C) μ-XRD pattern of the single isolated droplet. (D) Schematic representation of the bipolar configuration.

The pattern of Figure 2(C) represents the scattering of the isolated droplet and is obtained subtracting from the pattern of Figure 2(A) the contribution of the isotropic background due to the polymer matrix [i.e. the pattern of Figure 2(B)]. The details of this background correction are reported elsewhere [6]. 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 of the selected area. The anisotropy of the pattern 2(C) is associated with a director configuration possessing cylindrical symmetry and is similar to the typical diffraction patterns observed for axially-oriented nematics. The preferred orientation axis, **N**, is given by the straight line through the small angle peaks [i.e. the meridional line, Fig. 2(D)]. The dominant feature of the scattering in Figure 2(C) for the scattering vector $\mathbf{q} \parallel \mathbf{N}$ is the pair of small-angle diffuse peaks centered at $q = 0.218\,\text{Å}^{-1}$ arising from longitudinal correlations in the molecular arrangement and corresponding to a spacing $d = 2\pi/q = 28.8\,\text{Å}$. The two wide-angle diffuse crescents centered on the equatorial line ($\mathbf{q} \perp \mathbf{N}$) at $q \cong 1.4\,\text{Å}^{-1}$ are associated to the short-range liquid-like positional order of the molecules and correspond to an average molecular distance $\mathrm{d} \cong 4.5\,\text{Å}$. Differently from what observed for perfect axially-aligned samples, distinct arc-shaped profiles of both meridional and equatorial reflections are evident in the diffraction pattern, which indicate a distribution of angular orientations of the coherently-scattering nematic domains relative to the average **N**. This distribution reflects the curvature of the nematic director-field lines inside the bipolar droplet. The azimuthal intensity profile of the wide-angle diffuse crescents was used for the first time to determine experimentally the orientational distribution function of the nematic director inside to calculate the droplet order parameter, as illustrated in the following.

The concept of droplet order paramter was introduced by Kelly and Palffy-Muhoray [7] within a model formulated to describe the electrooptical response of PDLCs. This approach introduces a hierarchy of order parameters suitable to describe orientational order on different length scales. The nematic within a droplet is assumed to possess a local director configuration and order parameter. From this assumption a droplet director $\mathbf{N}_\mathrm{D}$ and droplet order paramter S_D are defined representing the average orientation of the nematic

$$S_D = \langle \{3[\mathbf{N}_\mathrm{D} \cdot \mathbf{n}(\mathbf{r})]^2 - 1\}/2 \rangle_{V_D} = \langle P_2(\mathbf{N}_\mathrm{D} \cdot \mathbf{n}(\mathbf{r})) \rangle_{V_D}, \tag{1}$$

where $P_2(\mathbf{N}_D \cdot \mathbf{n}(\mathbf{r}))$ is the second-order Legendre polynomial and the average is over the droplet volume V_D. $\mathbf{N}_D$ is parallel to the average orientation of the local director $\mathbf{n}(\mathbf{r})$ within the droplet and for the bipolar configuration it coincides with the symmetry axis **N**. S_D represents the degree of *geometrical* orientational order of the nematic within a droplet. For example, the spherical symmetry of the droplet leads to no preferred orientation for the droplet and $S_D = 0$. On the other hand, for an ideal uniform parallel configuration ($\mathbf{n} \| \mathbf{N}$ at each point within the droplet) $S_D = 1$. For the bipolar configuration, attempts have been made [7] to calculate $\mathrm{S_D}$ using analytical approximations to the true distribution of the director field (i.e. the one that minimizes the total free energy [8]). However, more reliable calculations can be done if the director field in the bipolar droplet is modelled by assuming that the molecules are oriented along a series of elliptical lines lying on a series of nested ellipsoids. For a sphere of radius R and assuming $\mathbf{N}_\mathrm{D}$ along z, the director field $\mathbf{n}$ is then described in terms of Cartesian vectors by

$$\mathbf{n} = (\lambda^2 \cos^2 \theta + \sin^2 \theta)^{-1/2}(\mathbf{i}\lambda \cos \theta \cos \varphi + \mathbf{j}\lambda \cos \theta \sin \varphi - \mathbf{k} \sin \theta). \tag{2}$$

Here, θ and φ correspond to the polar and azimuthal angles, respectively, of position within the droplet described in spherical coordinates $\{r,\theta,\varphi\}$ and λ is a radius vector ranging between 0 and 1, which spans the range of nested ellipsoids containing the elliptic lines. Comparison between this analytical expression and the result of numerical calculation indicate that the analytical equation is a good approximation to the true director field [9]. Equation (2) can readily be transformed to provide the local tilt angle of the director to the droplet axis, χ [Fig. 2(D)], as a function of the Cartesian coordinates, i.e. $\chi = -\cos^{-1}[1-(z/R)^2]^{1/2}$. Considering that $\mathbf{N}_\mathrm{D} \cdot \mathbf{n} = \cos\chi$, Eq. (1) for S_D takes the form

$$S_D = \frac{\int\limits_{r=0}^{R}\int\limits_{\theta=0}^{\pi}\left[\frac{3}{2}\frac{(R^2-r^2\cos^2\theta)^2}{(R^2-r^2\cos^2\theta)^2+(r^2\sin\theta\cos\theta)^2}-\frac{1}{2}\right]2\pi r^2\sin\theta\, dr\, d\theta}{4\pi R^3/3} \tag{3}$$

Numerical integration of Eq. (3) gives the value $S_D = 0.70$. Figure 3 shows the azimuthal intensity profile (at $q = 1.4\,\mathrm{\AA}^{-1}$) of the wide-angle equatorial crescents. The azimuthal spread of these diffuse peaks is the result of two distinct causes: (*i*) the curvature of the director-field lines inside the droplet and (*ii*) the thermal orientational disorder of the molecules. The latter contribution produces a distribution of molecular orientations around the local average direction $\mathbf{n}(\mathbf{r})$ and is always present, even for an ideal uniform parallel configuration ($S_D = 1$). In that case, the azimuthal intensity profile at constant $q, I_0(\psi)$, is related to the orientational distribution function of the molecules, $f(\beta)$, as [10]

$$I_0(\psi) = \int\limits_{\beta=\psi}^{\pi/2} f(\beta)\sec^2\psi(\tan^2\beta - \tan^2\psi)^{-1/2}\sin\beta\, d\beta \tag{4}$$

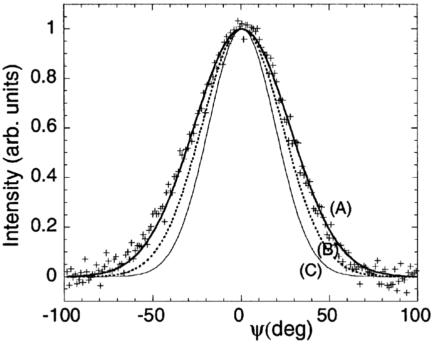

FIGURE 3 (A) Azimuthal intensity profile of the wide-angle equatorial crescents of the μ-XRD pattern of figure 2(C): symbols represent the experimental data and the full thin line gives the best fit by a Gaussian lineshape. (B) Theoretical intensity profile for a uniform parallel director configuration. (C) Deconvolution of A and B.

where the azimuth ψ is measured relative to the equatorial axis and $f(\beta)$ is defined such that $2\pi f(\beta)\sin\beta d\beta$ gives the fraction of molecules that have their long axis at an angle between β and $\beta + d\beta$ with respect to the local director **n**. On the other hand, following the same arguments leading to Eq. (4), a configuration with curved director-field lines in the ideal absence of thermal disorder gives an intensity profile $I_D(\psi)$ described by a similar equation

$$I_D(\psi) = \int_{\chi=\psi}^{\pi/2} f_D(\chi)\sec^2\psi(\tan^2\chi - \tan^2\psi)^{-1/2} sin\chi d\chi \tag{5}$$

where $f_D(\chi)$ is the orientational distribution function of the nematic director inside the droplet relative to the average axis. For a real general configuration with curved director-field lines and including thermal disorder, the contribution of elementary domains having different orientation **n** must be considered. If $G(\alpha)d\alpha$ is the fraction of the droplet volume where **n** is oriented at an angle between α and $\alpha + d\alpha$ with respect to **N**, then its contribution to the scattered intensity is given by $dI = I_0(\psi - \alpha)G(\alpha)d\alpha$. If we assume that the nematic order parameter S is not appreciably affected by the confinement and is constant everywhere within the droplet, then the scattered intensity $I(\psi)$ can be written as the convolution integral

$$I(\psi) = \int_0^{\pi} I_0(\psi - \alpha)G(\alpha)d\alpha. \tag{6}$$

This approximation is reasonable for micron sized droplets far from the N-I transition [5,11]. $G(\alpha)$ is proportional to $I_D(\alpha)$ so that experimental determination of the former allows us to determine $f_D\ (\chi)$ by inversion of Eq.(5). The function $G(\alpha)$ is then obtained by deconvolution of the experimental profile $I(\psi)$ with the function $I_0(\psi)$ representing the intrinsic spreading due to the thermal disorder. $I_0(\psi)$ can be easily modelled considering that in the nematic phase $f(\beta)$ closely conforms to the simple Maier-Saupe mean field distribution [12]. Accordingly, we may assume $f(\beta) = C\exp(m\cos^2\beta)$ where C is a normalization constant and m is a parameter depending on the temperature and the orientational potential energy. The room-temperature value of m is determined by imposing that the calculated nematic order parameter $S = \langle 3cos^2\beta - 1\rangle/2$ equals the experimental value 0.6 resulting from recent accurate optical-waveguide measurements in E7 bulk nematic [13], which gives $m = 4.45$. Then, numerical integration of Eq. (4) allows us to calculate $I_0(\psi)$ and the result is shown in Figure 3(B). The function $G(\psi)$ resulting from the numerical deconvolution of $I(\psi)$ and $I_0(\psi)$ is reported Figure 3(C). Finally, numerical inversion of the integral Eq.(5) gives $f_D(\chi)$ as shown in Figure 4.

The droplet order paramter is then calculated by means of Eq. (1), i.e. $S_D = \int_0^\pi P_2(\cos\chi)f_D(\chi)sin\chi d\chi/\int_0^\pi f_D(\chi)sin\chi d\chi$, which gives $S_D = 0.73$, in excellent agreement with the theoretical calculation. If the small difference between experimental and theoretical value is significant, it may be attributed either to slight imperfections of the spherical shape of the droplets or to small deviation from the condition of strong surface anchoring. In the latter case, such difference can be used in principle to get an indirect measurement of the anchoring energy, which represents a new exciting potential application of the μ-XRD technique.

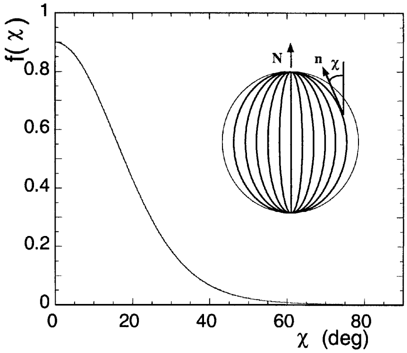

FIGURE 4 Orientational distribution function of the nematic director inside the bipolar droplet. The function is normalized such that $2\int_0^{\pi/2} 2\pi f(\chi)sin\chi d\chi = 1$.

An analysis similar to that described in this paper can be extended to other director configurations and used to discriminate among configurations that exhibit the same cylindrical symmetry but differ in the director orientational distribution function, as is the case for the bipolar and axial configurations.

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