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EPR Study of Order and Dynamics of the 5CB Liquid Crystal in an H-PDLC Device

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We have studied the effects of confinement on the order and dynamics of the 5CB liquid crystal (LC) inside nanosized droplets of a reflection-mode holographic-polymer dispersed LC (H-PDLC) device, consisting of alternating LC nanodroplets and polymer layers, forming a diffraction grating. Here we have investigated, taking advantage of the high sensitivity of the EPR spin probe technique, a series of temperatures spanning the nematic and isotropic phase of the LC. The occurrence of phase separation and the consequent formation of a diffraction grating was revealed by SEM images of the H-PDLC cross section and by the presence of a reflection peak around 565 nm. Differently from the case of BL038 LC based H-PDLCs, the results here indicate the absence of an ordered fraction of mesogens throughout the analysed temperature range. Taking into account a previous model of LC molecules arrangement in the same kind of device [Bacchiocchi, C., et al. (2009). J. Phys. Chem. B 113, 5391], we postulate the presence of very small droplets in which the surface anchoring constraints represent the dominant effect. This results in the hindrance of the LC uniform macroscopic alignment, providing a plausible explanation for the malfunctioning of these devices.

Keywords Bragg gratings; confined liquid crystals; phase separation; surface-induced order

I. Introduction

In a recent work [1] we have used the EPR spin probe technique to study the molecular organization and the local fluidity of the BL038 liquid crystal (LC) mixture inside the nanosized droplets of a commercially viable reflection-mode holographic-polymer dispersed LC (H-PDLC) device prepared with a prepolymer syrup of urethane acrylate oligomers. The quite complex spectra recorded clearly indicated the presence of uniformly aligned LC domains across a range of temperatures where bulk BL038 exhibits a nematic phase. The EPR spectra could be consistently analyzed only by assuming the presence of up to four

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spectral contributions which we attributed to different environments of various degrees of order, both at molecular and macroscopic level, where the spin probe could be located. We concluded by postulating a model where LC molecules with a very limited mobility form a layer at the nanodroplet interface and are in equilibrium with molecules in the remaining volume, the droplet cavity, exhibiting a faster dynamics. As the temperature increases, less and less molecules remain "frozen" on the surface layer, thus expanding the effective size of the cavity, lowering the constraints induced by the surface layer to the LC structure and allowing the molecule to align along the magnetic field. We expect the same to take place in the device under operational conditions when an electric field is applied. Surprisingly, no study has been reported so far on a similar commercial-grade H-PDLC device prepared with the 5CB LC, which has been extensively studied and, being a single component, with a sharp nematic–isotropic (N–I) transition, is expected to provide simpler spectra in an EPR study and possibly clarify some of the previous results and assumptions. Iannacchione et al. [2] used deuteron NMR, electron microscopy and optical studies of the diffraction efficiency to obtain information on the orientational order of 5CB in an H-PDLC and found an extremely broad N–I transition and low orientational order. The polymer was prepared from the dipentaerythrol-hydroxy-pentaacrylate monomer which is a typical acrylate used to make transparent films but is not the type of material considered for commercial applications in display and telecommunication. A preliminary study reported in a previous work [3] on a urethane acrylate H-PDLC device indicated that 5CB behaved differently from BL038 and did not phase separate during the curing process from the prepolymer syrup. A complete absence of phase separation appears to be strange since 5CB is one of the main components of the BL038 LC mixture which instead successfully phase separates. Since the role of the polymer is fundamental in determining the phase separation in an H-PDLC and is crucial in the optimization of such a device, in this work we use electron microscopy and optical studies of the transmission efficiency to show that phase separation of 5CB from the urethane acrylate oligomers mixture (see Experimental section) does in fact occur, then we use the EPR spin probe technique to obtain information on the nematic director configuration inside the nanodroplets, the local molecular order and dynamics.

II. Experimental

The H-PDLC device was prepared by photopolymerization of a prepolymer syrup that consisted of tri and hexafunctional oligomers EBECRYL 4866 and EBECRYL 8301 (Cytec, NJ, USA), both at a fraction of 23.85% w/w, 28.4% w/w of LC 5CB (EM Industries, NY, USA) doped with the spin probe (see below), 13.34% w/w photoinitiator (4% w/w Rose Bengal, 10% w/w of coinitiator N-Phenyl Glycine and 86% w/w of N-Vinyl Pyrrolidone) to sensitize the mixture to visible wavelengths and 10.56% w/w surfactant which is used in an actual device to improve the electro-optical response. The mixture was placed between two uncoated, alkali free, borosilicate glass slides (display-grade, Corning 1737, Corning, NY, USA), separated by 20 μm spacers forming an approximately 2 mm thick cell. The latter, held by the glass slides at the sides, was then exposed to a 532nm, 5 W, Nd:YAG Verdi laser (Coherent, CA, USA) using a reflection hologram setup to create a reflection grating where the droplet layers are parallel to the glass slides [4]. A capillary tube glued to the border of the cell was used to hold it in the chosen position and orientation within the EPR cavity (see experimental scheme in Fig. 1(a)). A SEM image of the sample cross section is shown in Fig. 1(b). The grating structure is visible at the centre of the image, the dashed white line is used as a reference to identify the layers which are less clearly visible compared to

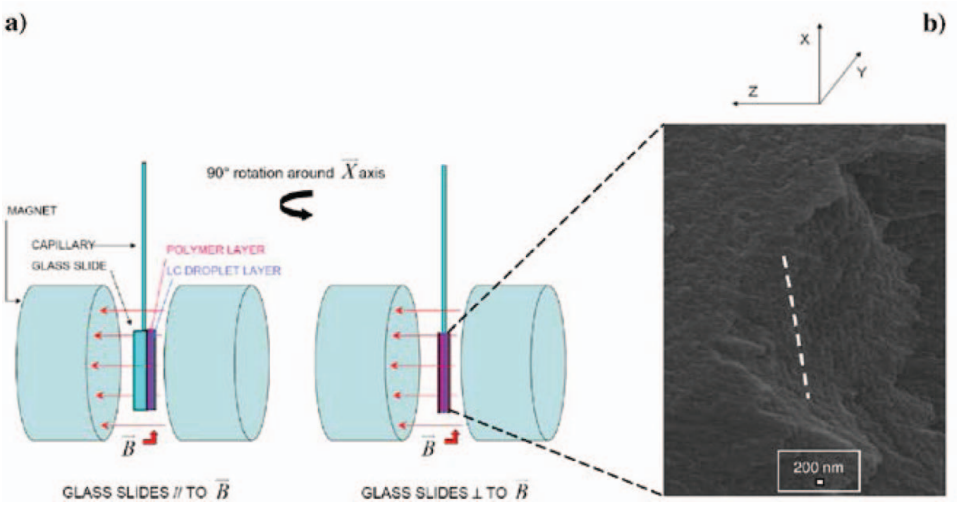

Figure 1. Scheme and laboratory reference frame of the EPR measurements. (a) Placement of the rectangular H-PDLC cell inside the instrument cavity in the parallel (//) or perpendicular (⊥) geometry. (b) Scanning electron micrograph of a cross section of the H-PDLC used in the EPR measurements. The grating structure is visible at the centre of the image, its orientation is indicated by the dashed white line.

the H-PDLC prepared with the BL038 LC [1]. Unfortunately the actual nanodroplets are not visible. To maximize the signal, 35 mm long cells were manufactured, to fully span the EPR cavity (25 mm long) with the central, uniformly photo-cured, portion, while the chosen width was 5 mm, that is, the largest dimension fitting inside the Dewar tube in the cavity. This rectangular cell could be rotated around the X axis of the laboratory frame (see the reference frame in Fig. 1). This allowed us to study the anisotropy of the director configuration with respect to a change in the orientation of the nanodroplet layers from parallel to the magnetic field (glass slides //: "parallel geometry") to perpendicular (glass slides ⊥: "perpendicular geometry"). In the temperature range 283.2–353.2 K investigated in this study, bulk 5CB, used as the LC component of the H-PDLC device, exhibits on heating the following phase sequence: Crystal–N (295.7 K), N–I (308.5 K), as reported by the manufacturer. It was used without any further purification.

The nitroxide spin probe, used for doping the LC, was the 3β-DOXYL-5α-cholestane free radical (CSL, Aldrich) which was employed in a number of previous studies [1, 5–7] where it proved to be a reliable probe to monitor the order and the dynamics of the LC system, due to its size, morphology and rigidity, which result in a strong orientation by the 5CB host. The CSL structure is shown in Fig. 2 together with the chosen ordering (x,y,z, solid line) and magnetic (x′,y′,z′, dashed line) molecular frames and the indication of its two main reorientational motions, tumbling and spinning, with the corresponding components of the rotational diffusion tensor: $D_\perp$ (reorientation of the molecular long axis) and $D_{//}$ (rotation around the long axis), respectively. The molecular magnetic frame (x′,y′,z′) was chosen according to the standard system of coordinates for the N–O paramagnetic moiety with the x′ axis along the N–O bond [5, 8] and the z′ axis perpendicular to the five-membered ring, i.e. parallel to the p_z orbital containing the unpaired electron density. According to a standard approach, the z axis of the ordering frame is considered parallel to the principal axis of inertia of the probe (its "long axis") and, to simplify the rotation which takes the

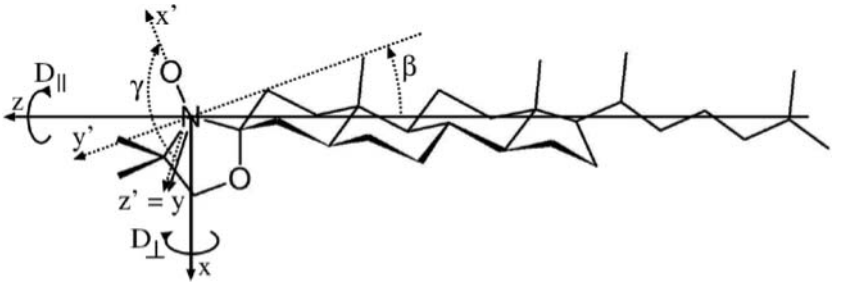

Figure 2. Chemical structure of the CSL spin probe together with the chosen ordering (x,y,z, solid line) and magnetic (x′,y′,z′, dashed line) molecular frames, the Euler angles, β and γ, between the molecular frames and the principal components, $D_\perp$ (reorientation of the molecular long axis) and $D_{//}$ (rotation around the molecular long axis), of the rotational diffusion tensor.

ordering into the magnetic frame [5], the y axis is considered parallel to the z′ axis. To reduce the correlation among variable parameters, the Euler angles, β and γ, between the molecular frames, were fixed in the fittings to 15° and 90°, respectively, in agreement with previous results obtained in related systems [1, 5–8]. The initial concentration of CSL present in the prepolymer syrup was set to 6×10^{-3} g_{CSL}/g_{BL038} which is six times larger than the limiting concentration typically suggested [9] to avoid Heisenberg spin exchange distortion effects, in order to compensate for the signal loss resulting from the free radical oxidation during the curing process, as described elsewhere [1]. In a typical acquisition, 100 to 200 scans were averaged to reach a S/N ratio larger than 100, and the resulting spectra displayed lineshapes essentially identical to the noisier spectra obtained in a set of test measurements of H-PDLC cells prepared with 1×10^{-3} g_{CSL}/g_{LC}, thus indicating the absence of spectral distortions. EPR spectra were acquired with a Bruker EMX spectrometer equipped with an ER 041XG microwave X-band (9.5 GHz) Gunn Diode bridge and a rectangular ER 4102 cavity. The samples were thermostated with a nitrogen flux through a variable temperature unit Bruker B-VT 2000. The temperature, monitored with a calibrated type T thermocouple (Comark Ltd.) kept in contact with the sample cell, showed a stability better than ±0.05 K. To study the effects due to annealing, spectra recorded from freshly prepared cells were compared with those recorded after either "field cooling" (FC) or "zero field cooling" (ZFC) the sample. This was done by heating it at 323.2 K (above the LC_{TNI}), then slowly cooling it to 298.2 K, which lies in the N phase of bulk 5CB, approximately 1 K/min, with the magnetic field either set at 6300 G (the highest available on the EPR spectrometer, $1\ G = 10^{-4}$ T) or turned off, and then equilibrating for 20 min. Finally, the cell was brought to the required temperature for the measurement. Images of cross sections of the H-PDLC have been recorded with a Zeiss Supra 50VP SEM, following the procedure adopted in a previous study [3] by freeze fracturing the cell and removing the LC with ethanol. Spectra of the percent transmittance of the H-PDLC have been recorded with an HR4000 high-resolution fiber optic spectrometer equipped with a white light source (Ocean Optics). The EPR spectra simulation program employed was based on a set of Fortran routines implementing the "slow tumbling" theory for a spin probe reorienting in a LC, developed by Freed and collaborators [9–11], combined with a software package [12] that optimizes the fit parameters for a series of spectra at the same time (global target analysis) using the Gauss-Newton-Marquardt non-linear least squares method [13].

III. Results and Discussion

Figure 3 shows a spectrum of the percent transmittance of the H-PDLC containing 5CB studied in this work compared to the one used in the previous study [1] containing BL038. The presence of a reflection peak around 565 nm reveals the formation of a diffraction grating and thus the occurrence of phase separation. The scattering loss difference at lower wavelengths between the 5CB and the BL038 H-PDLC spectra can be attributed to wavelength dependent Rayleigh scattering due to smaller droplet size. The droplet layers of 5CB H-PDLC were harder to discern during SEM imaging than those of BL038 H-PDLC, also supporting much smaller droplet sizes and lower phase separation. The difference in the wavelength of maximum reflection efficiency is related to the difference in the grating pitch, primarily due to a different phase separation between the two H-PDLCs.

The rigid-limit (RL) EPR spectrum of the 5CB H-PDLC cell recorded at 153.2 K in the parallel geometry is shown in Fig. 4, upper plot (green line, //). The spectrum is essentially identical to the RL spectrum of bulk 5CB (black line). Since the polarity of the environment experienced by the spin probe in the polymer is different to that present in the bulk of 5CB, with a consequent change in the hyperfine tensor [9], this result indicates that the spin probe is to be found mainly in the LC which therefore must phase separate, in contrast with what was suggested before [3], forming nanodroplets, as a result of the curing process. The lower plot of Fig. 4 is the RL spectrum recorded in the perpendicular geometry (green line, $\perp$) and is identical to the parallel one, as expected for an isotropic orientational distribution of locally oriented domains [14]. As a preliminary test of the interplay between the confinement and the ability of 5CB to self organize in the nanodroplets at 298.2 K, we compared a spectrum of the sample "as shipped" (Fig. 5, AS), recorded before any temperature treatment (no annealing), with one recorded after a quick zero field cooling (Q-ZFC) and after a slow one (S-ZFC). In case of some ordering effect due to the confinement,

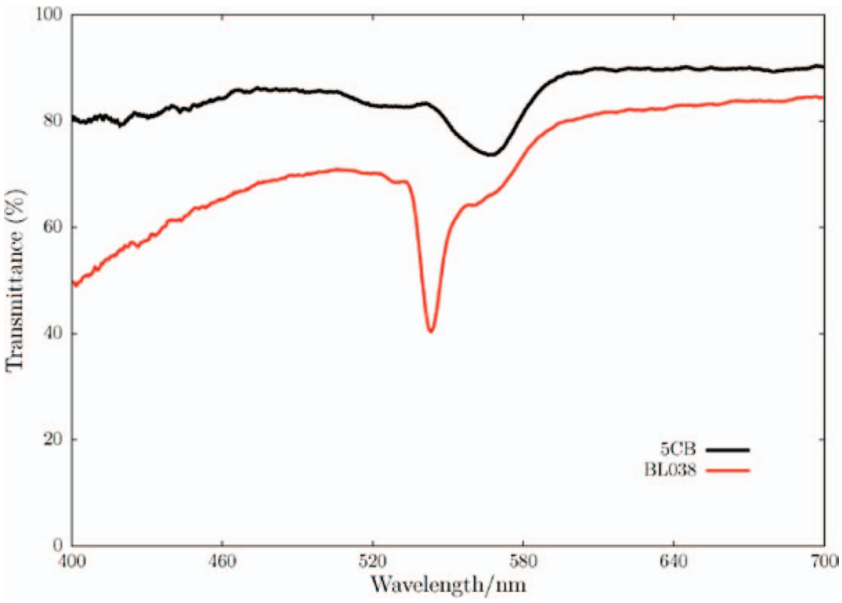

Figure 3. Spectrum of the percent transmittance of the H-PDLC containing 5CB (black line) studied in this work compared to the one previously studied [1] containing BL038 (red line).

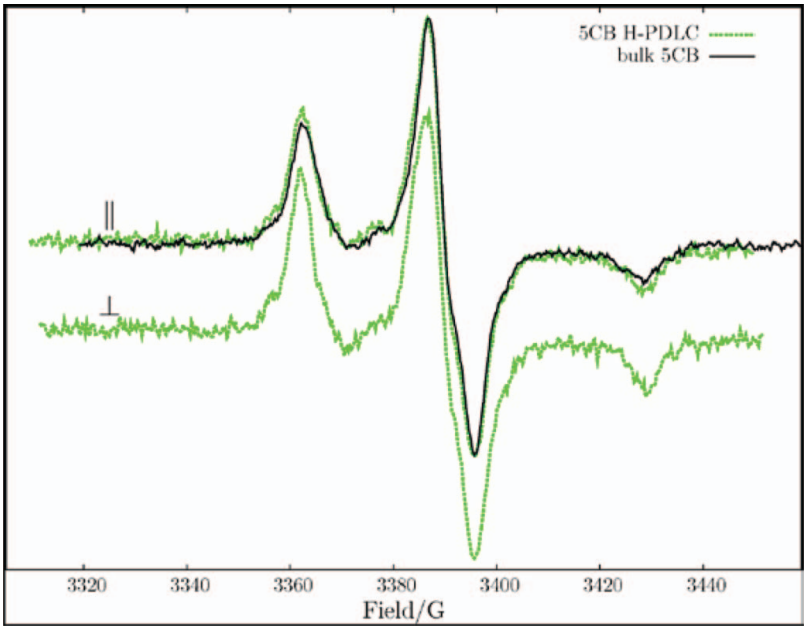

Figure 4. Typical rigid-limit spectra of the H-PDLC cell recorded at 153.2 K in the parallel (green line, //) and in the perpendicular (green line, ⊥) geometries compared to a typical rigid-limit spectrum of bulk 5CB at 153.2 K (black line).

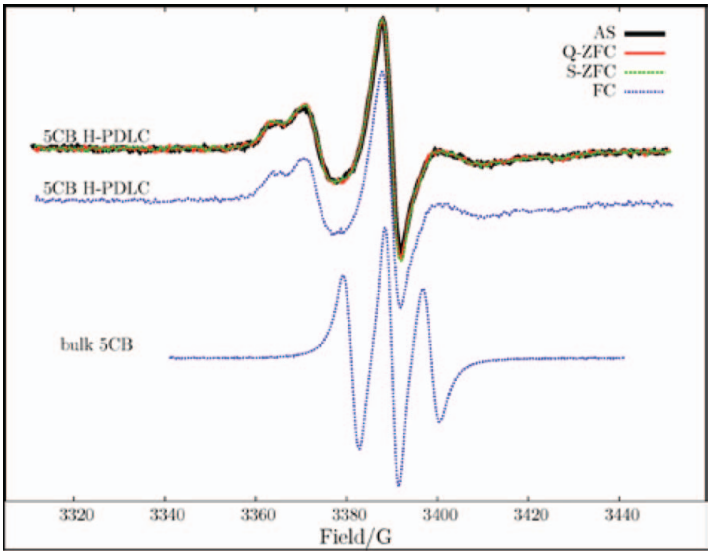

Figure 5. Upper plots: typical EPR spectra of the H-PDLC cell recorded at 298.2 K "as shipped" (AS, black line) or after various temperature treatments: quick zero field cooling (Q-ZFC, red line); slow zero field cooling (S-ZFC, green line); field cooling (FC, blue line). Lower plot: typical EPR spectrum of bulk 5CB at 298.2 K, in the nematic phase.

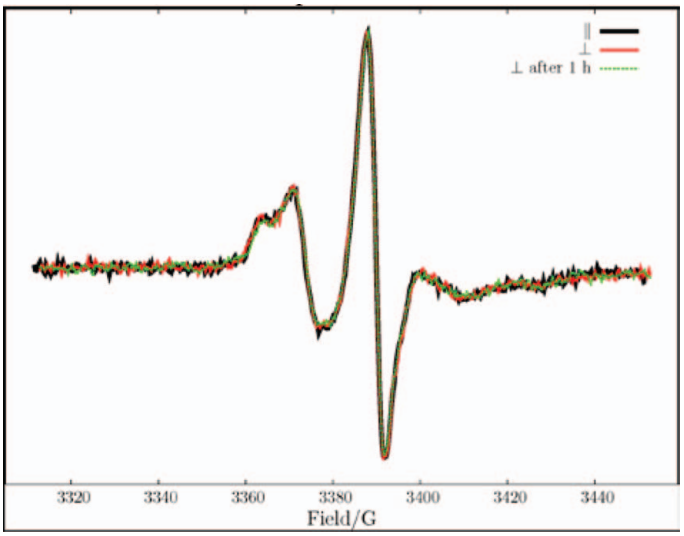

Figure 6. Typical EPR spectra of the H-PDLC cell recorded at 298.2 K after field cooling in the parallel geometry (//, black line), immediately after a 90° rotation to the perpendicular geometry (⊥, red line) and after 1 h in the perpendicular geometry at the highest field available on the EPR spectrometer of 6300 G (green line).

we would have expected some difference, but the spectra were identical. Then, to understand the influence of the field, we compared the sample after ZFC and after field cooling (FC). Also in this case the spectra were identical.

The spectra were instead very different from bulk 5CB which, at 298.2 K, is in the N phase. Since the spectra were independent of the temperature treatment, this suggests that the confinement did not induce any kind of ordering but rather it seemed to suppress the nematic

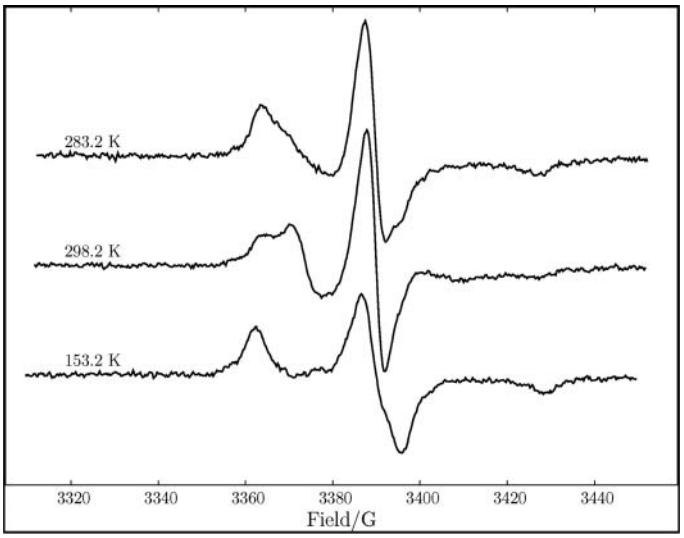

Figure 7. Typical EPR spectra of the H-PDLC cell recorded at 283.2 K after field cooling in the parallel geometry and at 298.2 K, compared to a typical rigid-limit spectrum at 153.2 K.

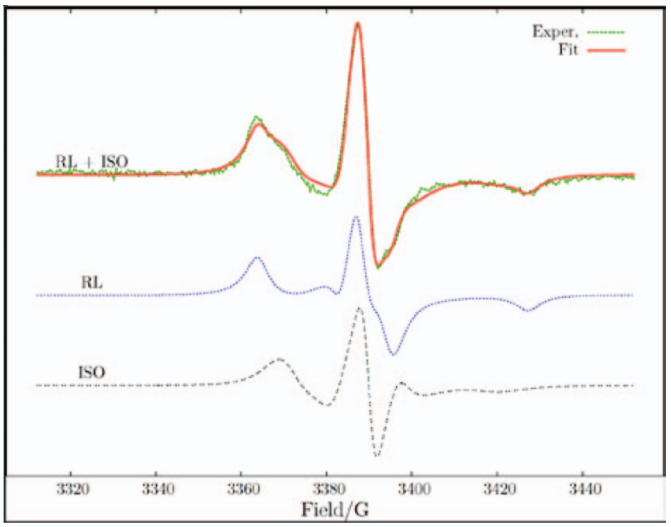

Figure 8. Typical EPR spectrum of the H-PDLC cell recorded at 283.2 K after field cooling in the parallel geometry (green line) and fit (RL + ISO, red line) to a model formed by two spectral components, one is rigid-limit (RL, blue line) the other is isotropic (ISO, black line).

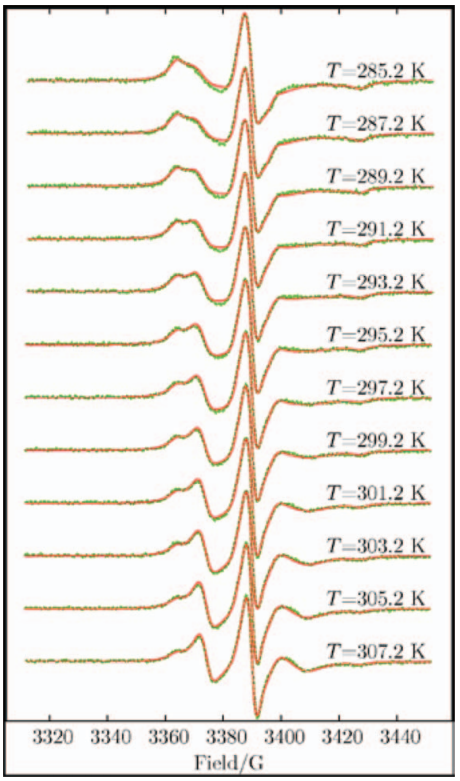

Figure 9. Temperature dependence of typical EPR spectra (green line) and fits (red line) to a 2-site model formed by a rigid-limit and an isotropic spectral component (see text for details). Spectra from 297.2 K to 307.2 K are in the range of the nematic phase of bulk 5CB.

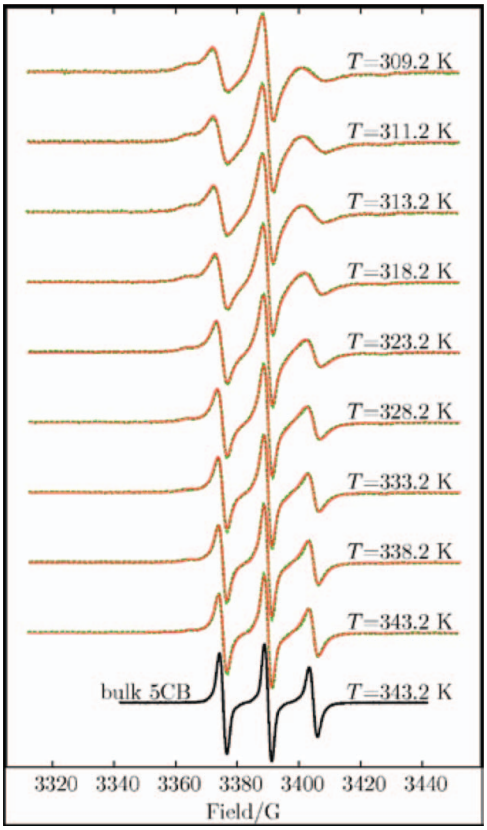

Figure 10. Temperature dependence of typical EPR spectra (green line) and fits (red line) to a 2-site model formed by a rigid-limit and an isotropic spectral component (see text for details). Spectra are in the range of the isotropic phase of bulk 5CB (black line).

ordering of bulk 5CB. To further verify the presence of some ordered fraction, we recorded a spectrum in the parallel geometry, after a FC also in the parallel geometry (Fig. 6, //), then we rotated the sample and quickly recorded a spectrum in the perpendicular geometry (Fig. 6, $\perp$). The result confirms that the macroscopic molecular organization of 5CB in the nanodroplets is isotropic since the two spectra were identical. By keeping the sample in the perpendicular geometry for 1 h at the maximum magnetic field available of 6300 G did not modify the spectrum, indicating that it was not possible to induce an alignment of 5CB in the nanodroplets, at least with this field strength. Typical spectra of the 5CB H-PDLC cell recorded in the temperature range 283.2–298.2 K had some similarities with the RL spectrum at 153.2 K. In particular the low field peak around 3365 G and the small, negative peak at high field around 3430 G (see Fig. 7). This suggests that a fraction of the sample might have a RL-like dynamics. Given the absence of an ordered fraction, as suggested by the preliminary spectra above, the remaining fraction is likely to be isotropic. According to these results, we performed a fit of the spectrum at 283.2 K using a 2-site model formed by a RL plus an isotropic (ISO) spectral component.

The resulting fit is shown in Fig. 8 and appears to be satisfactory. By adopting this model, a consistent temperature dependence of the best-fit parameters was recovered from

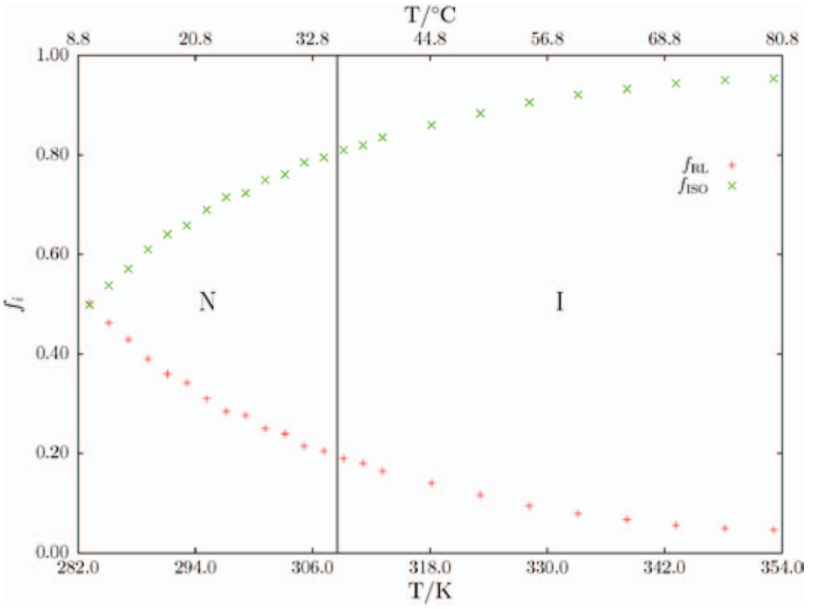

Figure 11. Temperature dependence of the fractional contributions, f_i, to the EPR spectra of the observed spectral components: rigid-limit (RL) and isotropic (ISO). The vertical line at 308.5 K indicates the T_{NI} of bulk 5CB.

the global analysis of the spectra recorded in the temperature range 283.2–353.2 K, after FC in the parallel geometry.

Results of the fits in the temperature range 285.2–307.2 K are presented in Fig. 9 (experimental: green line, fits: red line). Spectra from 297.2 K to 307.2 K are in the range of the N phase of bulk 5CB. The peak at the lowest field decreases consistently, according to a decrease of the RL fraction in the sample, whereas the neighbouring peak around 3375 G increases, according to an increase of the ISO fraction in the sample. Fits in the temperature range 309.2–343.2 K, where bulk 5CB is in the I phase, are reported in Fig. 10 (experimental: green line, fits: red line).

As the temperature increases, the RL component is still visible, albeit progressively smaller and smaller and the spectrum of 5CB in the H-PDLC device looks more and more similar to bulk 5CB (black line). The temperature dependence of the RL fraction recovered from the fits is shown in Fig. 11.

The consistent decrease of this fraction across the whole range of temperature confirms the validity of the fitting model and suggests the presence of a layer of LC molecules on the droplet surface with a very limited mobility. As the temperature increases, less and less molecules remain "frozen" in the surface layer thus reducing the RL spectral contribution. The consistent increase of the reorientational dynamics (Fig. 12) across the whole range of temperature also supports the proposed model. The slower dynamics within the nanodroplets with respect to bulk 5CB is also consistent with the expected behavior and with the results obtained in the previous study [1] of an analogous H-PDLC device, prepared with the BL038 LC.

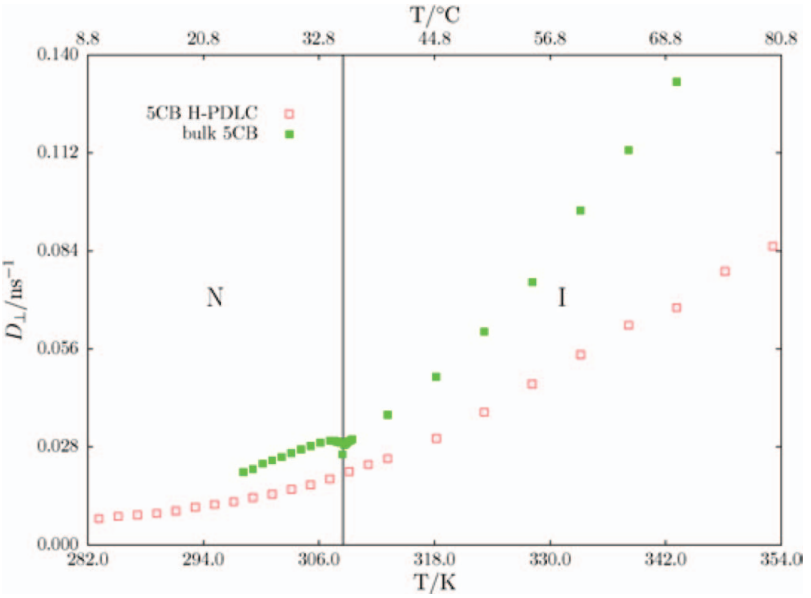

Figure 12. Temperature dependence of the tumbling diffusion coefficient, $D_\perp$, of the isotropic spectral component (open squares) compared to bulk 5CB (filled squares). The vertical line at 308.5 K indicates the T_{NI} of bulk 5CB.

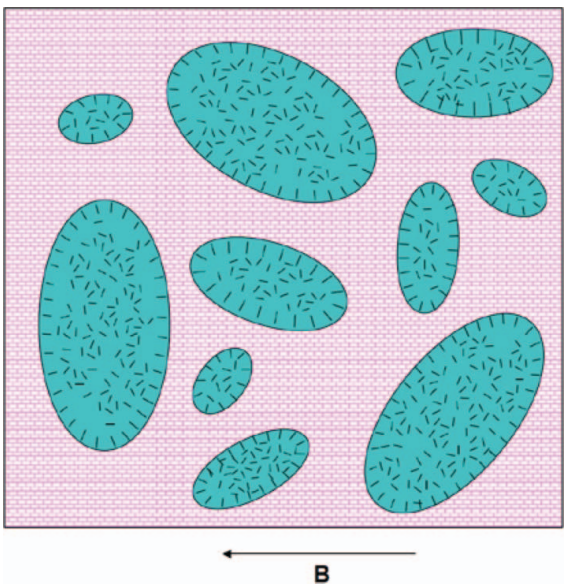

Figure 13. Model of the director configuration (black sticks) inside the postulated H-PDLC nanodroplets, across the studied temperature range, 283.2–353.2 K, formed by a surface layer with a very limited mobility and an isotropic phase in the droplet cavity.

IV. Conclusions

Our results indicate that the 5CB liquid crystal does phase separate from the prepolymer syrup as a result of the H-PDLC curing process, albeit not as well as the BL038. The occurrence of phase separation and the consequent formation of a diffraction grating was revealed by SEM images of the H-PDLC cross section and by the presence of a reflection peak around 565 nm. EPR spectra further confirmed the presence of liquid-like dynamics which would have not been observed in the absence of phase separation since the reorientational dynamics of 5CB in the H-PDLC device would have remained essentially frozen in the temperature interval studied. Instead, the dynamics was found to be slower than in bulk 5CB (Fig. 12), but still in the "fast motional regime" as indicated by the lineshapes of the spectrum of the 5CB H-PDLC at 343.2 K which appears to be quite similar to the spectrum of bulk 5CB (Fig. 10). In contrast with what was observed in a previous study [1] of an analogous H-PDLC device, prepared with the BL038 liquid crystal, in the present case no order, either macroscopic or only at molecular level, was found in the mobile fraction of the liquid crystal (i.e. potentially "switchable"), across the temperature interval studied. The 5CB nematic phase appears to be completely suppressed and no discontinuity is present in the temperature dependence of the reorientational dynamics (Fig. 12). According to our previously proposed model of the liquid crystal structure inside the nanodroplets of an H-PDLC device [1], the present result can be explained by assuming that the curing process led to the formation of nanodroplets of a very small size, of the order of only a few tenths of nm or less, which, we believe, was previously mistaken for the absence of phase separation. In these nanodroplets the constraints induced by the surface layer to the LC structure are dominant and do not allow for the onset of nematic order. The proposed model of the director configuration inside the postulated H-PDLC nanodroplets (Fig. 13) is formed by a surface layer with a very limited mobility and an isotropic phase in the droplet cavity.

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