# ESR Spin Probe Study of Nematic Order and Dynamics Inside HPDLC Droplets

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Electron Spin Resonance (ESR) spin probe spectroscopy is used to investigate the two phase Holographic Polymer Dispersed Liquid Crystal (HPDLC) system made of a liquid crystal (LC) confined periodically in a polymer matrix. HPDLCs are prepared using a two-beam laser interference set up at 532 nm wl on a prepolymer mix [1] consisting of LC, a monomer and a light sensitive photoinitiation dye. Polymerization at the bright regions of the interference pattern causes the diffusion of the liquid crystal to the dark regions forming a regular array of nanosized droplets embedded in a polymer matrix. A beam of light shone across the HPDLC reflects specific wavelengths of light, depending on the periodicity of the grating structure. These systems have extensive application in the fields of telecom and spectroscopy [2], and in reflective displays [3].

Several microscopic and spectroscopic techniques were used to study both droplets morphology and behaviour, ranging from SEM and AFM microscopy [2] to Nuclear Magnetic Resonance using deuterated 5CB LC [4] and protonated LC. A molecular-level information on the director configuration inside the droplets is still lacking and is fundamental to improve the diffraction properties and the switching performance of HPDLCs. To this purpose, ESR spin probe spectroscopy [5] was conducted on HPDLCs based on the commercial BL038 LC by doping the prepolymer mix with the CSL nitroxide free radical. Spectra were recorded at various temperatures ranging from the nematic to the isotropic phase of the LC to evaluate the effect of confinement on HPDLC local order and dynamics compared to bulk characteristics.

At 283 K, below the LC clearing temperature ($T_c$), the sample shows a peculiar equilibrium between a rigid-limit-like and an isotropic phase in approximately a 50:50 proportion. By increasing the temperature, the rigid-limit fraction decreases rapidly to about 5% while an ordered contribution, in the form of a relatively narrow distribution of nematic domains (quasi-monodomain), aligned along the magnetic field, begins to appear and can still be observed by a signature lineshape up to the $T_c$. The fractional contribution of this phase increases by field cooling the sample and decreases upon zero field cooling, with good reproducibility, and it occurs only along a direction parallel to the HPDLC droplet planes.

The results are consistent with the assumption of a distribution of droplets with an elongated shape (as shown by SEM) whose long axis is parallel to the layers and randomly oriented. The internal director configuration is bipolar-like. The LC local order is close to zero in the smaller droplets and increases in the larger. Only in the largest, the magnetic field is able to determine the observed quasi-monodomain.

References

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