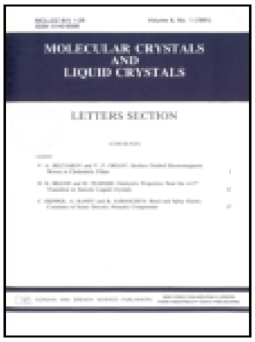

Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

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To cite this article: Corrado Bacchiocchi, Giulia Foschi, Isabella Miglioli, Saeedeh Shoarinejad, Alberto Arcioni & Claudio Zannoni (2015) Nematic Director Configuration, Local Order and Microviscosity in a PSLC Cell, Molecular Crystals and Liquid Crystals, 614:1, 2-10, DOI: 10.1080/15421406.2015.1049474

To link to this article: http://dx.doi.org/10.1080/15421406.2015.1049474

Mol. Cryst. Liq. Cryst., Vol. 614: pp. 2–10, 2015
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2015.1049474

Nematic Director Configuration, Local Order and Microviscosity in a PSLC Cell

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The director configuration, the local order and the molecular-level reorientational dynamics (microviscosity) of the 5CB liquid crystal (LC) inside a polymer-stabilized LC (PSLC) cell prepared with the 4,4′-bis(6-(acryloyloxy)hexyloxy)biphenyl (BAB6) diacrylic monomer have been studied with the EPR spin probe technique across the nematic and the isotropic phase of the LC. The cells made from glass slides, either clean or coated with an aligning layer, were filled with pure 5CB or with 0.5, 1.0 or 2.0 wt% of BAB6, either in the monomeric state or polymerized. Local orientational order parameter ($<P_2>$) in the non treated cells was always slightly lower than in the coated ones and both were lower than in the bulk LC. Order appeared to be independent of polymerization state or BAB6 concentration up to 1.0 wt%. Reorientational dynamics was essentially bulk-like in all cases, indicating that in our PSLC cells a full molecular mobility is retained. At the concentration of 2.0 wt%, in the coated cell with polymerized BAB6, the monodomain did not reform after a 90° rotation of the cell in the magnetic field, suggesting that the polymer network is, as expected, stabilizing the preexisting director configuration.

PACS numbers 42.70.Df; 42.79.Kr; 42.79.Ta; 61.30.-v; 61.30.Cz; 61.30.Eb; 61.30.Gd; 61.30.Pq; 76.30.-v; 76.30.Rn; 81.05.Qk; 85.60.-q; 85.60.Pg

Keywords confined liquid crystals; porous systems; phase separation; induced order; display devices; optical switches

I. Introduction

Polymer stabilized liquid crystals (PSLC) [1] are composite materials obtained by photopolymerization of a few percent concentration (typically 0.5 - 3%) of a suitable monomer (quite often a tetrafunctional diacrylate) mixed in a nonreactive low molar mass liquid

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crystal host. During the reaction the growing polymer network phase separates from the liquid crystal solvent, giving the material a gel-like physical appearance. If the polymerization is conducted in an ordered phase of the liquid crystal, the polymer network acquires the orientational order of the surrounding liquid crystal and will act, to some extent, as a template to stabilize the structure and the properties of the liquid crystal host [2].

These materials have initially attracted interest as a technological improvement of the pre-existing PDLC devices in applications like privacy windows and displays with faster switching rates, haze-free transparent state and larger viewing angle [3], bistable reflective mode displays [4–6] with lower threshold switching voltage [7, 8] and volume-stabilized ferroelectric and antiferroelectric liquid crystal displays [9]. More recently, polymer dispersions have been used in the stabilization of liquid crystal blue phases [10]. Prototype displays based on blue phases have been demonstrated (see e.g. [11] and refs therein).

The morphology of the network and how it is influenced by the temperature and orientational state of the liquid crystal during the polymerization and by the presence of flexible spacers in the monomer has been studied by scanning electron microscopy and cross-polarized light microscopy [12–14]. A commonly employed monomer is the diacrylic compound 4,4′-bis(6-(acryloyloxy)hexyloxy)biphenyl (BAB6), consisting of the 4,4′-bisacryloylbiphenyl (BAB) rigid anisotropic bead with 6 alkyl spacer chains. It was found that a disordered bead-like network is formed by BAB (without spacers) both in the nematic and the isotropic phase and by BAB6 (with spacers) in the isotropic phase of the LC host. Interestingly, BAB6 forms a more fibrous and ordered network in the nematic phase. This was explained assuming that, as the polymerization proceeds, BAB6 forms a more flexible network that (i) allows the yet unreacted monomers to keep their initial alignment and (ii) perturbs less the original order and director distribution of the LC host.

Fung et al. [15] analysed birefringence data on a PSLC formed by BAB6 in 4-*n*-pentyl-4′-cyanobiphenyl (5CB) in terms of the Landau-de Gennes approach using a simple model of an array of thin fibrils. The characteristic thickness of the fibrils was estimated to be around 4 nm, suggesting a very fine distribution of polymer networks.

Stannarius et al. [16] performed the first deuterium NMR study of the local director distribution and the nematic order in PSLC cells formed by BAB monomer and a 50/50% mixture of 5CB and 4-*n*-pentyloxy-4′-cyanobiphenyl (5OCB) showing that about 1 wt% of polymer is sufficient to stabilize the nematic director against the NMR field and suggesting that once the polymer network has formed its orientation is no longer influenced by the field. They also found that the nematic order is bulk-like with a lowering of about 1-2 K of the T_{NI}.

Local dynamic processes of the liquid crystal host have been studied via NMR proton spin-lattice relaxation [17]. The relaxation rate observed in the pure liquid crystal exhibited only a small variation in the MHz regime in the presence of the polymer network, but showed a significant change in the kHz regime. This was attributed to a slower exchange of liquid crystal molecules between a more ordered layer at the polymer surface and the disordered bulk, in the assumption of a finely distributed network with fibers of a few nanometers in diameter.

Electrooptic studies [14] found that networks formed by highly oriented fibers exhibit higher threshold voltage and switching hysteresis compared to bead-like networks with larger pore sizes, formed preferentially at higher temperatures.

The importance of the polymer network at the nanometer scale prompted us to adopt the EPR spin probe technique that can provide molecular-level information on the ordering, the director distribution and the reorientational dynamics of a suitable stable nitroxide free radical dissolved in the liquid crystal host. We have previously employed this technique in investigation of silica nanoparticles dispersed in nematics [18, 19] as well as of Holographic Polymer Dispersed LC (H-PDLC) [20, 21], where a nematic is embedded in nanosized pores. In both these systems the spin probe technique was key to understanding at molecular level ordering and dynamics of the probe and indirectly the matrix. Here the application of the method is complicated by the fact that the nitroxide radical added to the prepolymer mixture can take part in the polymerization evolution. Nitroxide radicals can react directly with carbon centered radicals and can control polymerizations. In particular, it has been shown that a small concentration of a nitroxide radical, less than 1%, is able to significantly reduce the shrinkage of an acrylate-based polymer [22]. The presence of the nitroxide radicals should therefore reduce the aggregation at the initial stage of the network formation, prevent bead-like structures and favour a more fiber-like and flexible network that should exhibit a larger orientational coupling with the liquid crystal host [14]. Here we aim at studying the liquid crystal as affected by a polymer network rather than the details of a specific network, so the effect of the nitroxide on the network itself is probably not so important. It is, however, not so obvious that enough spin probes can survive this active participation in the polymerization without being completely consumed. Our work thus serves first to demonstrate the feasibility of the approach even in this case and then proceeds to extracting order and dynamics for the probe in the nematic perturbed by the polymer network.

II. Experimental

The host liquid crystal 5CB was obtained from Merck KGaA (Darmstadt, Germany). This compound exhibits, on heating, the nominal phase sequence: Crystal – N (295.7 K), N – I (308.5 K), as reported by the manufacturer, and was used without further purification. The nitroxide spin probe, used for doping the LC mixture, was the 3β-doxyl-5α-cholestane free radical (Aldrich, hereafter referred to as CSL), which was employed in a number of previous studies [19, 20, 23, 24] 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 results in a strong orientation by the 5CB host. The CSL structure is shown in Figure 1 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.

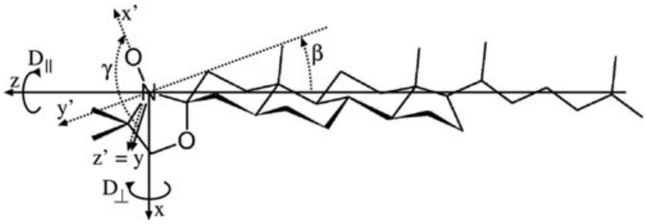

Figure 1. Chemical structure of the CSL spin probe together with the chosen ordering (x,y,z, solid line) and magnetic (x$'$,y$'$,z$'$, dashed line) molecular frames, the Euler angles, β and γ, between the molecular frames and the principal components, $D_\perp$ (reorientation of the molecular long axis) and $D_\|$ (rotation around the molecular long axis), of the rotational diffusion tensor.

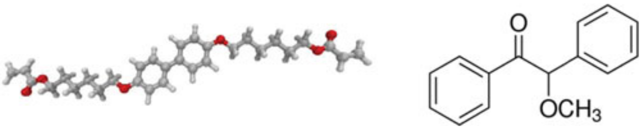

Figure 2. Model rendering of the BAB6 monomer (left) and chemical structure of the photoinitiator BME (right).

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 [23, 25] 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 ordering into the magnetic frame [23, 25], 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 [19, 20, 23–25].

The monomer mixed in the LC host was the BAB6 mesogenic diacrylic monomer, synthesized in Prof. L. Giorgini group. The free-radical photo-polymerization was carried out using the photoinitiator benzoin methyl ether (BME, also a generous gift of Prof. L. Giorgini) and curing the samples inside the Dewar tube in the EPR instrument cavity by irradiation with UV light ($\lambda = 365$ nm) for a period of time depending on the monomer concentration. The typical BME concentration was 10 wt% of the monomer. The chemical structures of BAB6 and BME are shown in Figure 2. A model rendering of the resulting polymer, *p*(BAB6), is presented in Figure 3.

In order to compensate for the signal loss resulting from the free radical oxidation during the polymerization process, the typical initial concentration of CSL present in the prepolymer mixture was set to 1×10^{-3} g_{CSL}/g_{5CB}, which is anyway the limiting concentration typically suggested [26] to avoid Heisenberg spin exchange distortion effects.

Four BME/CSL/5CB samples were prepared either without monomer or with 0.5, 1.0 or 2.0 wt% of BAB6. The cells used for the measurements were formed by two parallel rectangular glass slides separated by two plastic 110 μm spacers and sealed at the ends. We prepared two series of cells: in the first the glass slides were just cleaned with sulphuric

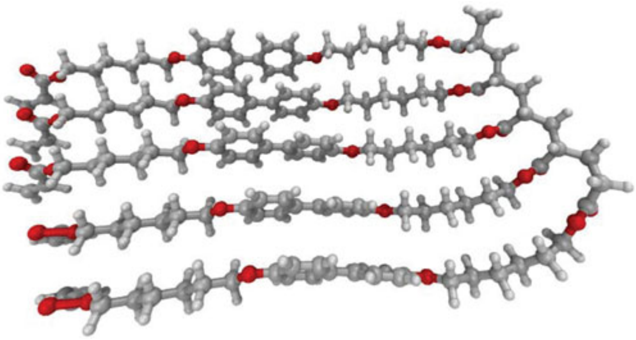

Figure 3. Model rendering of *p*(BAB6).

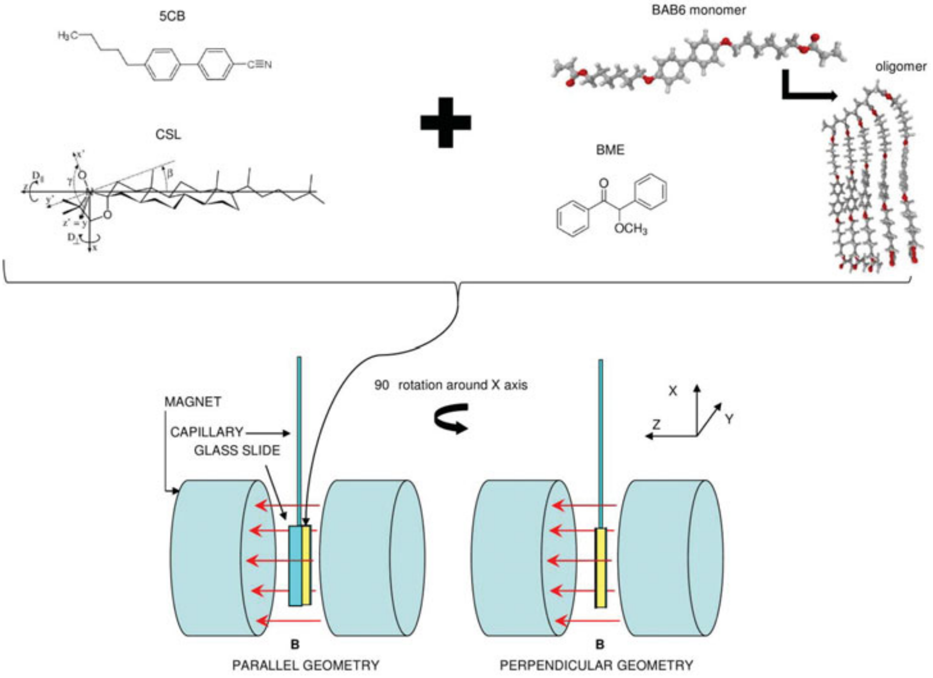

Figure 4. Scheme and laboratory reference frame of the EPR measurements. Placement of the rectangular cell inside the instrument cavity in the parallel (∥, left) or perpendicular (⊥, right) geometry.

acid, while in the second they were also coated with a suitable aligning material (polyvinyl formal) and rubbed to achieve a homogeneous orientation of the sample in the direction of the short edge of the cell. One cell of the first type and one of the second were filled with the samples without monomer, whereas, for each BAB6 concentration, we prepared four cells under different conditions: uncoated - unpolymerized (UU type), uncoated - polymerized in the isotropic phase at 323.2 K and under the action of a magnetic field of 3390 G (UP type), coated - unpolymerized (CU type), coated - polymerized in the supercooled nematic phase at 288.2 K and 6300 G (CP type).

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 Figure 4). To maximize the signal, 40 mm long cells were manufactured, to fully span the EPR cavity (25 mm long) with the central 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 Figure 4). This allowed us to study the anisotropy of the director configuration with respect to a change in the orientation of the polymer network from parallel to the magnetic field (glass slides ∥: parallel geometry) to perpendicular (glass slides ⊥: perpendicular geometry).

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 4102ST 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.

For each sample, EPR spectra were recorded in the temperature range 288.2 - 343.2 K both in a heating and in a cooling run. Before a typical run, a first spectrum, hereafter referred to as NFC, was recorded at 298.2 K, immediately after the preparation of the cell, and then the sample was kept in the cavity under the action of a magnetic field of 6300 G, which is the highest field available in our instrument, and was subjected to the same programmed temperature cycle taking it from 298.2 K (N phase) to 323.2 K (I phase) and then cooling it down slowly to 288.2 K at an average rate of 1 K/min. This "field cooling" (FC) procedure was able to fully anneal the LC to form a monodomain in all samples. 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 [26–28], combined with a software package [29] that optimizes the fit parameters using the Gauss-Newton-Marquardt non-linear least squares method [30].

III. Results and Discussion

In a preliminary experiment a cell was prepared with 5CB and only the photoinitiator. Spectra, recorded at various temperatures, were identical to those of pure 5CB, thus indicating that the photoinitiator does not perturb the local order or the director distribution.

Since the conditions that favour a monodomain distribution of the nematic director are a major topic of this work, another series of preliminary spectra were recorded to ascertain whether the 5CB can be aligned and form a monodomain in a similar way in the cell confined geometry compared to a typical EPR capillary. At all the concentrations studied, the FC at 6300 G produces a monodomain at 298.2 K in a 1.8 mm internal diameter capillary and in the cells. To ensure stability and reproducibility of the results, care was taken to record spectra immediately after FC at 6300 G. FC spectra could be typically fitted to a nematic monodomain model that was then used throughout the main experimental data analysis.

To study the ability of the polymer network to stabilize the initial nematic monodomain structure, we compared spectra recorded from uncoated PSLC cells, at various concentrations of BAB6, polymerized in the I phase at 323.2 K (UP type cell) with coated cells polymerized, with the same concentrations of BAB6, in the supercooled N phase at 288.2 K and 6300 G (CP type cell) with the rubbing direction aligned along the magnetic field.

In a typical experiment, a first NFC spectrum was recorded immediately after the preparation of the cell, then a series of two FC processes were done, to ensure that a repeated heating of the cell to the I phase did not change the spectra after the FC. The cell was then rotated by 90° in the magnetic field and a spectrum was immediately recorded (AR). A final spectrum was recorded 30 min after the rotation (30minAR).

Figure 5 shows spectra recorded as described above in the CP type cell at 0.5 wt% BAB6. NFC, FC and before rotation (BR) spectra were all identical and typical of a nematic monodomain indicating that the freshly prepared CP cell exhibits, as expected, the alignment even before the FC. The spectra recorded after the rotation did not change, showing that, at this polymer concentration, the combined effect of the alignment layer and the network is not able to keep the original director orientation. This same result was obtained also with the CP type cell at 1.0 wt% BAB6.

Spectra recorded in the CP type cell at the higher concentration of 2.0 wt% BAB6 are presented in Figure 6. Also in this case, NFC, FC and BR spectra were all identical and substantially indicating a nematic monodomain but, immediately after the rotation, the spectrum (AR) was clearly different, indicating that the polymer network is hindering

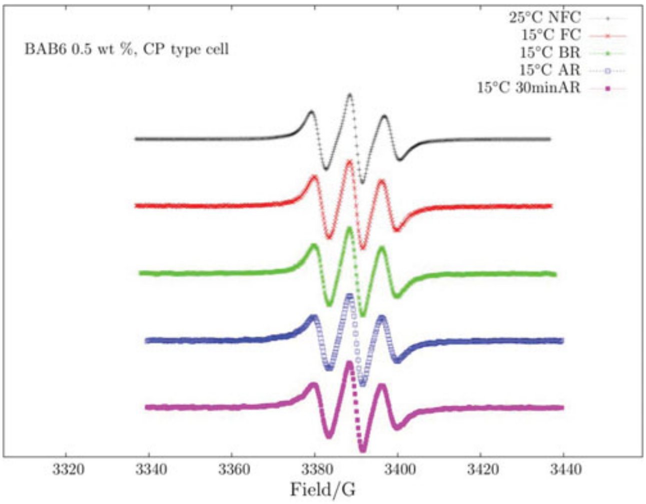

Figure 5. EPR spectra in the N phase of 5CB + 0.5 wt% BAB6 in the coated PSLC cell, polymerized in the supercooled N phase at 288.2 K and 6300 G (CP type cell, see text for details) recorded at 298.2 K before "field cooling" (NFC) and at 288.2 K after "field cooling" (FC); after a second "field cooling", before rotation (BR); immediately after rotation (AR) and 30 min after rotation (30minAR).

the rotation of the director and thus the reformation of a monodomain along the magnetic field. Moreover, 30 min after the rotation the spectrum did not exhibit a further change, suggesting that the network is able to stabilize the LC structure.

Figure 7 shows spectra recorded in the UP type cell at 2.0 wt% BAB6. The NFC spectrum is a typical isotropic polydomain which is the expected result since this sample

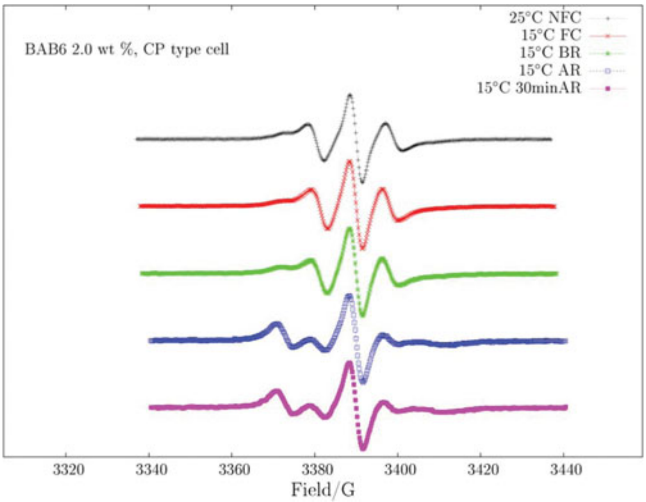

Figure 6. EPR spectra in the N phase of 5CB + 2.0 wt% BAB6 in the coated PSLC cell, polymerized in the supercooled N phase at 288.2 K and 6300 G (CP type cell, see text for details) recorded at 298.2 K before "field cooling" (NFC) and at 288.2 K after "field cooling" (FC); after a second "field cooling", before rotation (BR); immediately after rotation (AR) and 30 min after rotation (30minAR).

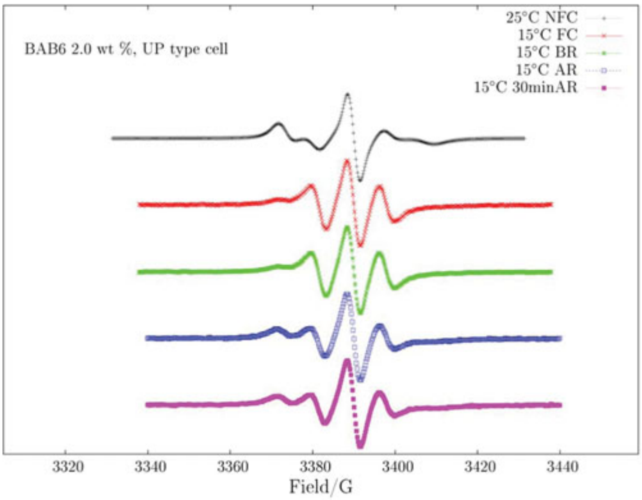

Figure 7. EPR spectra in the N phase of 5CB + 2.0 wt% BAB6 in the uncoated PSLC cell, polymerized in the I phase at 323.2 K (UP type cell, see text for details) recorded at 298.2 K before "field cooling" (NFC) and at 288.2 K after "field cooling" (FC); after a second "field cooling", before rotation (BR); immediately after rotation (AR) and 30 min after rotation (30minAR).

was polymerized in the I phase. The FC process is able to form a monodomain (FC) indicating that the magnetic field is able to overcome the disordering effect of the polymer network. After the rotation the spectrum (AR) is different from the BR one, but the change is small compared to that observed in the CP cell at 2.0 wt% BAB6 (Figure 6). In fact, the AR and BR spectra share the same lineshapes typical of a monodomain. Also in this cell, 30 min after the rotation the spectrum did not exhibit a further change, suggesting that this type of network has retained the ability to stabilize the LC structure, but to a lesser extent.

IV. Conclusions

The ability of a polymer network formed by the 4,4′-bis(6-(acryloyloxy)hexyloxy)biphenyl (BAB6) diacrylic monomer to stabilize the nematic monodomain structure of the 5CB liquid crystal was studied with the EPR spin probe technique in cells with different surface treatment, polymer concentrations and polymerization procedure. Sample preparation showed, in all cases, good reproducibility: spectra recorded from samples prepared in the same conditions were always identical. At all BAB6 concentrations studied, each freshly prepared cell formed a monodomain after field-cooling (FC). After a 90° rotation in the magnetic field the monodomain immediately reformed in all types of cells at concentrations of BAB6 up to 1.0 wt% indicating that, at these lower concentrations, the polymer network was not able to stabilize the LC structure. At 2.0 wt% in the UP type cell the monodomain reformed only partially and did not reform at all in the CP type cell. This appears therefore to be the lower threshold concentration for this type of network to be able to stabilize the LC structure, with a larger effect exhibited by a polymer network formed in the N phase.

Acknowledgments

We thank MIUR, INSTM, EU, the University of Bologna and the CINFO Computer Centre, University of Camerino for support. We are grateful to Prof. L. Giorgini (University of Bologna) for the generous gift of the BAB6 monomer and the BME photoinitiator.

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