PHYSICAL REVIEW E **67**, 041709 (2003)

Anchoring behavior, orientational order, and reorientation dynamics of nematic liquid crystal droplets dispersed in cross-linked polymer networks

Frédérick Roussel[1,*] and Bing M. Fung[2]
[1]*Laboratoire de Thermophysique de la Matière Condensée, Equipe de l'UMR CNRS 8024, Université du Littoral-Côte d'Opale, MREID, 59140 Dunkerque, France*
[2]*Department of Chemistry, University of Oklahoma, Norman, Oklahoma 73019*

(Received 21 November 2002; published 17 April 2003)

The orientational ordering and the electro-optical properties of nematic liquid crystal (LC) droplets confined to cross-linked polymer networks are investigated as a function of the anchoring conditions at the polymer-liquid crystal interface. Normal alignment (homeotropic) or parallel alignment (planar) inside LC droplets was controlled by using acrylate polymers with appropriate side chains. Drastic changes in the reorientation dynamics of the confined nematic liquid crystal phase are observed, as well as in the orientational ordering of the phase-separated LC which was investigated by ^{13}C-NMR (nuclear magnetic resonance) spectroscopy. The cross-link density of the polymer network also affects the orientational ordering and the electro-optical properties of the confined LC phase. Faster switching times and higher-order parameters were found for samples with LC droplets exhibiting planar anchoring.

DOI: 10.1103/PhysRevE.67.0417XX PACS number(s): 61.30.−v, 42.70.Df, 76.60.Cq

Surface interactions at liquid-solid interfaces are of main scientific interest from a fundamental standpoint and find numerous potential technological applications. Ordered fluids such as liquid crystals (LC) in contact with a solid substrate often adopt a preferred direction of alignment, which is called surface anchoring [1,2]. This phenomenon has been known for several decades, and is widely used to develop LC display devices [3]. However, the direction of alignment depends on subtle molecular interactions between the LC and the host that are still not well understood. For a nematic LC, three preferred alignments have been observed, i.e., the director **n** is oriented normal to the interface (*homeotropic* anchoring), parallel to the interface (*planar* or *homogeneous* anchoring), or along a tilted direction [1]. When the LC compound is confined either to porous inorganic materials (e.g., nucleopore membranes, porous glasses, or aerosils) or to polymer matrices [e.g., polymer-dispersed liquid crystals (PDLC) and polymer-stabilized liquid crystals], the geometry of the LC phase is strongly influenced by the shape and the size of the cavity [4]. Figure 1 displays two schematic nematic director fields in spherical cavities exhibiting *homeotropic* (right) and *planar* (left) anchoring. Due to confinement to a curved geometry, topological defects appear in the director-field configuration leading to structures referred to as radial (left) and bipolar (right), respectively. In the case of PDLC systems, Amundson and Srinivasarao [5], and Zhou *et al.* [6] demonstrated the ability to tailor the anchoring energy by making small changes in the side group of polyacrylate matrices without significantly changing the sample morphology. By this means, one expects to exercise significant control over the electro-optical properties of PDLC-based display devices. The cavity surface is then a strong determining factor of the director-field configuration that is closely related to the order parameter of the confined LC phase. In a previous report, ^{13}C-NMR (nuclear magnetic resonance) spectroscopy has been successfully used to probe the orientational ordering of a confined nematic LC in a homopolyacrylate matrix [7]. In this paper, the electro-optical behavior and the orientational ordering of nematic droplets confined to cross-linked polyacrylate networks are investigated as a function of the anchoring boundary conditions at the polymer-liquid crystal interface.

The liquid crystal chosen for this study, 4-*n*-pentyl-4′-cyanobiphenyl (5CB, Aldrich) is a single-component nematic well characterized from an optical, a thermodynamical, and a structural (NMR) point of view. 5CB exhibits a nematic phase between the crystalline and isotropic states in the temperature range of 23–35.3 °C. The polymer precursor is composed of a mixture of a monofunctional monomer to tailor the anchoring conditions at the polymer-LC interface, and a multifunctional monomer to provide cross-links to the polymer network. In order to investigate the influence of the network density on the physical properties of the confined LC phase, three different multifunctional monomers were used: a trifunctional monomer [pentaerythritoltriacrylate (PE3A, Aldrich)], and two difunctional monomers having the same structure, but with different spacer lengths between the two reactive acrylate moieties [polyethyleneglycoldiacrylate of molecular mass of M_n

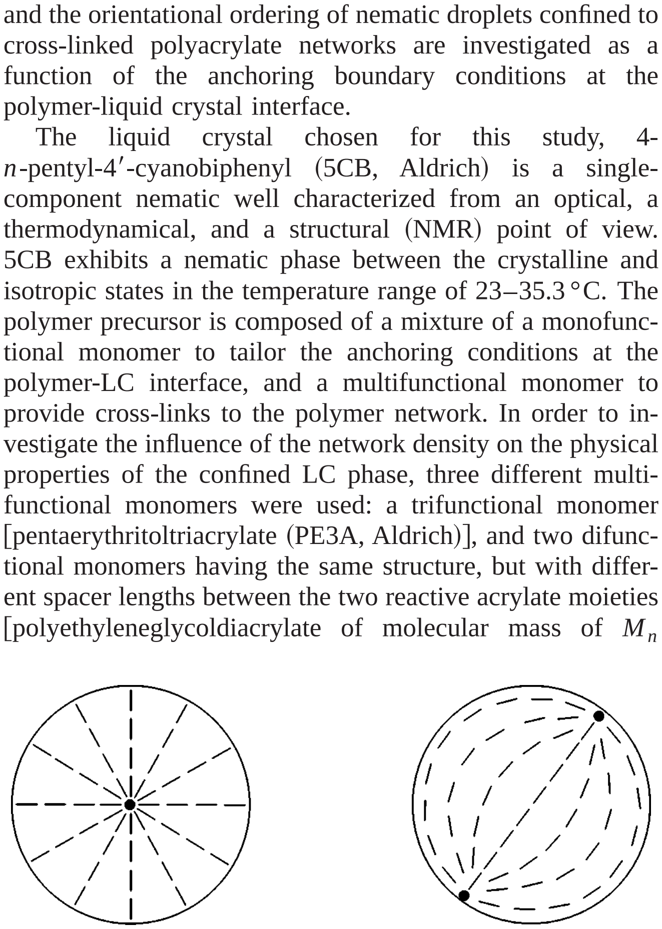

FIG. 1. Nematic director fields in spherical cavities: radial (left) and bipolar structures (right).

---

[*] Corresponding author. Email address: Frederick.Roussel@purple.univ-littoral.fr

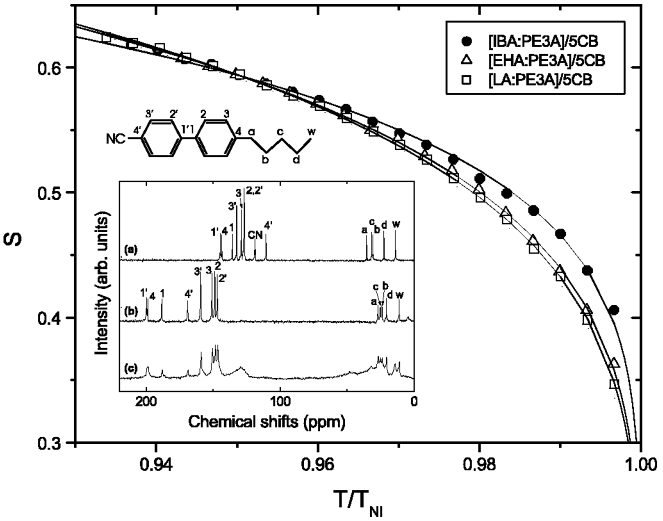

FIG. 2. Order parameter of nematic 5CB confined to various cross-linked polymer networks inducing *planar* anchoring (IBA:PE3A) and *homeotropic* anchoring [(EHA:PE3A) and (LA:PE3A)], respectively. Inset: NMR spectra of isotropic 5CB (a), nematic 5CB (b), and nematic 5CB confined to a (IBA:PE3A) cross-linked polymer network in the (60:40) wt % ratio (c).

$\sim$575 g mol^{-1} (P2A575, Aldrich) and $M_n\sim$700 g mol^{-1} (P2A700, Aldrich), respectively]. The choice for monofunctional acrylate is driven by the need for planar or homeotropic anchoring at room temperature. Two monofunctional acrylate monomers with alkyl side groups [ethylhexylacrylate (EHA, Aldrich) and laurylacrylate (LA, Aldrich)] were used to induce homeotropic anchoring, whereas isobornylacrylate (IBA, Aldrich) was employed to obtain planar anchoring conditions [5]. In order to control the macromolecular architecture, the molar fraction of acrylate function in the various monofunctional-multifunctional monomer mixtures was kept constant (8.7×10^{-3} mol) so that the polymer networks and cross-link densities could be compared. The ultraviolet sensitive photoinitiator Darocur 1173 (Ciba) was added to the monomer mixtures at a concentration of 1 wt %. The liquid crystal and the monomer mixtures were mixed together in 60:40 wt % ratio until formation of a single-phase solution. Samples for NMR experiments were prepared by filling standard 5-mm tubes with the monomer-LC mixtures; the height of the sample size was ca. 3 cm. For the electro-optical measurements, 25 μm commercial cells (EHC, Japan) were filled with the same mixtures. The photopolymerization process was initiated with a Hg-Xe arc lamp operating at $\lambda=365$ nm with a beam intensity of 17.5 mW cm^{-2}. As polymerization proceeded, the solution supersaturated, microdroplets of 5CB formed and were trapped by solidification of the polymer matrix. As estimated by optical microscopy, films prepared with a given multifunctional acrylate exhibit approximately similar drop size.

The ^{13}C-NMR experiments were performed at 100.58 MHz on a Varian UNITY/INOVA 400 NMR spectrometer ($|\mathbf{B}_0|=9.5$ T) equipped with an indirect detection probe [7]. The inset of Fig. 2 displays typical NMR spectra of isotropic 5CB (a), nematic 5CB (b), and nematic 5CB confined to a (IBA:PE3A) cross-linked polymer network (c). Using the SPINAL-64 broadband proton decoupling sequence [8], all PDLC samples exhibit high resolution spectra such as (c) indicating that the nematic director field inside the droplets is obviously aligned along with the magnetic field $\mathbf{B}_0$. The chemical shifts of the observed signals in the nematic phase (δ_{nem}) [spectrum in inset (b)] are considerably different from those in the isotropic state (δ_{iso}) [spectrum in inset (a)], and are determined by the order parameter tensor and the anisotropic chemical shift tensor. For many cases, a semiempirical equation can be used to describe the relationship between the chemical shift anisotropy ($\Delta\delta=\delta_{nem}-\delta_{iso}$) and the order parameter S [7,9]

$$S=\alpha\Delta\delta+\beta, \tag{1}$$

where α and β are empirical constants. To estimate the order parameter S using Eq. (1), the chemical shift anisotropy $\Delta\delta$ of each aromatic carbon is measured from the NMR spectra recorded at several given temperatures. Using calculated values of α (ppm^{-1}) and β (unitless) reported in the literature [9], S can be determined. Figure 2 displays the evolution of S of the mesogenic core as a function of the reduced temperature T/T_{NI} for 5CB droplets confined to cross-linked polymer networks based on the same multifunctional acrylate (PE3A), but with different monofunctional monomers inducing either planar or homeotropic anchoring [(IBA:PE3A)/5CB, (EHA:PE3A)/5CB, and (LA:PE3A)/5CB]. In Fig. 2, the symbols represent averages of experimental data of the eight aromatic carbons of the 5CB molecules, and the solid lines are the best fit curves using the Haller equation [10]

$$S(T)=S_0\left(1-\frac{T}{T_{NI}}\right)^F, \tag{2}$$

where S_0 is the limit of the order parameter with decreasing temperature and F may be considered as an indication of how quickly a molecular segment reaches the limit of the order parameter as a function of change in temperature. Significant differences in S vs T/T_{NI} are observed depending on the type of monofunctional acrylate used for the polymer network formulation. These changes seem to be closely related to the anchoring conditions at the polymer-LC interface. For planar anchoring (IBA:PE3A), the confined LC phase is more ordered compared to that with homeotropic anchoring [(EHA:PE3A) or (LA:PE3A)]. These results can be explained by the droplet director-field configuration. When the LC molecules are tangential to the polymer surface, i.e., bipolar configuration, the whole droplet including the two points defects (‘‘boojums’’) rotate and align upon application of the magnetic field $\mathbf{B}_0$ [11]. This reorientation process (alignment of the bipolar axis in $\mathbf{B}_0$) has obviously minimal effect on the bipolar configuration of the droplets, meaning that the geometry of the confined LC phase remains nearly identical.

When the LC molecules are perpendicular to the surface, i.e., radial structure, a first-order transition is expected in which the droplets adopt an aligned configuration in the magnetic field $\mathbf{B}_0$ with an equatorial disclination line [11]. In other words, the radial ‘‘hedgehog’’ structure containing a

TABLE I. Parameters for the temperature dependence of S for the LC phenyl rings obtained from fitting the experimental data to Eq. (2). R is the correlation factor. Experimentally, the limiting value of S_0 cannot be reached due to phase transition of LC into a solid. The factor F describes how fast S changes with temperature; in the present work for 5CB in different polymer matrices, a smaller value of F corresponds to larger S in the temperature range studied.

PDLC system	S_0	F	R
(IBA:PE3A)/5CB	0.931	0.150	0.989
(EHA:PE3A)/5CB	1.040	0.187	0.987
(LA:PE3A)/5CB	1.072	0.197	0.989
(IBA:P2A575)/5CB	1.021	0.178	0.988
(EHA:P2A575)/5CB	1.042	0.190	0.988
(LA:P2A575)/5CB	1.061	0.194	0.986
(IBA:P2A700)/5CB	1.058	0.196	0.987

point defect at the center of the droplet transforms into an axially symmetric structure with a ring defect. This ring defect obviously induces a larger distortion of the nematic director field compared to that of a bipolar configuration reducing the averaged order parameter of the confined LC phase. Another important point concerns the anchoring conditions at the polymer-LC interface. Indeed, the homeotropic anchoring results from the interdigitation between alkyl ends of mesogens and alkyl side groups of polyacrylate matrices [5,7,12,13]. Several studies demonstrated that there is a substrate-induced order in the LC surface layer [14]. This process is mostly driven by short range molecular interactions. Therefore, a competition between the aligning effect of the external magnetic field and the surface anchoring is present, and it may reduce the order parameter of the confined LC phase. If one considers the two samples prepared with various alkyl side chain lengths, i.e., hexyl -C_6- (EHA:PE3A)/5CB, and dodecyl -C_{12}- (LA:PE3A)/5CB, one can see small but distinct changes in S (Fig. 2) showing that a longer alkyl side chain (C_{12}) induces a decrease in the order parameter of the confined LC phase. This means that for droplets with homeotropic anchoring conditions, the interdigitation of the alkyl chains of the polymer side groups with the LC molecules may also alter the averaged orientational ordering of the phase-separated LC domains. Similar behaviors were observed for another PDLC system based on the same monofunctional monomers (IBA, EHA, LA) but with a different multifunctional acrylate, i.e., P2A575. As evidenced in Table I, values obtained from nonlinear least-squares fits of experimental data to Eq. (2) show that the order parameter of the confined LC phase is higher for planar anchoring (IBA:P2A575)/5CB than for homeotropic anchoring [(EHA:P2A575)/5CB and (LA:P2A575)/5CB]. Again, the effect of the length of the alkyl polymer side chain on S is indicated by a decrease of the order parameter with increasing chain length. The network cross-link density also influences the orientational ordering of the confined LC phase. By changing the spacer length between two consecutive cross-links (P2A575→P2A700), S drops by a factor of almost 10%. This behavior may be explained by a smaller imprinting of the nematic order onto polymer interfaces when the cross-link density is lower [15].

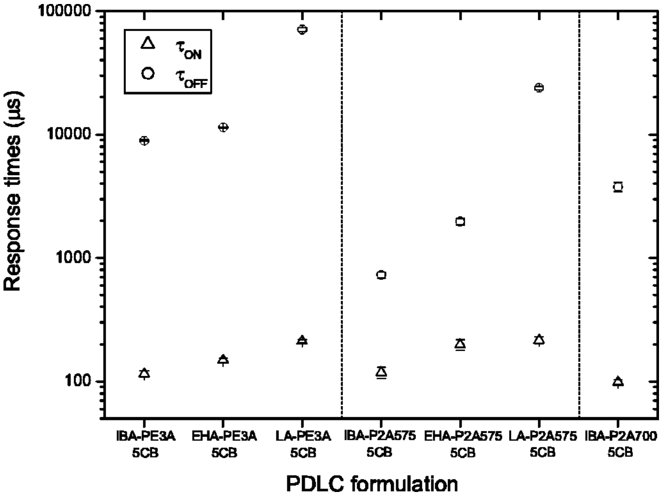

FIG. 3. Switching times of confined 5CB as a function of the polymer network formulation. τ_{ON} and τ_{OFF} are the rise time and fall time, respectively. Measurements were performed at $T/T_{NI} = 0.97$.

Considering the elastic free energy of a nematic LC phase confined to a spherical geometry [16], and assuming that an electric field **E** and a magnetic field $\mathbf{B}_0$ are formally equivalent, the nematic director-field configurations are expected to be identical upon application of either **E** or $\mathbf{B}_0$. In order to corroborate the orientational ordering with the reorientation dynamics (switching times) of the confined nematic phase upon application of an external electric field **E**, the electro-optical properties of the various PDLC films were determined from time-resolved, forward transmittance of a He-Ne laser beam passing through the film, while applying 100-Hz sinusoidal voltage pulses ($V_{pp} = 140$ V) across the film [17]. For a given multifunctional monomer, various PDLC films exhibit a similar contrast (difference of transmittance between the electric field ON and OFF states), indicating that the sample morphology remains almost identical when small changes in the side group of polyacrylate matrices are made. These results are in good agreement with optical microscopy observations as well as with previous studies reported in the literature [5]. Figure 3 displays the rise time (τ_{ON}) and fall time (τ_{OFF}) for various PDLC formulations. For both PE3A- and P2A575-based PDLC films, the switching times (τ_{ON}, τ_{OFF}) behave in a similar way depending on the anchoring conditions at the polymer-LC interface. Indeed, films with LC droplets having planar anchoring exhibit faster reorientation dynamics upon application or removal of the electric field **E** compared to films with LC droplets having homeotropic anchoring. It should be pointed out that the transition occurring in the defect structure of a radial droplet as a function of the applied field may increase the switching time, even though there is no critical field characterizing the transition between the hedgehog and the aligned structure [14]. If one combines the switching time measurements with the order parameter values determined from ^{13}C-NMR experiments, it appears that droplets with a higher-order parameter have faster reorientation dynamics. In their theoretical model to describe the electro-optic response of PDLC films, Kelly and Palffy-Muhoray [18] stated that the characteristic response time for bipolar LC droplets is $\tau \equiv \Gamma R_e^2 / K \epsilon^2 S S_d$, where Γ is a viscous torque, R_e^2 is the mean squared curvature of the director field in the cavity, K is the LC elastic constant, ϵ is the LC dielectric constant, and SS_d is the degree of orientational order of confined LC molecules. In other words, a decrease in the orientational order of the confined LC phase will induce an increase in the dynamic response time of PDLC films. Our experimental results are generally in agreement with this assessment. A comparison between the differences in τ_{ON} and the differences in S is interesting. If one considers the PE3A and P2A575 systems exhibiting the largest difference in S (LA and IBA), ΔS values are for both systems in the range of 0.011 ($T/T_{NI} = 0.97$). Interestingly, differences in τ_{ON} are also similar, i.e., ≈ 90 μs. These results seem to indicate that for a given difference in S, one should expect a given difference in τ_{ON}. Such a relationship is not observed for τ_{OFF} indicating that other factors such as the droplet shape and/or the viscosity of the phase-separated LC phase also play an important role in dictating τ_{OFF}. As one can see in Fig. 3, the alkyl side-chain length of the polyacrylate matrices strongly influences the reorientation dynamics, particularly the relaxation time (τ_{OFF}). When the side-chain length increases from -C_6- (EHA) to -C_{12}- (LA), τ_{OFF} is at least ten times larger. This behavior could be explained by the lower-order parameter of LA-based PDLC films, but an alternative explanation may stem from surface anchoring conditions. Previous works on alkyl brush surfaces have generally shown that homeotropic anchoring is best achieved when first alkyl chains are long ($\geqslant C_6$), and second mesogens are perpendicular to the surface [12,13]. Therefore, increasing the side-chain length should enhance the interdigitation process leading to larger interactions in the LC surface layer. However, it should be also considered that interdigitation of long alkyl chains with LC molecules may increase the viscosity of the nematic phase leading to slower switching times. Another possible explanation may arise from a difference in droplet shape. Radial anchoring is best achieved in spherical cavities, whereas a bipolar configuration usually takes place in ellipsoidal droplets which are known to exhibit faster reorientation dynamics compared to spherical ones [4]. Finally, the switching time measurements show that a decrease in the cross-link density (P2A575→P2A700) leads to an important increase in $\tau_{OFF}(\times 5)$. As previously discussed, this behavior can be correlated either to a smaller surface imprinting for a polymer network with a lower cross-link density, or to a change in droplet shape.

In summary, we have shown that the order parameter of a LC phase confined to cross-linked polymer networks is closely related to the anchoring condition at the polymer-LC interface. Higher-order parameters were found for samples with LC droplets exhibiting planar anchoring. These results were corroborated to switching time measurements. It appears that droplets with a higher S have faster reorientation dynamics upon application of an electric field.

The EU program Interreg, the MJENR, and the CNRS are acknowledged for financial support. The work of B.M.F. was supported by the U.S. National Science Foundation (Grant No. DMR-0090218).

[1] B. Jérôme, in *Handbook of Liquid Crystals*, edited by D. Demus, J. Goodby, G.W. Gray, H.W. Spiess, and V. Vill (Wiley-VCH, Weinheim, 1998), Vol. 1, p. 535.
[2] G. Barbero and G. Durand, in *Liquid Crystals in Complex Geometries*, edited by G.P. Crawford and S. Žumer (Taylor and Francis, London, 1996), p. 21.
[3] S.M. Kelly and M. O'Neill, in *Handbook of Advanced Electronics and Photonic Materials and Devices*, edited by H.S. Nalwa (Academic Press, Boston, 2000), Vol. 7, p. 1.
[4] G.P. Crawford and S. Žumer, *Liquid Crystals in Complex Geometries* (Taylor and Francis, London, 1996).
[5] K.R. Amundson and M. Srinivasarao, Phys. Rev. E **58**, R1211 (1998).
[6] J. Zhou, D.M. Collard, J.O. Park, and M. Srinivasarao, J. Am. Chem. Soc. **124**, 9980 (2002).
[7] F. Roussel, C. Canlet, and B.M. Fung, Phys. Rev. E **65**, 021701 (2002).
[8] B.M. Fung, K. Ermolaev, and A.K. Khitrin, J. Magn. Reson. **142**, 97 (2000).
[9] T.H. Tong, B.M. Fung, and J.-P. Bayle, Liq. Cryst. **19**, 333 (1997).
[10] I. Haller, Prog. Solid State Chem. **10**, 103 (1975).
[11] S. Candau, P. LeRoy, and F. Beauvais, Mol. Cryst. Liq. Cryst. **23**, 283 (1973).
[12] J.E. Proust, L. Ter-Minassian-Saraga, and E. Guyon, Solid State Commun. **11**, 1127 (1972).
[13] G.P. Crawford, R.J. Ondris-Crawford, J.W. Doane, and S. Žumer, Phys. Rev. E **53**, 3647 (1996).
[14] M. Vilfan *et al.*, Phys. Rev. E **59**, R4754 (1999); P. Ziherl *et al.*, *ibid.* **61**, 2792 (2000); C. Chiccoli *et al.*, *ibid.* **62**, 3766 (2000); M. Vilfan *et al.*, *ibid.* **66**, 021710 (2002)
[15] K.R. Amundson, Phys. Rev. E **59**, 1808 (1999).
[16] S. Žumer and J.W. Doane, Phys. Rev. A **34**, 3373 (1986); J.H. Erdmann, S. Žumer, and J.W. Doane, Phys. Rev. Lett. **64**, 1907 (1990); G.P. Crawford and J.W. Doane, Condens. Matter News **1**, 5 (1992).
[17] F. Roussel, R. Chan Yu King, and J.-M. Buisine, Eur. Phys. J. E (to be published).
[18] J.R. Kelly and P. Palffy-Muhoray, Mol. Cryst. Liq. Cryst. **243**, 11 (1994).