

Virtual surfaces, director domains, and the Fréedericksz transition in polymer-stabilized nematic liquid crystals

Pavel A. Kossyrev, Jun Qi, Nikolai V. Priezjev, Robert A. Pelcovits, and Gregory P. Crawford^{a)}

Department of Physics, Brown University, Providence, Rhode Island 02912

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The critical field of the Fréedericksz transition and switching dynamics are investigated for polymer-stabilized nematic liquid crystals as a function of polymer concentration. A simple phenomenological model is proposed to describe the observed critical field and dynamic response time behaviors as a function of concentration. In this model, the polymer fibrils form director domains, which are bounded by “virtual surfaces” with a finite anchoring energy. © 2002 American Institute of Physics. [DOI: 10.1063/1.1515136]

Polymer-stabilized liquid crystals (PSLCs) are composed of a polymer network dispersed in a nematic liquid crystal. They are promising materials for many display configurations. Small amounts of reactive monomer polymerized in a nematic liquid crystal create an aligned polymer network that under some circumstances can provide a memory effect.¹ The polymer network structure captures details of the nematic director prior to photopolymerization. We present results on the influence of the polymer network on the switching behavior of a homogeneously aligned nematic liquid crystal.

Previous studies calculated the critical field of the Fréedericksz transition in PSLC systems by modeling the polymer morphology as a collection of planes or bundles parallel to the substrates,^{2,3} or collectively as an effective field.⁴ The model of the polymer matrix as a series of planes perpendicular to the x , y , and z axes of the Cartesian coordinate system was introduced by Hikmet and Boots.⁵ None of these models explicitly accounts for the observed dependence of the critical field on the polymer concentration. We introduce a phenomenological model which describes the dependence of the critical field and the response time on the polymer concentration, and accounts for the change in the polymer network's characteristic length and anchoring strength.

Consider a homogeneous cell of PSLC sandwiched between two transparent indium tin oxide (ITO) coated glass plates with a $5\ \mu\text{m}$ cell gap thickness. The glass substrates are coated with rubbed polyimide (Nissan-0821) such that the nematic directors on both surfaces are anchored parallel to the plates. We prepared two sets of PSLCs using the low molecular weight nematic liquid crystal BL038 (EM Industries) and diacrylate monomers LC242 (BASF) and RM257 (EM Industries). Both monomers have negative dielectric anisotropy ($\epsilon_a \approx -2$) and a stable nematic phase in the range of temperatures: $65\text{--}118\text{ }^\circ\text{C}$ for LC242 and $70\text{--}126\text{ }^\circ\text{C}$ for RM257. A low percentage (2% of monomer weight) of photoinitiator Darocur-1173 (Ciba) was used. In our studies we investigated the concentration range where the diacrylate monomers are dissolved in liquid crystals at room temperatures ($\leq 6\%$ of the monomer by weight). When a diacrylate

monomer is polymerized with UV in a liquid crystal solvent, the orientation and order of the resultant network depend on the orientation and order of the liquid crystal,¹ which can be slightly different from the liquid crystal alignment prior to photopolymerization due to the formation of the polymer network. Nevertheless, we assume that the polymer network has homogeneous alignment identical to the alignment of the liquid crystal prior to photopolymerization.^{3,4}

A schematic illustration of the experimental setup for measuring the transmission properties of a PSLC cell is shown in Fig. 1(a). The cell is situated between a pair of parallel polarizers, with the nematic director oriented 45° to the transmission axes of the polarizers. Glass plates coated with ITO serve as the electrodes to apply 1 kHz square ac

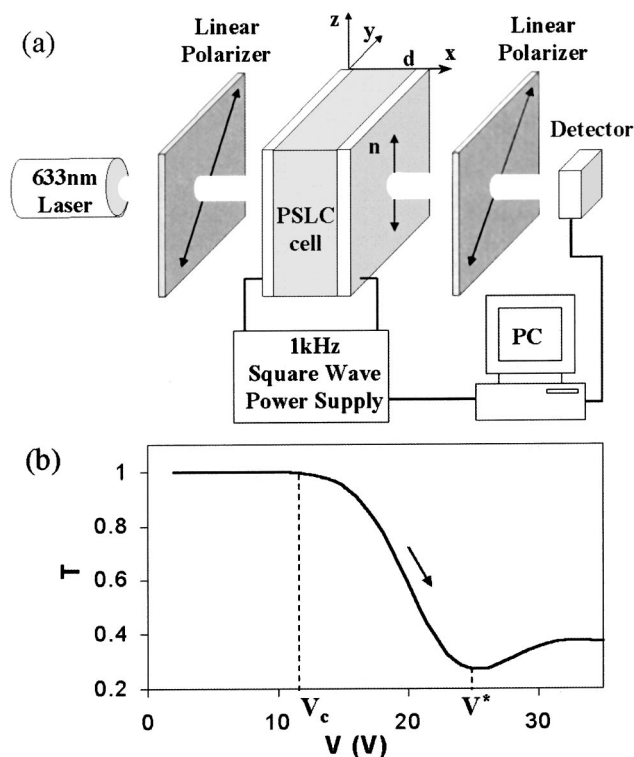


FIG. 1. (a) Experimental apparatus for measuring the transmission properties of a homogeneously aligned PSLC cell. The cell is situated between parallel polarizers oriented 45° to the nematic director n inside the cell. (b) Example of transmittance vs applied voltage scans.

^{a)}Also with: Division of Engineering; electronic mail: gregory_crawford@brown.edu

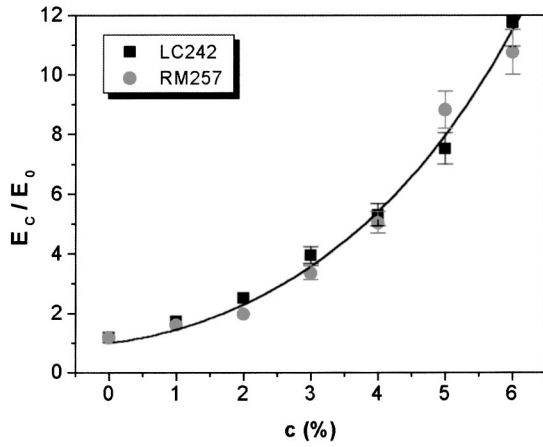


FIG. 2. Critical field vs concentration for two PSLC prepared using BL038 and diacrylate monomers LC242 and RM257. E_c is the critical field normalized to the critical field E_0 in the homogeneous cell filled with pure BL038. The solid curve represents the based on Eq. (5). Error bars, where not shown, do not exceed the symbol size.

voltage, V . In the field-off state, the cell exhibits phase retardation $\Gamma = 2\pi/\lambda(n_e - n_o)d \approx 4\pi$, where $n_e = 1.799$ and $n_o = 1.527$ are the extraordinary and ordinary refractive indices, respectively, of the BL038 at 589 nm, $d = 5 \mu\text{m}$, is the cell gap thickness, and $\lambda = 633 \text{ nm}$ is the wavelength of the incident laser light. Due to uniform alignment of the liquid crystal and the polymer network, the light intensity of the cell transmitted, $I = \frac{1}{2} \cos^2(\Gamma/2)$, is maximized in the field-off state with the present arrangement of polarizers. A transparent cell can be switched to an opaque state when an electric field is applied due to the creation of director domains in the cell.⁶ By application of the field only a portion of the molecules reorient. Those molecules, which are in close vicinity to the polymer network, remain less influenced by the field due to anchoring to the polymer. In this way domains with different orientations of the nematic director can be created. The phase retardation of the reoriented molecules becomes $\Gamma = 2\pi/\lambda \int [n_e(\theta) - n_o] dx$, where the integral is over the domain size and $n_e(\theta)$ is given by $[1/n_e(\theta)]^2 = (\sin \theta/n_o)^2 + (\cos \theta/n_e)^2$. The angle $\theta = \theta(x, y)$ is the tilt angle of the director with respect to the z axis [see Fig. 1(a)], which depends on positions x and y of the molecule in the domain and the field strength. The transmittance $T = I(V)/I(V=0)$ of the cell in the field-on state is affected by two factors: scattering by the nematic director domains and the change in phase retardation. The scattering leads to a decrease in the transmittance and to the opaqueness of the PSLC cells. The change in phase retardation gives rise to oscillations in the transmittance. An example of the transmittance versus applied field is shown in Fig. 1(b).

By monitoring the transmittance of the cells as a function of the voltage applied we determine the critical voltage V_c of the Fréedericksz transition, and hence the critical field $E_c = E_c(c)$ for each concentration c of the polymer. The results of the critical field of the Fréedericksz transition for both types of PSLC are shown in Fig. 2. We normalized our data to the critical field $E_0 = \pi/d\sqrt{K/(\epsilon_a\epsilon_0)} = 0.24 \text{ V}/\mu\text{m}$ for homogeneously aligned BL038 in the absence of a polymer network ($c=0$), where $\epsilon_a = \epsilon_{\parallel} - \epsilon_{\perp} = 16.4$ is the dielectric anisotropy of the BL038 at 1 kHz, ϵ_0 is the permittivity of

the free space, and $K = 20.7 \text{ pN}$ is the Frank elastic constant for BL038 in the one constant approximation.

To explain these results we assume that the polymer network is composed of polymer fibrils oriented parallel to the nematic director in the field-off state. The density of the fibrils (the number of polymer fibrils per unit volume) is proportional to the concentration of the dissolved diacrylate monomer. By assuming that the polymer fibrils are perfectly straight we can treat the problem as two dimensional. We model the domains of the nematic director in the field-on state by rectangles of dimension a along the x axis and b along the y axis. We consider the Fréedericksz transition in the PSLC cell of cell gap thickness d in context of the transition in each of these identical rectangles defined by the director domains. Within each rectangular domain the total free energy density (per unit volume) of nematic liquid crystal can be expressed as

$$f_v = \frac{K}{2} \left[\left(\frac{\partial \theta}{\partial x} \right)^2 + \left(\frac{\partial \theta}{\partial y} \right)^2 - \frac{\epsilon_a \epsilon_0 E^2}{K} \sin^2 \theta \right], \quad (1)$$

where $\theta(x, y)$ is the distortion angle of the nematic director with respect to the z axis. By minimizing the total free energy, we obtain the differential equation for the distortion angle,

$$\frac{\partial^2 \theta}{\partial x^2} + \frac{\partial^2 \theta}{\partial y^2} + \frac{\epsilon_a \epsilon_0 E^2}{K} \sin \theta \cos \theta = 0. \quad (2)$$

Assuming strong anchoring boundary conditions at the surface of the domain, i.e., $\theta=0$ at $x=0, a$ and $y=0, b$ the critical field E_c , is obtained by solving Eq. (2):

$$E_c = \sqrt{\frac{\pi^2 K}{\epsilon_a \epsilon_0} \left[\left(\frac{1}{a} \right)^2 + \left(\frac{1}{b} \right)^2 \right]}. \quad (3)$$

We assume that lengths a and b decrease with an increase in concentration as $1/a = 1/d + 1/\xi$ and $1/b = 1/\xi$, where the characteristic length ξ is determined by the polymer network. The average distance between the centers of the randomly distributed polymer fibrils changes with the polymer concentration as α/\sqrt{c} , where we express c in %, and α will be determined from the data. Therefore, if we denote the diameter of the polymer fibrils by β [see Fig. 3(b)], the polymer characteristic length ξ can be expressed as $\xi(c) = \alpha/\sqrt{c} - \beta$. With finite surface anchoring, which is the case on the perimeter of each of the rectangular director domains, lengths a and b have to be modified. We assume that the surface anchoring energy per unit area takes Rapini–Papoular form:⁷

$$f_s = 1/2 W \sin^2 \theta, \quad (4)$$

where W is the anchoring strength on the surfaces of the rectangular domains. The boundary conditions at finite anchoring are^{7,8} $(d\theta/dx)_a \pm W/K \sin \theta \cos \theta = 0$ and $(d\theta/dy)_b \pm W/K \sin \theta \cos \theta = 0$, where the derivatives are taken on the perimeter of the rectangles. Hence the critical field with finite anchoring can be approximated as

$$E_c(c) \approx \sqrt{\frac{\pi^2 K}{\epsilon_a \epsilon_0} \left[\left(\frac{1}{d} + \frac{1}{\xi + 2K/W} \right)^2 + \left(\frac{1}{\xi + 2K/W} \right)^2 \right]}. \quad (5)$$

This expression is valid when $K/W < 10\xi$.⁹ In comparing the elastic energy, Eq. (1), and the surface energy, Eq. (4), of the

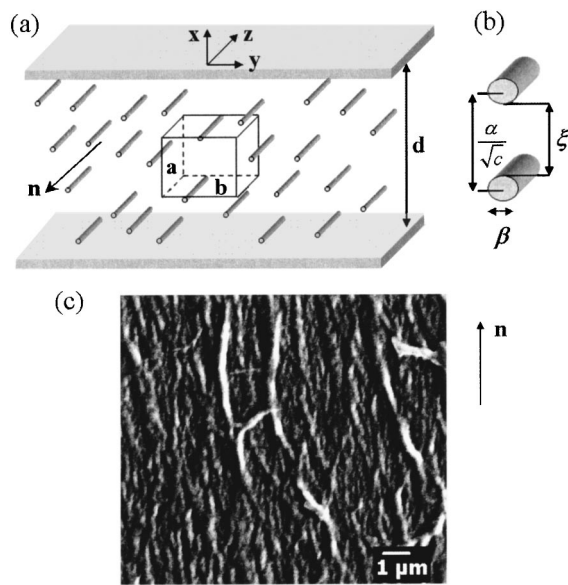


FIG. 3. (a) Polymer network shown as a collection of fibrils parallel to the nematic director n in the field-off state (z axis). The electric field E was applied along the x axis perpendicular to the glass substrates. The director domains are modeled by parallelepipeds with a rectangular cross section of dimensions a along the x axis and b along the y axis. (b) The average distance between the centers of polymer fibrils at concentration c is α/\sqrt{c} , and the diameter of a fibril is β . (c) SEM picture of the aligned 3% RM257 polymer network (the nematic director orientation is vertical).

nematic liquid crystal on the boundaries of the nematic director domains where we assign the virtual surfaces $f_v\beta \approx f_s$ [or, equivalently, $K(\theta/\xi)^2\beta \approx W\theta^2$], we conclude that $2(K/W) = A(\xi^2/\beta)$, where A is a constant. As can be seen from the above expression, the anchoring strength W is concentration dependent due to the dependence of ξ on the concentration. At concentration $c=0$, the critical field in Eq. (5) reduces to the original Fréedericksz critical field, $E_c(c) = E_0 = \pi/d\sqrt{K/(\epsilon_a\epsilon_0)}$, as expected. The polymer morphology was studied by scanning electron microscopy (SEM). Polymer feature sizes on the order of 50 nm are prominent in the SEM image for a 3% RM257 sample [Fig. 3(c)]. Due to removal of the liquid crystal, which is necessary for taking the SEM image, the polymer network collapsed considerably, resulting in some grosser features (collections of fibrils). By fitting the experimental data (the diameter of the polymer fibrils $\beta=0.05 \mu\text{m}$ was fixed) to the critical field of expression (5) we obtain $\alpha=0.21 \mu\text{m}$ and $A=23.92$. The fit is shown in Fig. 2 by the solid line. As our model assumes that the polymer fibrils do not touch each other, we can evaluate the polymer concentration above which our model is not valid by setting $\xi=0$. We find that this criterion corresponds to $c=17.72\%$. This concentration is already sufficiently high for the nematic liquid crystal to form a droplet like structure in the polymer matrix similar to polymer-dispersed liquid crystals (PDLC),¹ for which our model is not relevant. The anchoring strength value from our model $W(c) = 1.95 \times 10^{-6} (1/\sqrt{c} - 0.24)^{-2} \text{ J/m}^2$ would cross over to a concentration independent value in the PDLC case.

Another way to test the validity of our model is to measure the switching behavior of the PSLC. The time off τ_{off} is

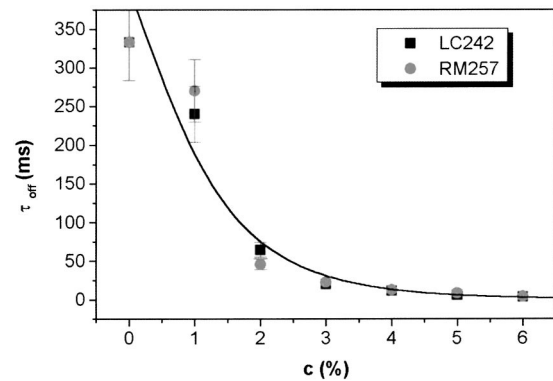


FIG. 4. Time off results for both types of PSLC as a function of the polymer concentration. The solid curve represents the fit based on Eq. (6). Error bars, where not shown, do not exceed the symbol size.

related to the critical field E_c defined in Eq. (5) by

$$\tau_{\text{off}} E_c^2 = \frac{\pi^2 \gamma}{\epsilon_a \epsilon_0}, \quad (6)$$

where γ is the rotational viscosity of the liquid crystal. For each concentration the time off was measured after application of a field with strength corresponding to voltage V^* [see Fig. 1(b)], where the light transmittance T reaches its first minimum, to insure that for each concentration of the polymer the phase retardation is the same at the maximum voltage applied V^* . Figure 4 shows the experimental results and fit corresponding to Eq. (6). By considering the identical domains in our model, the time off is effectively averaged over domains of all sizes. From the fit we calculate the rotational viscosity of BL038 to be 0.33 Pa s. Although γ has not been measured for BL038, the calculated value of γ from the fit is comparable to the measured rotational viscosity of other mixtures in the BL series (e.g., $\gamma=0.374$ Pa s for BL087). The time off of ≈ 3 ms is achievable for 6% polymer concentration. The comparable measured values of the critical field and the time off for the two types of PSLC studied (LC242 and RM257) suggest the existence of a common polymer network morphology and influence on the nematic host.

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¹Liquid Crystals in Complex Geometries, edited by G. P. Crawford and S. Zumer (Taylor and Francis, London, 1996).

²C.-C. Chang, L.-C. Chien, and R. B. Meyer, Phys. Rev. E **56**, 595–599 (1997).

³R.-Q. Ma and D.-K. Yang, Phys. Rev. E **61**, 1567 (2000).

⁴M. J. Escuti, C. C. Bowley, G. P. Crawford, and S. Zumer, Appl. Phys. Lett. **75**, 3264 (1999).

⁵R. A. M. Hikmet and H. M. J. Boots, Phys. Rev. E **51**, 5824 (1995).

⁶R. A. M. Hikmet, J. Appl. Phys. **68**, 4406 (1990).

⁷A. Rapini and M. J. Papoular, J. Phys. Colloq. **30**, C4 (1969).

⁸J. Nehring, A. R. Kmetz, and T. J. Scheffer, J. Appl. Phys. **47**, 850 (1976).

⁹L. M. Blinov and V. G. Chigrinov, *Electrooptic Effects in Liquid Crystal Materials* (Springer, New York, 1993), Chap. 3, pp. 111–113.