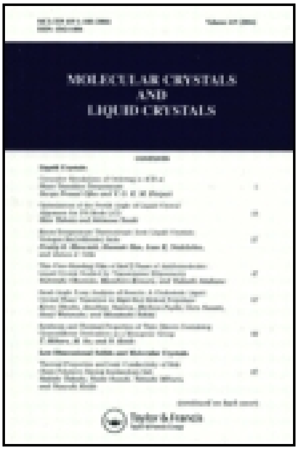

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Freedericksz Transition Measurements on Polymer-Stabilized Liquid Crystals

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Electric-field Freedericksz transition experiments were performed on homogeneous nematic samples of pentylcyanobiphenyl in which an anisotropic cross-linked polymeric network was formed. The studied geometry yields the splay elastic constant from the threshold voltage, Vc. Specimens in which the network was polymerized with the field OFF exhibited an increase in Vc; those in which the network was formed with the field ON, i.e. in the homeotropic alignment, showed a decrease in Vc. These observations are interpreted in terms of a model which assumes that the nematic elasticity is coupled to that of the network. Thus, Vc depends on the longitudinal component of the network elasticity, as well as on the Frank elastic constant. From this relationship, values of network elastic modulus can be estimated.

Keywords: Polymer stabilized liquid crystal; Freedericksz transition; splay elastic constant; network elasticity

INTRODUCTION

Recently, the incorporation of polymer networks into liquid crystal displays has attracted interest because of the possibility of markedly improving device performance [1,2]. Such systems are referred to as polymer-stabilized liquid crystals (PSLC). The properties of these materials have been extensively studied [3–8]. Of particular relevance to the present work is the observation that a polymer network can lower the operating voltages of a twisted nematic (*TN*) cell. Thus, Bos *et al.* [9] found that significant decreases in the threshold voltage of a *TN* device could be achieved by

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doping a liquid crystal with a photo-curable monomer, and applying voltage to the cell during the photo-curing process. The mechanism of this phenomenon is unclear, but it is presumed that the polymer network formed in the presence of an applied field, i.e. in homeotropic alignment, has the effect of inducing some degree of pre-tilt of the director when the nematic returns to homogeneous alignment in the OFF state [9].

In an effort to gain insight into the molecular origin of the increase in pre-tilt angle, we have investigated the influence of the polymer network on the splay Freedericksz transition threshold of polymer-stabilized liquid crystal specimens. We find that the threshold voltage increases when the network is formed with the field OFF, and decreases when the network is formed with the field ON. Recently, a theoretical analysis was reported on the Freedericksz transition threshold of a doubly-anchored liquid crystal polymer brush immersed in a nematic solvent [10]. These authors found [10] that there is a coupling between the nematic elasticity and the configurational elasticity of the tethered chain. Stimulated by this result, we propose the hypothesis that the change in threshold voltage in PSLCs arises because of the coupling between the nematic elasticity and the entropic elasticity of the anisotropic polymer network. By applying the theoretical treatment [10] to the present experimental results, it is possible to extract information about the network modulus from the Freedericksz threshold voltage. We explore the dependence of the network modulus, obtained in this way, on monomer concentration and sample thickness.

EXPERIMENTAL METHODS

The reactive monomer, 4,4′-bis(acryloyloxy)biphenyl (99% pure as determined by HPLC analysis), at a selected concentration was added to the nematic, pentylcyanobiphenyl (5CB, purchased from BDH Ltd and used as received) with a small amount of benzoin methyl ether as photoinitiator. The sample cell was constructed from two ITO coated glass slides separated by mylar spacers. Homogeneous alignment of the mixtures was produced by coating the glass surfaces with rubbed polyimide. The mixtures were introduced into the sample cell by capillary action. The filled cell was sealed with a five-minute epoxy (Devcon). A Carl Zeiss optical polarizing microscope was used to assess sample homogeneity. A mercury spot lamp, 100 watt power and wavelength $\lambda = 360$ nm, was used as the UV source for initiating the polymerization. The lamp was placed 0.3 meters from the homogeneous sample cell. Two kinds of samples containing polymer networks were prepared: one type was polymerized in the homogeneous alignment, the other was polymerized in the presence of an AC electric field (sinusoidal wave with frequency = 3000 Hz, $V_{\rm rms} = 7$ volts) applied across the sample cell.

Freedericksz transition measurements were performed using methodology described in detail elsewhere [11]. Briefly, the capacitance of the sample cell was monitored while an increasing bias voltage was applied. The frequencies of the bias voltage and the probe signal were, respectively, 50 Hz and 1000 Hz. The sample was placed in an oven whose temperature was kept 5°C below the clearing temperature by a temperature controller (YSI model 72) accurate to 0.2°C. When the bias voltage is applied to the nonconductive homogeneous nematic monodomain, which has a positive dielectric anisotropy, the director tends to become aligned parallel to the applied field. This director realignment only occurs above a threshold voltage V_c. A discrete increase is observed in the sample cell capacitance at the transition because of the attendant increase in sample dielectric constant. Under strong anchoring between the substrate and the nematic, the threshold voltage is related to the splay elastic constant:

$$V_c^2 = K_{11}\pi^2/(\Delta\varepsilon\,\varepsilon_0) \tag{1}$$

As discussed below, we are interested in understanding how the presence of the polymer network modifies this relationship.

RESULTS AND DISCUSSION

Figure 1 shows the Freedericksz transition measurements for samples polymerized in the absence of an electric field. For comparison we also show a representative result for a sample prior to polymerization. The latter was indistinguishable from the corresponding observation for pure 5CB. Clearly, for these samples, the presence of the polymer network, formed in the homogeneous alignment, increases the threshold voltage. Moreover, as the polymer concentration increases, there is trend towards higher values of V_c. Another phenomena, evident at higher concentration, is that the transition becomes broader, and, also, the asymptotic value of the capacitance at high field decreases. The latter effect indicates that the applied voltage can no longer bring the entire specimen into alignment with the field.

In Figure 2, we exhibit the measurements for samples polymerized in the presence of an applied field (7 Volts/cm). Here a very different picture is seen. The threshold voltage decreases in the presence of the network, and, in addition, there is a progressive increase in the initial value of the capacitance prior to the transition. Indeed at a polymer concentration of

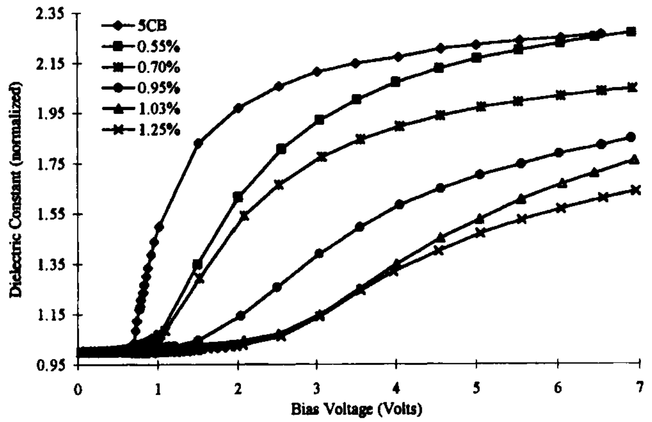

FIGURE 1 Effect of monomer concentration on the Freedericksz transition of PSLC networks. Planar samples polymerized with electric field OFF. Calculated dielectric constant values are normalized to the initial value.

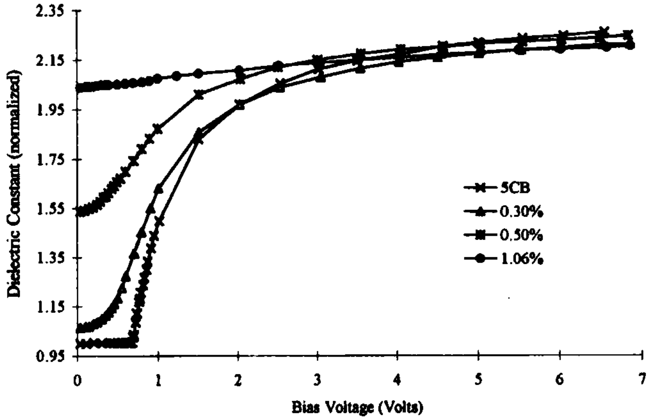

FIGURE 2 Effect of monomer concentration on the Freedericksz transition of PLSC networks. Planar samples polymerized with electric field ON. Calculated dielectric constant values of the sample after polymerization are normalized to the initial dielectric constant before polymerization.

1.06% w/w, there is scarcely evident a transition. Obviously, the surface anchoring is no longer able to overcome the tendency of the nematic to align with the network, and hence with the applied field.

As a working hypothesis, we propose to interpret these observations on the basis that there is a coupling between the nematic elasticity and the entropic elasticity of the polymeric network. As alluded to earlier, the rationale for this approach lies in the analysis of Halperin and Williams [10] of the Freedericksz transition threshold for a doubly-anchored LCP brush immersed in a nematic solvent. The situation we are considering is that of an anisotropic polymeric network, uniaxially-oriented along the director. For such a network the distances between crosslinks must be spatially-anisotropic, being larger along the director than perpendicular to it. It appears to us that an argument essentially identical to that of Halperin and Williams can be applied to a uniaxially-oriented anisotropic network, swollen by a nematic solvent, when subjected to an orthogonal electric field, or an orthogonal shear deformation. This presumes a coupling between the orientation of the anisotropic network and that of the nematic. For an ideal network which obeys Gaussian statistics and undergoes affine deformation [12], the free energy per network strand can be expressed by an equation of the form [10]:

$$\frac{F_{\text{net}}}{kT} = \left(\frac{K\Sigma}{kTH}\right)Q^2 + \frac{\xi_\perp^2}{\xi_{\perp 0}^2} + \frac{\xi_\parallel^2}{\xi_{\parallel 0}^2} - \frac{\Sigma|\Delta\varepsilon|E^2}{kT}\left(Q^2 - \frac{1}{4}Q^4\right) \tag{2}$$

Here k is the Boltzmann constant, T is absolute temperature, K is the splay elastic constant, Σ is the area per network strand, H is the sample thickness, Q is an order parameter which characterizes the anchoring strength, $\Delta\varepsilon$ is the dielectric anisotropy, E is the electric field strength, $\xi_\parallel$ and $\xi_\perp$ are the distances between crosslinks parallel and perpendicular to the director, respectively, for the deformed network, and $\xi_{\parallel_0}$ and $\xi_{\perp_0}$ are the corresponding distances for the undeformed network.

If the network is subjected to a shear strain $\delta = \Delta/H$, then we may write [10] $\xi_\perp = (\Delta\text{-}H\tan\theta)/\cos\theta$ and $\xi_\parallel = H/\cos\theta$, where θ is the angle between the director and the normal to the direction of the applied field or applied shear. Substituting these equations into eq. (2), retaining terms to second order on θ, and minimizing with respect to θ, one obtains [10]:

$$\delta = \theta/(1+\theta^2) \tag{3}$$

Upon substitution into eq. (2), it follows that [10]:

$$F = \mu_{\parallel} + \mu_e \delta^2 \tag{4}$$

where $\mu_{\parallel} = kTH/\Sigma\xi^2_{\parallel_0}$ is the component of the network elasticity along the director, and μ_e is the effective modulus in the presence of the field:

$$\mu_e = \mu_{\perp}(\mu_n + \mu_{\parallel} - \sigma_E)/(\mu_n + \mu_{\parallel} + \mu_{\perp} - \sigma_E) \tag{5}$$

where $\mu_{\perp} = kTH/\Sigma\xi^2_{\perp_0}$ is the network elasticity perpendicular to the director, $\mu_n = K/H^2$ is the elasticity contribution arising from the nematic solvent, and $\sigma_E = |\Delta\varepsilon|E^2$ is proportional to the electric "Maxwell" stress. The Freedericksz transition occurs at $\mu_e = 0$, i.e. when $\mu_n + \mu_{\parallel} = \sigma E^*$. In the absence of polymers the transition takes place when $\sigma E^* = \mu_n$. Thus we deduce that for a polymer-stabilized nematic, polymerized in the homogeneous orientation, with the field off, the threshold voltage in the splay Freedericksz transition is:

$$V_c^2 = (\pi^2/\Delta\varepsilon\varepsilon_0)[K^0_{11} + \mu_{\parallel}H^2] \tag{6}$$

where K^0_{11} is the splay elastic constant of the nematic solvent.

If the sample is polymerized in the homeotropic orientation, i.e. with the field ON, then, in the OFF state, we expect there may be a degree of pre-tilt, determined by the balance of forces between the polymer elasticity, $\mu_{\parallel}$, and the surface anchoring strength. Under these conditions, it appears that the Freedericksz threshold is determined by the equation $\sigma E^* + \mu_{\parallel} = \mu_n$, leading to the following expression for the threshold voltage:

$$V_c^2 = (\pi^2/\Delta\varepsilon\varepsilon_0)[K^0_{11} - \mu_{\parallel}H^2] \tag{7}$$

Adopting eqs. (6) and (7), it becomes possible to determine the modulus $\mu_{\parallel}$ from the Freedericksz threshold. Note that, in applying equation (6) and (7), for such dilute system, we can safely assume $\Delta\varepsilon$ to be that of pure solvent. Results of such analyses are shown in Figure 3, where $\mu_{\parallel}$ is plotted against polymer concentration. The magnitude of $\mu_{\parallel}$ ranges from ~ 0.1 dynes/cm^2 at $c \sim 0.30\%$ w/w to ~ 2.0 dynes/cm^2 at $c \sim 1.25\%$ w/w, which are reasonable values for weak gels. From Figure 3, we note that the moduli determined for the networks polymerized with field ON are quite consistent with those for networks polymerized with field OFF. We note that the networks formed in these PSLC mixtures are phase-separated, and the relatively low

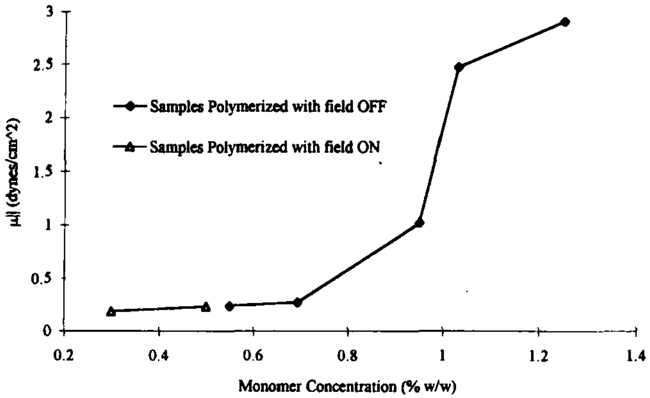

FIGURE 3 Effect of monomer concentration on network modulus of elasticity, $\mu_{\|}$, for cells of 12.5 μm thick. These values were estimated from the threshold voltage, Vc, using equations (6) and (7), for samples polymerized with the field OFF and ON, respectively.

experimental precision of the measured moduli is attributed to the poor reproducibility of such materials.

Figure 4 shows the Freedericksz transition measurements of planar samples polymerized with field OFF for different cell thickness. The monomer concentration in Figure 4a and 4b were 0.95 and 1.25%, respectively. A clear trend, common to both sets of data, is that the Vc values increase with cell thickness, and with monomer concentration. Similarly, with increasing cell thickness and monomer cencentration, the asymptotic value of the dielectric constant at high field decreases, and the transition becomes broader. Evidently, at high monomer concentration and for the thick cells, the applied field is not able to bring the sample into complete homeotropic alignment.

The threshold voltage values from Figure 4 were used in equation (6) to determine the network elastic modulus, $\mu_{\|}$, for each thickness and monomer concentration. These results are shown in Figure 5. For each thickness, as expected, $\mu_{\|}$, increases with increasing monomer concentration. However, it is evident that $\mu_{\|}$, as estimated by our model, decreases with increasing cell thickness. This is surprising since we would expect for a network of specific cross-link density and degree of anisotropy to observe the same value for $\mu_{\|}$, since it is a material constant independent of sample thickness. The reason for this discrepancy is not understood at present. One possibility is that the degree of alignment of the network depends on sample thickness. Specifically, the degree of alignment may decrease in the thicker cells leading to a

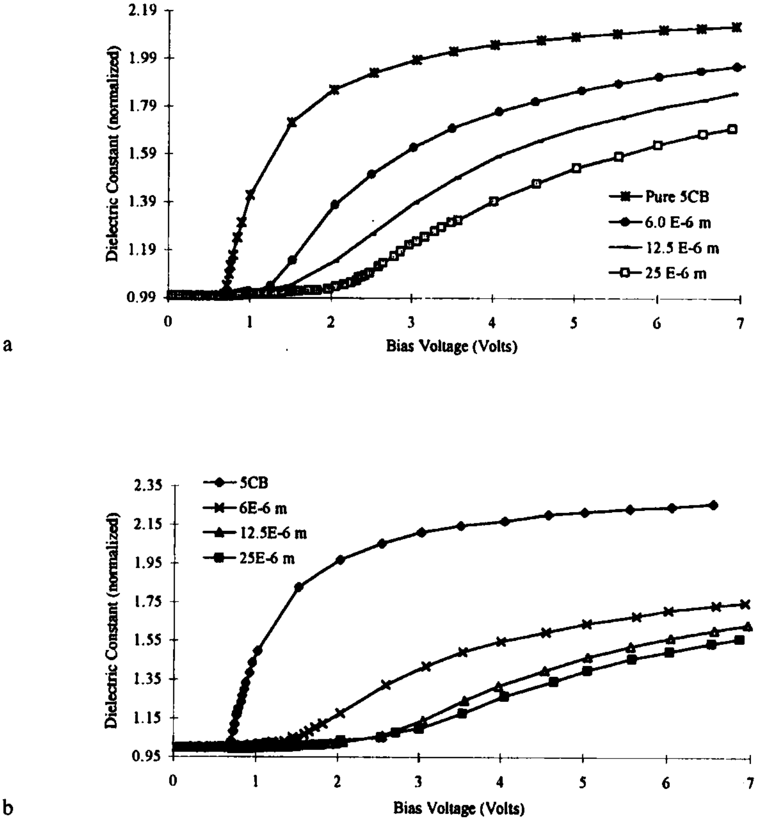

FIGURE 4 Effect of cell thickness on the Freedericksz transition of PSLC networks. Figure 4a and 4b, correspond to monomer concentration 0.95 and 1.25% respectively. Planar samples polymerized with electric field OFF.

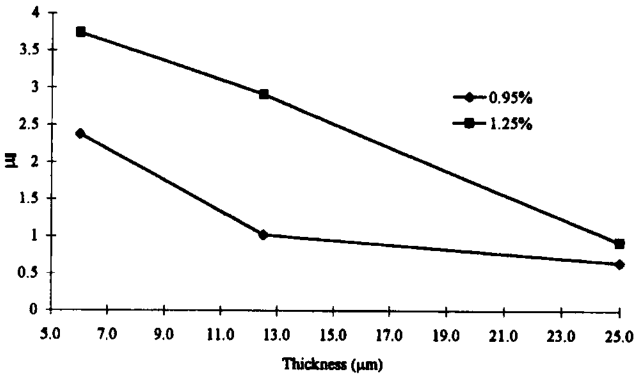

FIGURE 5 Effect of cell thickness and monomer concentration on μ_l values, calculated from Vc values in Figure 4 using equation (6).

decrease in $\mu_{\parallel}$. Another possibility is that the strength of the coupling between the nematic and the network varies depending on sample thickness. Further work will need to be done to address these questions.

CONCLUSIONS

Splay Freedericksz transition measurements on anisotropic PSLC networks showed increase in Vc for samples polymerized under no electric field and a decrease in Vc for those that were polymerized with the field ON. These effects were interpreted using a model which assumes the Frank nematic elasticity is coupled to the longitudinal component of the network elasticity. This analysis yields estimates of the network elasticity modulus. Experimental results indicate that the network modulus determined in this way increases with monomer concentration and decreases with sample thickness.

Acknowledgements

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References

[1] D. K. Yang, L. C. Chien and J. W. Doane, *Appl. Phys. Lett.*, **60**, 3102 (1992).
[2] D. K. Yang, L. C. Chien and J. W. Doane, *Proc. Soc. Info. Display XXIV*, 887 (1993).
[3] R. A. M. Hikmet, *Liq. Cryst.*, **9**, 405 (1991).
[4] R. A. M. Hikmet, *Molec. Cryst.*, **198**, 357 (1991).
[5] R. A. M. Hikmet and J. A. Higgins, *Liq. Cryst.*, **12**, 831 (1992).
[6] R. A. M. Hikmet, *J. Appl. Phys.*, **68**, 4406 (1990).
[7] R. A. M. Hikmet and B. H. Zwerver, *Molec. Cryst.*, **200**, 197 (1991).
[8] R. A. M. Hikmet and B. H. Zwerver, *Molec. Cryst., Liq. Cryst.*, **12**, 319 (1992).
[9] P. Bos, J. Rahman and J. W. Doane, SID Digest XXIV, 887 (1993).
[10] A. Halperin and D. R. M. Williams, *Phys. Rev. E* **49**, R986 (1996).
[11] D. Gu, S. R. Smith, A. M. Jamieson, M. Lee and V. Percec, *J. Phys. II (France)* **3**, 937 (1993).
[12] J. J. Aklonis and W. J. MacKnight, *Introduction to Polymer Viscoelasticity* (John Wiley & Sons, New York, 1983). 2^{nd} ed. Chap. 6, pp. 109.