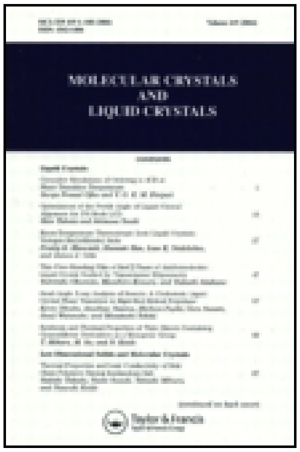

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OPTICAL FIELD INDUCED SCATTERING IN POLYMER DISPERSED LIQUID CRYSTAL FILMS

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Abstract Polymer dispersed liquid crystals are composite materials consisting of inclusions of liquid crystalline materials dispersed in a polymer binder. If the refractive indices of the constituent liquid crystal and polymer are appropriately matched, then films of these materials may be switched between an optically scattering state and a non-scattering transparent state[1-2] by the application of electric fields which reorient the liquid crystal in the inclusions. In this paper we discuss the response of these materials to intense laser radiation, and examine the mechanisms associated with optical field induced reorientation.

INTRODUCTION

Polymer dispersed liquid crystal (PDLC) films are composite materials consisting of a liquid crystalline material dispersed in a polymer matrix. The liquid crystal, which may be a pure material or a mixture, is usually dispersed in the form of nearly spherical inclusions with diameters ranging from 0.1 to 10 μm. The mechanism for forming these droplets is phase separation of the initial polymer-liquid crystal mixture. The phase separation can be induced by polymerization, thermal quenching or solvent evaporation.[3]

When the liquid crystal in the droplets is in the nematic phase, the optical properties of the PDLC film may be changed considerably by the application of a low-frequency external electric field, which reorients the liquid crystal in the inclusions. This effect makes these materials well suited for a variety of optoelectronic applications.[4] Optical field induced reorientation has been studied extensively in homogeneous samples with planar geometry.[5-8] Other geometries have yet to be considered. In this study, we report observations of changes in the optical transmittance of PDLC films due to the effects of optical fields on the liquid crystals in the inclusions. These results are interpreted on the basis of a simple theoretical model. The reorientation of the liquid crystal in the inclusions is similar to the Freedericksz transition in planar samples.

THEORY

In a uniaxial homogeneous nematic liquid crystal, one may define the director $\hat{n}$ as a unit vector along the direction of the principal axis of a second rank tensor which describes a material property, such as the magnetic susceptibility. Alternately, it may be viewed as the direction of average orientation of the symmetry axes of the constituent molecules. If $\hat{\ell}$ is a unit vector along the symmetry axis of the i'th molecule, the orientational order parameter S is given by

$$S = < \frac{1}{2}\left(3(\hat{n}\cdot\hat{\ell})^2 - 1 \right)> \qquad (1)$$

where $< >$ denotes the ensemble average. The anisotropy of physical properties described by second rank tensors is proportional to S.

If the director field is not uniform, the free energy density associated with the elastic distortion is given by[9]

$$F = -\frac{1}{2}\left[K_1(\nabla\cdot\hat{n})^2 + K_2(\hat{n}\cdot\nabla\times\hat{n})^2 + K_3(\hat{n}\times\nabla\times\hat{n})^2\right] \qquad (2)$$

where K_1 K_2 and K_3 are the elastic constants associated with the canonical deformations of splay, twist and bend.

In the absence of external fields, the director configuration of the liquid crystal in the inclusions is determined by elastic and surface torques. Microscopic observations of the samples under study indicate that surface anchoring at the liquid crystal polymer interface gives rise to homogeneous alignment. That is, the director is tangential to the interface at the interface, and the resulting director configuration is nearly cylindrically symmetric.

Rather than calculating the detailed form of the distortion, we define a "droplet director" $\hat{N}_D$ for each droplet as the unit vector along the principal axis of the volume averaged susceptibility for the droplet. Equivalently, it may be viewed as the average direction of the nematic director $\hat{n}$ in the droplet. We define the "droplet order parameter" S_D as

$$S_D = < \frac{1}{2}\left(3(\hat{N}_D\cdot\hat{n})^2 - 1\right) >_D \qquad (3)$$

where $< >_D$ denotes the volume average over the droplet. The average anisotropy of physical properties described by second rank tensors for the droplet is proportional to S_D. (We have assumed here for simplicity that the droplet is uniaxial;

that is, that $<n_x^2> = <n_y^2>$ in a coordinate system where $\hat{N}_D$ is along the z axis. The definition of a general tensor order parameter for the droplets is straightforward.)

The free energy of the liquid crystal in an inclusion contains contributions from orientational, elastic, external field and surface effects. We assume that the orientational order of the liquid crystal given by S is a constant (except possibly at the cores of defects), and that the sole effect of surface interactions is to ensure homogeneous alignment.

We have calculated explicitly, in the one elastic constant approximation ($K_1 = K_2 = K_3 = K$), the elastic energy for a droplet whose shape is an ellipsoid of revolution with eccentricity δ^2. We considered two director configurations, such that droplet director $\hat{N}_D$ was either parallel or perpendicular to the symmetry axis $\hat{L}$ of the ellipsoid. The director configuration for both cases is as follows. The intersection of a plane perpendicular to $\hat{N}_D$ with the ellipsoid is an ellipse. If a family of ellipses are constructed in this plane so that their major and minor axes are parallel to those of the original ellipse and with the same eccentricity, then the director is everywhere tangential to these ellipses. We have also assumed that there is a central defect with an isotropic core with core radius r_c along $\hat{N}_D$. Linear extrapolation between the two values of the elastic energy corresponding to the two orientations of $\hat{N}_D$ results in the following expression for the elastic contribution to the average free energy density in the droplet

$$F_{elastic} = \frac{1}{2}\,\frac{K}{R_{eff}^2}\left(1-\delta^2(\hat{N}_D\cdot\hat{L})^2\right). \tag{4}$$

Here $1/R_{eff}$ is the effective average curvature of the director field in the droplet, and $\hat{L}$ is along the symmetry axis of the cavity shape. We expect that for other configurations, the elastic free energy density will have the same form to lowest order. A similar expression for the elastic energy has been proposed in Ref. 4. For the director field described above, if $r_c/R << 1$, $R_{eff}^2 = R^2/(12(\ell n(2R/r_c)-1))$. It is more straightforward to calculate R_{eff} for the case of a spherical droplet with a radial director configuration; this gives $R_{eff}^2 = R^2/12$, where R is the droplet radius.

Equation (4) thus provides a simple expression for the elastic energy of a droplet in terms of the orientation of the droplet director.

The average free energy density in a uniaxial droplet due to a static electric field $\bar{E}_{DC}$ is

$$F_{electric} = -\frac{1}{2}\varepsilon_o E_{DC}^2\left(\bar{\varepsilon} + \frac{2}{3}\Delta\varepsilon S_D\left[\frac{1}{2}(3(\hat{N}_D \cdot \hat{E}_{DC})^2 - 1\right]\right) \tag{5}$$

where $\varepsilon = (\varepsilon_{\parallel} + 2\varepsilon_{\perp})/3$ is the average dielectric permittivity, and $\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$ is the dielectric anisotropy.

Similarly, the average free energy density due to optical fields is, approximately,

$$F_{opt} \simeq -\frac{I}{c}\left(\bar{n} + \frac{2}{3}\Delta n S_D\left[\frac{1}{2}(3(\hat{N}_D \cdot \hat{E}_{opt})^2 - 1\right]\right) \tag{6}$$

where I is the intensity, c is the speed of light, $n = (n_e + 2n_o)/3$ is the average index of refraction, $\Delta n = n_e - n_o$ is the refractive index anisotropy, and $\hat{E}_{opt}$ is a unit vector along the direction of polarization.

We assume that the effect of the static and optical fields on the order parameter S of the liquid crystal is negligible, and consequently the dielectric (and refractive index) anisotropy is a constant. We further assume that the effect of the fields on the droplet order parameter S_D is negligible; calculations describing this effect will be published elsewhere. Under these assumptions, the effect of the applied fields and of the shape of the cavity containing the liquid crystal droplet is to exert a torque on the droplet director.

If the static field $\hat{E}_{DC}$ and the optical field $\hat{E}_{opt}$ are perpendicular, and if the symmetry axis $\hat{L}$ of the cavity shape is paralell to $\hat{E}_{opt}$, then the average free energy density due to all contributions becomes, in units of $K\delta^2/R_{eff}^2$,

$$F = F_o + \frac{1}{2}\left(1 - \left(\frac{E_{DC}}{E_{th}}\right)^2 + \frac{I}{E_{th}^2}\left(\frac{2\Delta n}{c\varepsilon_o\Delta\varepsilon}\right)\right)\theta^2 + O(\theta^4) + \ldots \quad (7)$$

Here θ is the angle between $\hat{N}_D$ and $\hat{L}$, and

$$E_{th} = \frac{\delta}{R_{eff}}\sqrt{\frac{K}{\varepsilon_o\Delta\varepsilon S_D}}. \quad (8)$$

The form of the free energy is similar to that for the Freedericksz transition in the case of planar samples, and we therefore expect similar behavior. In the absence of an optical field, an applied field $E > E_{th}$ will give rise to reorientation of the droplet director. The response times may be calculated using the same approach as for planar samples,[11] since the free energy epressions have the same form. The turn-on time is

$$\tau_{on} = \frac{\gamma R_{eff}^2}{K\delta^2\left(\left(\frac{E}{E_{th}}\right)^2 - 1\right)}, \quad (9)$$

while the relaxation time if the field is removed is

$$\tau_{off} = \frac{\gamma R_{eff}^2}{K\delta^2}, \tag{10}$$

where γ is the effective viscosity. It is worth noting that since R_{eff} is expected to be proportional to the droplet radius R, τ_{off} decreases as R^2 as the droplets become small, while E_{th} increases only as $1/R$. If the applied field is not perpendicular to the symmetry axis $\hat{L}$ of the cavity, then there will not be a transition, but the droplet director will continuously rotate as the field is applied.

If the applied field is sufficiently large, the droplet director aligns essentially parallel to the field. If the ordinary index of the liquid crystal is matched to the refractive index of the polymer binder, then the PDLC film is transparent in this configuration. In the absence of an applied field, the orientational distribution of the symmetry axes of the droplet directors is assumed to be random. In this case, because of the refractive index mismatch, light will be scattered from the droplets and the film is opaque.

If the sample in the transparent state is subjected to the optical field of a normally incident laser beam, then it may be switched to the scattering state at sufficiently high laser intensities. From Eq. (6), the optical field will have a significant effect on the orientation of the droplet directors if

$$I \gtrsim \frac{1}{2} \frac{E_{th}^2 c\, \varepsilon_0 \Delta\varepsilon}{\Delta n} \tag{11}$$

Detailed calculations of the alignment of droplet directors in the presence of fields and the effect on the scattering cross-section of the droplets will be presented elsewhere.[12]

EXPERIMENT

PDLC films were formed by mixing by weight 9.8% Epon 828, 18.3% MK107, 30.9% Capcure 3-800, and 41.0% E7. Epon 282 is the reaction product of epichlorohydrin and bisphenol A, MK107 is the diglycidyl ether of cyclohexane. Capcure 3-800 is a trifunctional mercaptan terminated liquid polymer, and E7 is a eutectic liquid crystal mixture of cyanobiphenyls and triphenyls. The components were mixed forming a clear homogeneous solution. Glass spacers of 26 μm were added to the solution which was poured onto a 1"×1"×0.043" glass slide with a transparent layer of conducting indium tin oxide. A second glass slide, also with a conducting electrode, was placed on top of the solution, and was pressed to contact the glass spacers forming a 26 μm film. The glass sandwich was placed in a 72°C oven for 5 hours. The sample is opaque white on cooling to room temperature. The mean droplet radius is 1.7±0.3 μm, and the volume fraction of the inclusions is approximately 25%. Since the densities of the liquid crystal and the polymer are very nearly equal, ~16% of the liquid crystal in the sample has remained dissolved in the polymer binder.

The transmittance of the sample as function of applied voltage is shown in Fig. 1. The transmitted intensity was measured using a 10 mW He-Ne laser and a 1kHz sinusoidal voltage. The transmittance starts to increase significantly at voltages greater than 4.8V. Calculating the voltage corresponding to E_{th} from Eq. (8) gives 48V, where we have assumed $\delta = 0.41$

(corresponding to 1.1 length-to-breadth ratio of the droplet shape), ${R_{eff}}^2/R^2 = 12$, and $S_D=0.75$.[13] We have also made allowances for the dielectric mismatch between the liquid crystal and the polymer. This is the predicted threshold voltage for a film with all droplet shape symmetry axes perpendicular to $\hat{E}_{DC}$, and with all droplets the same size. This value is one order of magnitude larger than the voltage where observed transmittance starts to increase. Since in our sample the droplet shape symmetry axes are assumed to be randomly distributed, the apparent threshold voltage is expected to be lower, similar to the case of pretilted planar cells.[14]

The estimated values of δ^2 and ${R_{eff}}^2/R^2$ may also contribute to the discrepancy; independent determination of these quantities is planned. The transmittance as a function of time is shown in Fig. 2; the applied voltage is a 1kHz burst with a

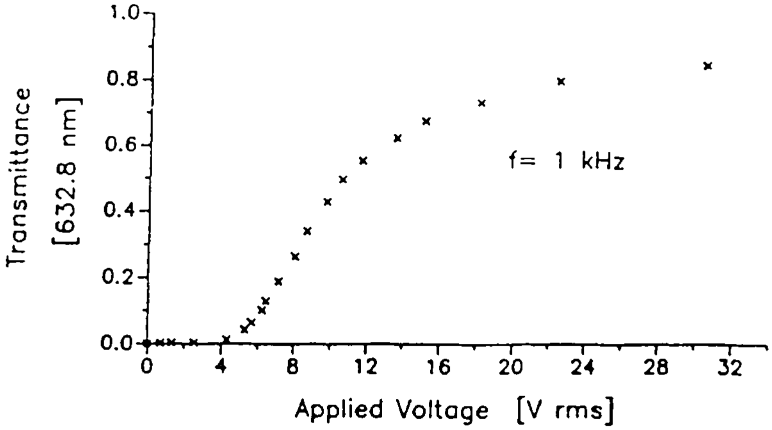

FIGURE 1. Sample transmittance as function of applied voltage.

duration of 80ms. Two characteristic times may be observed for both turn-on and turn-off of the film. We conjecture that the fast process is associated with effects of the applied field on the droplet order parameter S_D (neglected in the current theory), while the second is associated with the reorientation of the droplet director N_D. The time constant τ_{on} from Eq. (9) diverges as the voltage approaches the threshold voltage, and this increase can be clearly seen in Fig. 2.

Since the refractive indices of the liquid crystal in the inclusions as well as that of the polymer vary with temperature, the transmittance of the film is temperature dependent. This effect is particularly pronounced at the nematic-isotopic transition at 42.5°C. The transmittance of the sample with an applied voltage of 28.3V and 1kHz is shown in Fig. 3.

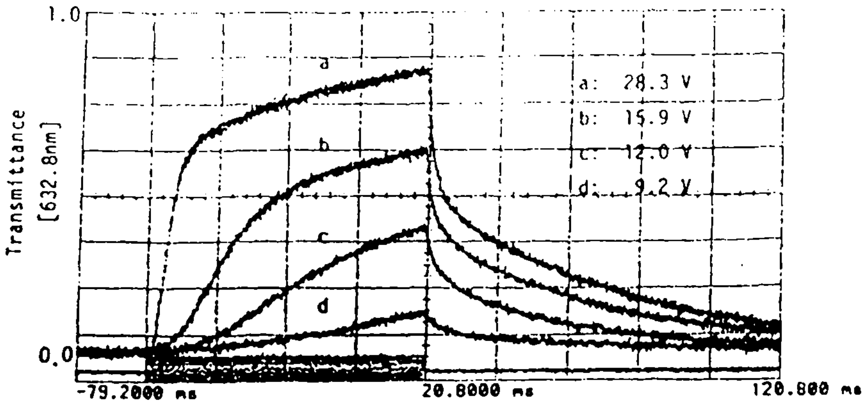

FIGURE 2. Sample transmittance as function of time. The on-time of the applied voltage is shown at the bottom.

The experimental arrangement for the study of the optical field induced scattering[15] is shown in Fig. 4. The pump beam is from a CW Ar^+ laser with vertical polarization. The beam is controlled by a pulse generator driven shutter, and is focused to a beam radius of 95 μm at the sample. The transmittance of the sample is obtained by monitoring the intensity of the probe beam from the 10 mW He-Ne laser. The sample transmittance for vertical and horizontal probe beam polarizations is shown as a function of time in Fig. 5. The pump beam intensity is 20.8 kW/cm^2 and its duration is 43.6 ms; the applied votage is 27.9V at 1kHz. The incident probe beam intensity for both beams was the same. The minimum transmittance as a function of pump beam intensity is shown in Fig. 6 for both polarizations.

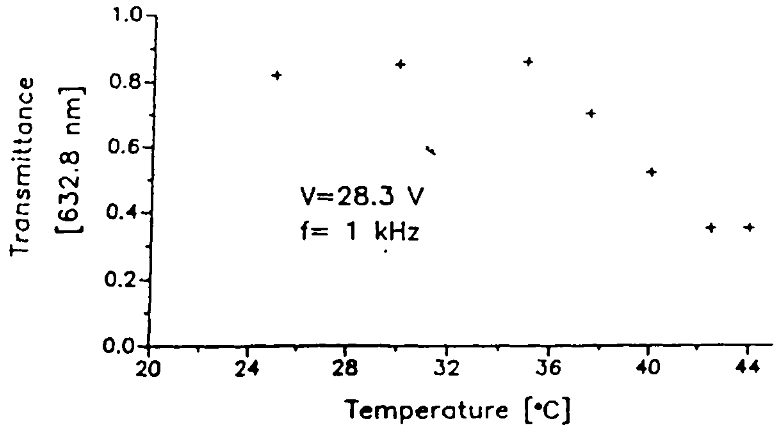

FIGURE 3. Sample transmittance as function of temperature.

DISCUSSION AND CONCLUSIONS

The response of the sample to the optical field of the pump beam is the result of both field induced reorientation of the liquid crystal in the sample and laser heating. The contributions of these two mechanisms are difficult to separate.

As can be seen from Fig. 3, if the sample was heated into the isotropic regime from room temperature, the transmittance would first increase slightly, then decrease to the value of 0.35. On cooling, the reverse process is expected to take place. Instead, as shown in Fig. 5, we see the transmittance reduced to values as low as 0.04, and we observe that the increase of the transmittance over its room temperature value occurs only

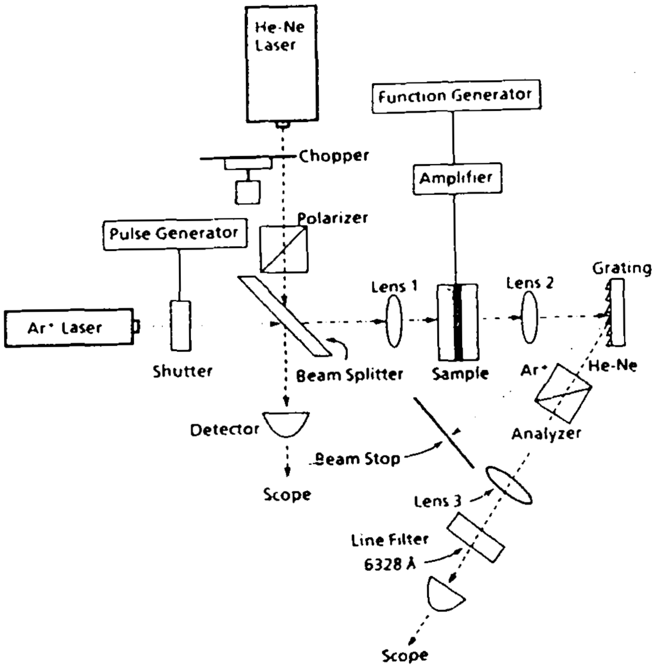

FIGURE 4. Experimental arrangement.

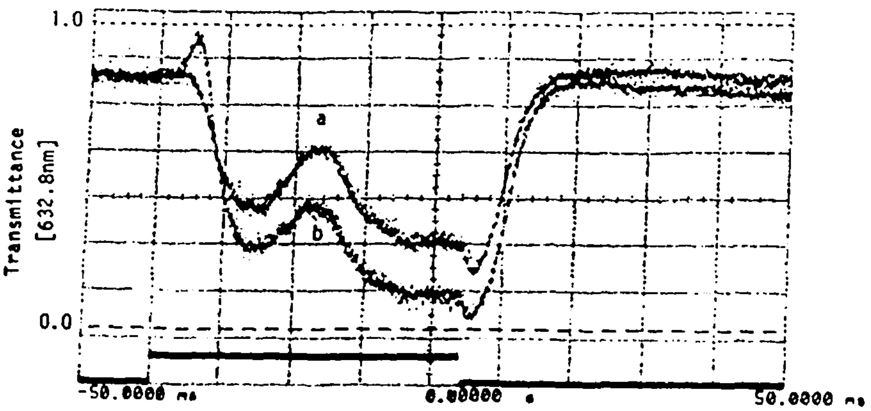

FIGURE 5. Sample transmittance as function of time. Trace "b" corresponds to parallel and trace "a" to perpendicular polarizations of the pump and probe beams. The on-time of the pump beam is shown at the bottom.

when the pump beam is turned on. We have also estimated the average thermal conductivity and the specific heat per volume for our sample, these are 0.18 J/smK and 2.0×10^6 J/m^{3}K respectively. This gives a thermal diffusivity of 9×10^{-8} m^2/s, and, since the pump beam radius is 95 μm, a thermal diffusion time of 0.1 s. Most of the features of the response occur on time scales shorter that this. We also note that if only thermal effects were present, the response would be independent of the probe beam polarization, in contrast with our observations.

The laser intensity where optical field induced reorientation is expected to take place is 43 kW/cm^2 from Eq. (11), where we have used the experimentally observed value of E_{th}. From

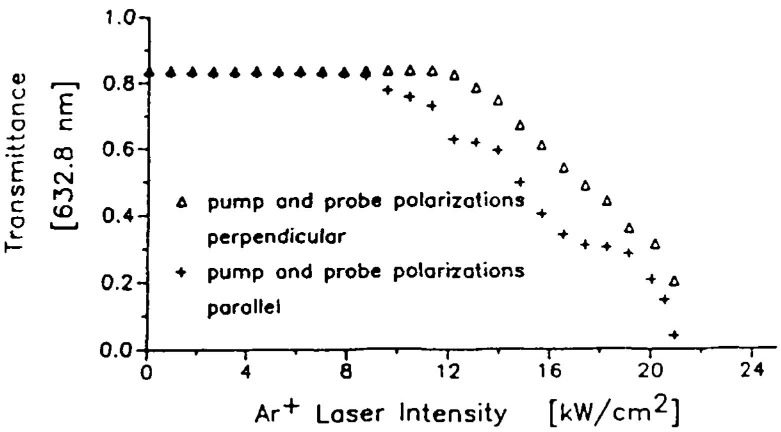

FIGURE 6. Minimum transmittance as function of pump beam intensity.

Fig. 6, the intensity where the transmittance of the sample begins to decrease is approximately 10 kW/cm^2. The discrepancy may in part be due to thermal effects; that is, due to changes in the elastic and dielectric properties of the liquid crystal with sample heating. In addition, again the effect of the optical field on the droplet order parameter, the random distribution of the droplet shapes and the size polydispersity have not been taken into account. If optical field induced reorientation occurs, we expect the director to align along the pump beam polarization and scattering of the probe beam to occur due to the resulting refractive index mismatch. We expect this scattering to be smaller if the probe beam is polarized perpendicular to the pump beam; this has been observed as shown in Figs. 5 and 6.

In summary, we have observed strong optical field induced scattering in PDLC films in the presence of a low frequency applied bias voltage. We have measured a reduction in the transmittance of the sample from 0.83 to 0.04 due to the effect of a focused Ar^+ laser. The effect is reversible, and we have found no discernible laser damage for pulse durations of 70ms or less. The predictions of the simple theory presented here qualitatively agree with the experimental observations. Before quantitative agreement can be expected, however, the effects of droplet orientation and size and shape variations must be taken into account. Better estimates of the effective curvature of the director field, droplet order parameter and shape anisotropy parameter are also needed; work to determine these is currently under way.

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