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Effects of off-state alignment in polymer dispersed liquid crystals

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Partial off-state alignment of the liquid crystal in polymer dispersed liquid crystal (PDLC) droplets was obtained by the application of electric or magnetic fields during their formation. Photopolymerization was used to induce phase separation of the liquid droplets from monomer/liquid crystal solutions. Substantial director directionality was retained in these PDLC films after removal of the fields used during their formation. This alignment affected both the off-state and the on-state electro-optic properties of the films. Transverse electrical fields (5 to 60 V across a 15 μm thickness) applied during PDLC formation from a solution of E7 (BDH Ltd) in a monomer resulted in PDLC films with progressively lower off-state scattering and lower threshold voltage. Strong longitudinal magnetic fields (9 to 14 T) applied during PDLC formation with these materials resulted in strong polarization effects in the light scattering off-state. In the infrared region, where there is less light scattering than in the visible region, the longitudinally aligned films shows tunable birefringent electro-optic effects while retaining the fast time response characteristics of PDLC films with small droplet sizes.

1. Introduction

Films of polymer dispersed liquid crystal (PDLC) in which liquid crystal droplets are formed spontaneously upon polymerization of a monomer/liquid crystal solution are of particular interest for electro-optic applications [1–6]. These films have properties which are similar to those of encapsulated nematic films made by evaporation of solvent from an emulsion containing liquid crystal droplets and polymer [7–9]. The formation of nematic droplets by evaporation of solvent from a solution containing liquid crystal-polymer has also been reported [10]. Doane *et al.* [3] have described the formation of directionally aligned nematic droplets in thermally cured epoxy PDLC films formed in the presence of magnetic and electric fields. In this report, we report studies of the properties of PDLC films formed by ultraviolet (U.V.) initiated polymerization of monomer/liquid crystal solutions [4, 6] in the presence of applied electric or magnetic fields which caused partial alignment of the nematic droplets in the polymer film. Light scattering, polarization, and birefringent electro-optic effects were studied with these poled PDLC films.

2. Experimental

In this series of experiments, the PDLC films were made from solutions of E7 (BDH Ltd) dissolved in the U.V.-curable monomer mixture described by Vaz *et al.* [4] in a 1 : 1 volume ratio. The polymerization induced phase separation process was obtained by U.V. exposures made with radiation from a 200 W medium pressure mercury arc, collimated with a lens system on to cells containing the liquid crystal/monomer solution. The exposure intensity measured at 365 nm was typically in the 10–20 mW/cm^2 range, and exposure times of about three minutes were used. Sandwich

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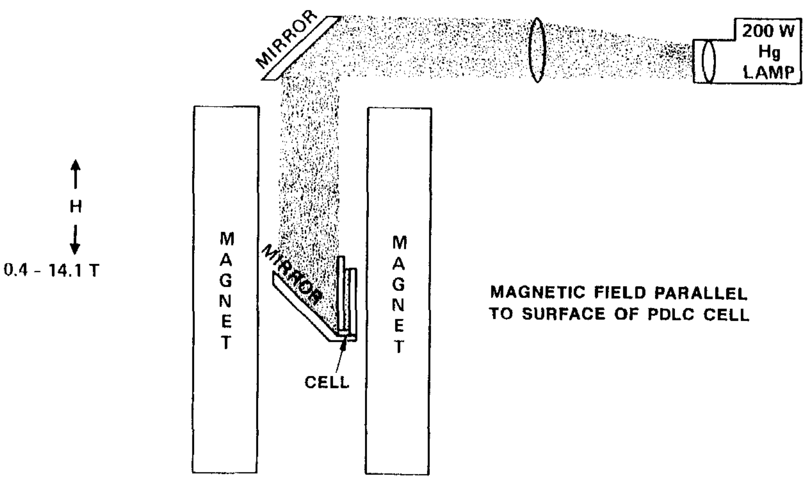


Figure 1. Schematic of U.V. exposure set-up to form PDLC films by polymerization induced phase separation in the presence of an applied magnetic field from a superconducting magnetic, showing the arrangement in which a lateral field is applied parallel to the cell surfaces.

cells were made of glass coated with indium tin oxide (ITO) separated by perimeter spacers, typically in the 6–13 μm range, and filled with the liquid crystal/monomer solution. In the magnetic field experiments, cells were used which were pre-sealed at the edges and then flow filled by capillary action just before use. For a given set of experiments with different cells, the thickness and exposure times were kept constant. For both the poling voltages and the test voltages a 100 Hz A.C. signal was used. For the magnetic field alignment studies, a superconducting magnet was used in which fields in the 0·4–14·1 T range were applied while the U.V. activated phase separation process was used to form the PDLC films. Figure 1 shows a schematic diagram of the U.V. exposure of a cell made with a lateral magnetic field parallel to the glass/ITO surfaces. A similar arrangement was used for U.V. exposures with the magnetic field transverse to the surfaces by removing the internal mirror and rotating the cell to a horizontal position. The electro-optic characteristics of the PDLC films were studied on an optical bench system, using for the visible region a collimated green light (centred at 550 nm) normal to the cells and a detector with an acceptance angle of ±2°. The per cent transmission (% T) was measured with reference to a glass cell containing a thin layer of mineral oil. In this system the transmission of light to the detector was reduced by light scattering (although most of it is forward scattered), and the contrast ratio (calculated by $\%\,T_{on}/\%\,T_{off}$) was highly dependent on the small acceptance angle of the detector [11, 12]. The same optical bench system was used for the infrared electro-optic studies, except that the light from the tungsten bulb was filtered with a narrow band 1·06 μm interference filter and the cell was placed between a set of infrared polarizers (Polaroid HR-Infrared), with the nematic droplet alignment direction (the magnetic field direction during phase separation) rotated 45° to the plane of polarization, in a typical tunable birefringent cell arrangement. Qualitative assessment of the surface alignment of the nematic in the PDLC droplets was made by observing the laser (632·8 nm) scattering patterns from PDLC films placed between parallel polarizers, applying the interpretation proposed by Stein *et al.* [13] for studies of spherulites in polyethylene films. Similarly, the cloverleaf scattering pattern [13] from laser illumination of PDLC films between crossed polarizers was used to estimate the approximate size of the nematic droplets, by calibration with scanning electron microscopy from a series of different PDLC films [14].

3. Results and discussion

3.1. *Electric field studies*

The effects of applying a transverse electric field across a cell during U.V. activated polymerization induced phase separation are shown in the electro-optic curves in figures 2 and 3. When no voltage was used during phase separation, the random director alignment in the PDLC droplets gave a highly scattering off-state, which was cleared by an applied field across the PDLC film. This high transmission on-state was obtained because when the monitoring light is normal to the cell with a strongly field aligned PDLC, the refractive index of the nematic (which approaches n_0) nearly matches that of the polymer film host. As the phase separation formation voltage was increased, these PDLC films showed increased off-state transmission, lower threshold voltages, and lower saturation voltages. This was due to increased off-state alignment of the nematic droplets caused by the applied field during polymerization induced phase separation. At a low phase separation formation voltage of 5 V, the PDLC transmission curve in figure 2 showed only a few per cent off-state transmission, a high on-state transmission, and substantially reduced threshold and saturation voltages as compared to the film formed without an applied field. This is particularly useful for lowering the operating voltage of a PDLC cell, especially in displays where the scattered light is viewed and a high contrast ratio depends primarily on high transmission in the on-state [11]. It is very interesting to note that in figure 2 polymerization induced phase separation voltages of 5–10 V had a strong effect on the PDLC films, whereas the same film formed in the absence of a field showed no % T difference up

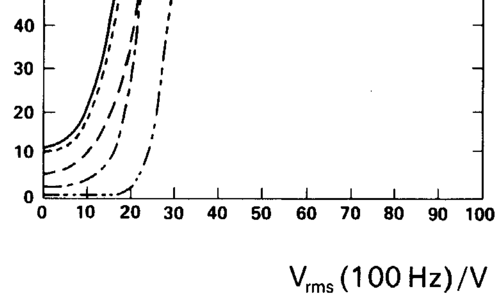


Figure 2. Electric field effect during phase separation on the electro-optical characteristics at 23°C of PDLC films formed in 13 μm thick cells with 20 mW/cm^2 at 365 nm for three minutes. The solid line indicates a voltage of 30 V during polymerization induced phase separation, ···· = 20 V, --- = 10 V, —·— = 5 V and —··— = 0 V.

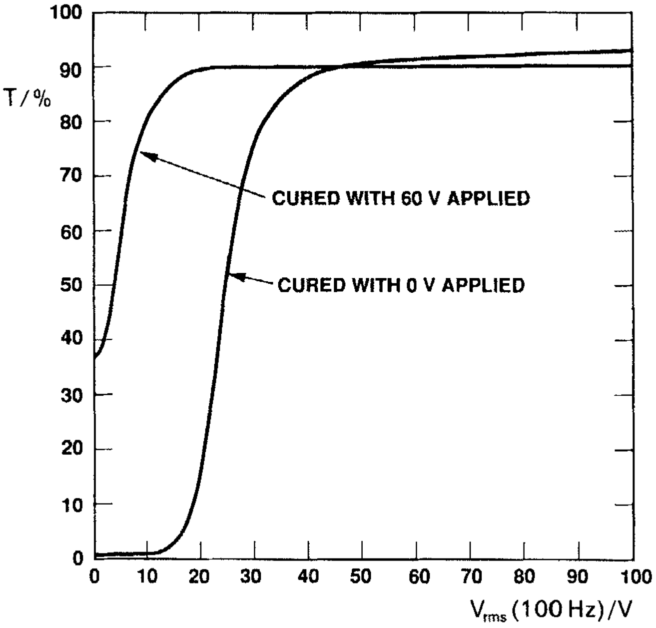


Figure 3. Electric field effect during phase separation on the electro-optic characteristics at 23°C of PDLC films formed in 13 μm thick cells with 15 mW/cm^2 at 365 nm for three minutes.

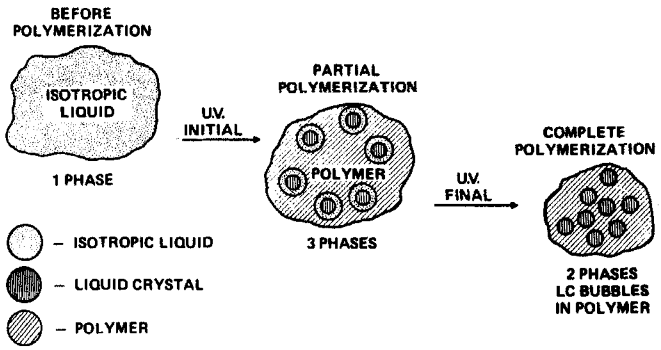


Figure 4. Diagram showing a possible three phase system in the polymer induced phase separation formation of PDLC films.

to about 18 V. This indicates to us that the nematic droplets formed initially during phase separation are more easily field-aligned than after the polymer is completely cured. One way to view this effect is illustrated in figure 4, in which we suggest that as polymerization first proceeds the solubility of the liquid crystal decreases, and the droplets initially formed may be surrounded by fluid nematic/monomer which has not yet undergone polymerization and phase separation. We would expect nematic droplets surrounded by fluid (or a soft polymer gel) to be more readily aligned by a field than ones which are surrounded by a solid polymer interface.

Initially we considered two models for the effect of applied fields during polymerization induced phase separation on the director alignment in the resultant PDLC films, and these models are illustrated in figure 5. Model A assumes that the initially formed nematic droplets tend to be ellipsoidal in shape, due to the directional nematic

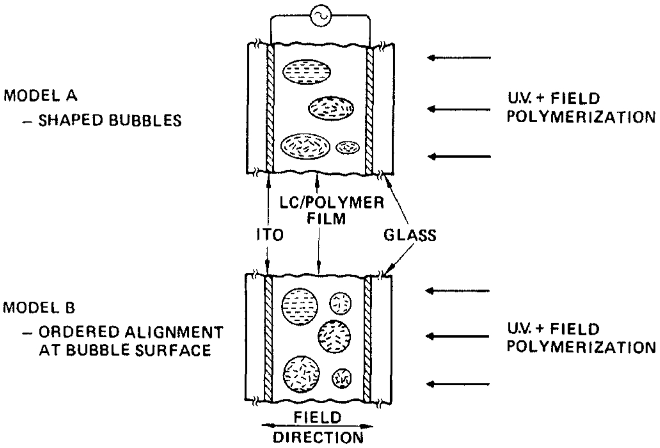


Figure 5. Models considered for the effect of field alignment during phase separation on the off-state shape and alignment of nematic droplets in PDLC films.

alignment as they form while the polymer is solidified around them. Model B assumed that the nematic droplets remain mainly spherical in shape (or are distorted by the polymer) and that the phase separation field affects the directional alignment at the liquid crystal polymer interface as it forms. We did not observe evidence, using scanning electron microscope pictures, for an increased number of ellipsoidal-shaped droplets in a PDLC film (about 55 μm thick) formed in the presence of a 30 V field as compared to a film formed withut an applied field. We favour model B as being the more likely situation. The effect of temperature on the optical bench transmission of PDLC films seemed to be more consistent with model B. The voltage-on (% T_{on}) and voltage-off (% T_{off}) conditions are shown as a function of temperature in figure 6(*a*) for a normal film and in figure 6(*b*) for a film formed with a transverse field of 60 V applied during its phase separation formation. In both cells, the observed heating effect was reproducible after cooling the cell and reheating it during the electro-optic observations. The high % T_{on} observed in both cells at 50°C, which is just below the PDLC clearpoint, is believed to correspond to the match of the field refractive index of the nematic droplet with that of the polymer [15]. The normal PDLC cell in figure 6(*a*) showed increased % T_{off} in the 40–50°C range. We are not sure what causes this, but it may be that the nematic droplet is dissolving somewhat into the polymer matrix at high temperatures and blurring the sharpness of the index difference at the interface between the two phases. The PDLC cell in figure 6(*b*), with partially aligned off-state, showed a dramatic temperature dependence on the % T_{off}, especially just below the clearpoint. It appears that the induced transverse off-state alignment improved in the 30–50°C range, and then disappeared completely just above 50°C. The latter may be due to liquid crystal solubility in the polymer causing the droplet to shrink enough to eliminate the effectiveness of the aligned liquid crystal/polymer interface. The reversibility of this temperature effect appears to be more consistent with model B, in which the interfacial alignment boundary might collapse at high temperatures and recover upon cooling, than in model A where the effect would correspond to a reversible change from ellipsoidal to spherical droplets.

Because the PDLC films formed with a transverse *E* field showed lower threshold voltages (see figures 2 and 3) and lower % *T* in the isotropic state (see figure 6 (*b*))

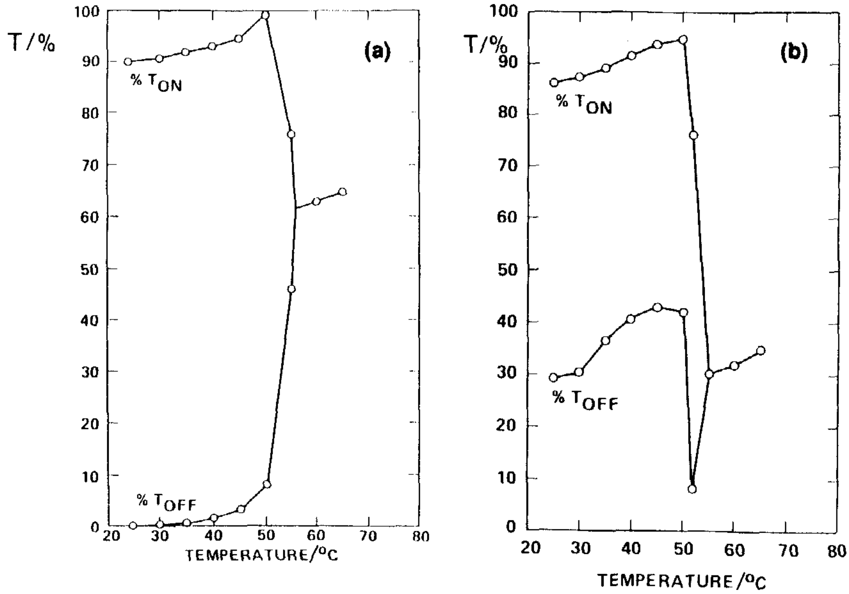


Figure 6. Temperature effect on off-state and on-state (60 V) transmission (~ 550 nm) of PDLC films: (*a*) normal PDLC film: (*b*) PDLC film formed with 60 V transverse electrical field during phase separation.

than normal PDLC films, we also considered the possibility that the field might induce larger size droplets. However, the cloverleaf scattering patterns from laser illumination of PDLC films between cross polarizers [13] were approximately the same for films formed at 60 V as those at zero field, in each case the droplets were estimated to have a size distribution centred at about 1·5 μm in diameter. Decay times (to 50 per cent of the on-state intensity) of 3·7, 3·8, and 11·2 ms were observed for matched thickness PDLC films formed at 0, 10 and 60 V respectively. The longer decay time from droplets formed with 60 V transverse fields could be consistent with either larger size droplets or with less restoring torque due to the pre-alignment in the droplet.

Another important observation was that the laser scattering patterns of PDLC films between parallel polarizers were altered by the E field polymerization induced phase separation formation. Without a formation field, the scattering pattern corresponded to tangential nematic droplet alignment, and with increased formation fields they showed increased evidence for the presence of radial director alignment as well [13]. Radial director alignment has been predicted to show less scattering than tangential director alignment, according to theoretical analysis both for droplets appreciably smaller [16] and larger [17] than the wavelength of the light beam. Thus the decreased scattering of PDLC films formed in the presence of transverse E fields may be related to field-induced radial director alignment. One possible cause for the radial alignment might be that the large resistivity difference between the polymer and the nematic droplet could cause local off-normal E fields across some droplets as they are formed. We have measured the resistivities of the PDLC film and components at 100 Hz with a 0·1 V signal, and the results are shown in table 1.

Table 1. Resistivity comparisons of a PDLC film and its components.

Film or layer	Resistivity/Ω cm
Polymerized monomer	$6{\cdot}1 \times 10^{10}$
PDLC film (1 : 1 monomer/nematic)	$1{\cdot}1 \times 10^{10}$
Nematic (BDH-E7)	4×10^{9}
Monomer	$7{\cdot}5 \times 10^{8}$
Monomer/nematic solution (1 : 1)	$3{\cdot}9 \times 10^{8}$

3.2. *Magnetic field studies*

The application of a strong transverse magnetic field during U.V.-induced polymerization induced phase separation caused PDLC electro-optic effects similar to those of the transverse electrical fields shown in figure 2, resulting in higher off-state transmission and lower threshold voltages. Typical examples of partially aligned PDLC samples formed with transverse magnetic fields during phase separation are shown in figure 7 for samples polymerized in the presence of 0·4 and 14·1 T fields respectively. The PDLC films formed at 14 T had transmission properties similar to those formed in the presence of transverse electrical fields in the 10–20 V range, although the full on-state transmission was slightly higher. However, there was no indication of radial director alignment in these samples.

The application of lateral magnetic fields, applied during phase separation as illustrated in figure 1, caused partial surface-parallel directional alignment of the director in the off-state. This is shown by the contrast ratio measurement in figure 8,

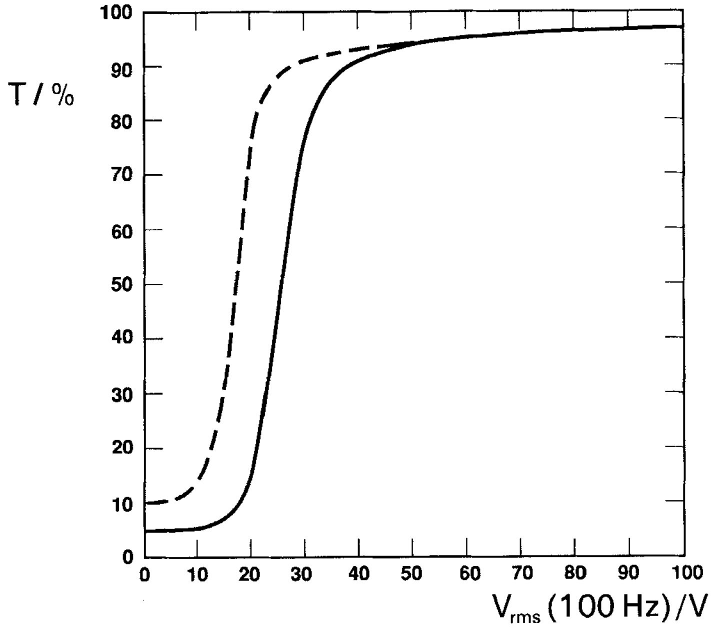


Figure 7. Effect of transverse magnetic field during phase separation on the electro-optic curves for PDLC films, using 13·4 μm thick films and U.V. exposures of 15 mW/cm^2 at 365 nm for phase separation. The solid line indicates a magnetic field of 0·4 T and the broken line 14·1 T.

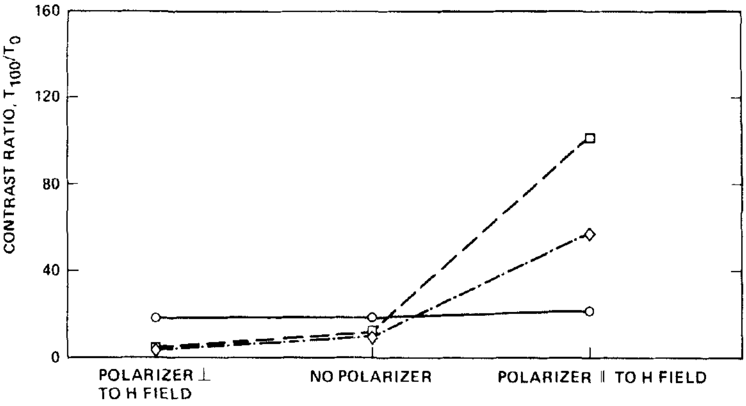


Figure 8. Effect of lateral magnetic field during phase separation field on the contrast ratio of PDLC films with various polarizer positions, using 13·0–13·7 μm thick films and U.V. exposures of 15 mW/cm^2 at 365 nm for phase separation.

where high contrast ratios were obtained when the polarized light incident on the PDLC film was parallel to the direction of the magnetic field during phase separation. This is because these aligned nematic droplets showed higher scattering of this polarization in the off-state, and less off-state scattering of polarized light perpendicular to the direction of the magnetic field using during phase separation. The partially fixed alignment direction of the director in the droplets was clearly indicated by the fact that the cloverleaf laser scattering pattern (from the PDLC film between crossed polarizers) rotated as the sample was rotated, whereas in a normal sample (with random alignment) this pattern remained stationary as the sample was rotated [13]. Although both models A and B can be considered for the magnetic field phase separation alignment effects, we favour model B in analogy with the electrical field phase separation alignment effects discussed previously.

We have also examined the infrared tunable birefringent effect with a PDLC cell aligned with a strong lateral magnetic field during phase separation. Because these

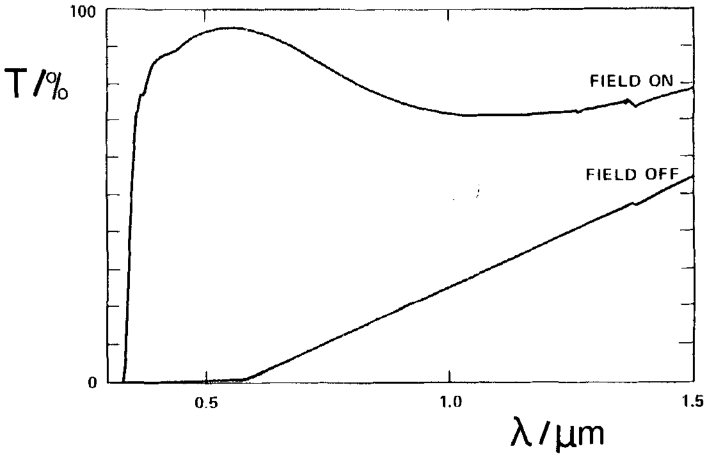
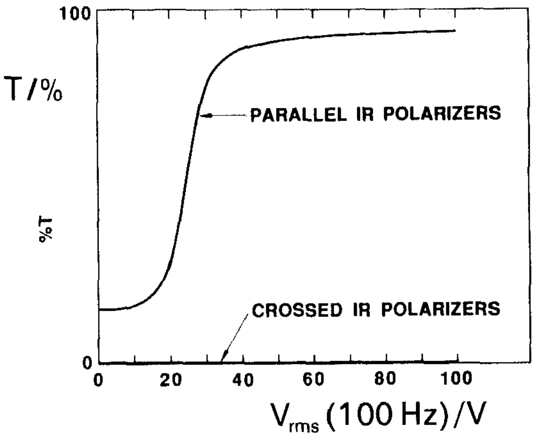
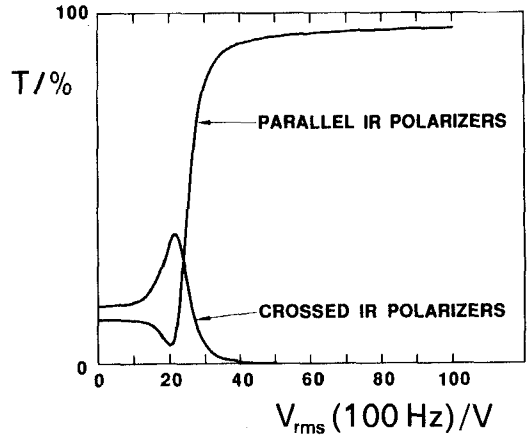


Figure 9. Spectrophotometer transmission curves of on-state and off-state of a normal PDLC film.

.C films were made in glass cells, we were restricted to use of the near infrared :e even though there is still substantial light scattering by the PDLC film. This is vn by the spectrophotometer transmission curves in figure 9 for a normal PDLC formed without a magnetic field. The off-state scattering decreases above 0·6 μm ie wavelength of light approaches the nematic droplet size in the PDLC film, but : is still quite a lot of scattering at 1·06 μm which was the near-infrared wavelength ioice for the optical components we had on hand. The crossed polarizer curve in e 10 showed that a normal PDLC cell exhibits no appreciable depolarization of inscattered light at 1·06 μm, while the parallel polarizer curve showed that the ired light scattering resulted in an off-state transmission of about 15% *T* in our :al bench system (which had a small acceptable angle). The electro-optical curve ;ure 10 showed that the infrared scattering decreased as increased voltages caused alignment of this normal PLDC film, just as in the visible wavelength range. Both es in figure 11, from a PLDC cell with partial lateral director off-state alignment



re 10. Electro-optic scattering effects at 1·06 μm of a non-aligned PDLC film, 13·2 μm thick, formed with 15 mW/cm^2 at 365 nm with 0·4 T lateral field.



:e 11. Electro-optic tuneable birefringent and scattering effects at 1·06 μm of a 13·2 μm thick PDLC film with lateral off-state alignment from phase separation with 15 mW/cm^2 at 365 nm with 14·1 T lateral field.

Table 2. Response times of PDLC cells at $1{\cdot}06\,\mu$m for normal scattering effect and for tunable birefringent effects, using cells made as for the results shown in figures 10 and 11.

	Mode	Voltage	On-time	Off-time
Tunable birefringence (crossed polarizers)	Front slope	0–22 V	10 ms	26 ms
	Back slope	40–22 V	30 ms	2 ms (22–40V)
Light scattering (parallel polarizers)	Front slope	0–65 V	< 1 ms	8 ms

made with a 14 T magnetic field during phase separation, showed a tunable birefringent effect even though it is partially obscured by light scattering. The off-state birefringence of this sample is shown by the presence of an off-state transmission through both crossed and parallel polarizers (aligned 45° to the lateral magnetic-field poling direction). Although light scattering effects are also present, the % T maximum through crosssed polarizers and the minimum through parallel polarizers shows the existence of the infrared tunable birefringent effect in the electro-optic curves in figure 11.

The use of PDLC films in the infrared region is advantageous because the response times are controlled by the nematic droplet size rather than the thickness of the cell. Thus, if the polymer medium is sufficiently transparent, relatively thick PDLC films can be used to modulate the infrared light while retaining fast response times [18]. Table 2 shows that fairly fast response times were obtained for the films used to obtain the results in figures 10 and 11. The full voltage (0–65 V) 1.06 μm light scattering response times from figure 10 showed a frame time (on-time plus off-time) of about 9 ms. (Intermediate voltage modulation would be slower). The partial voltage response times in table 2 for the tunable birefringent cell from figure 11 showed frame times in the 32–36 ms range, which is relatively fast. It would be of interest to design the PDLC composition and droplet size specifically for the infrared birefringent effect. Such an optimization would include the formation of off-state aligned nematic droplets considerably smaller in size than the infrared wavelength, and a choice of components so that the refractive index matching of the nematic droplet and the polymer films occurred at the first birefringent peak instead of at full saturation voltages as is normally used in light scattering PDLC films.

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