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A Light Control Film Composed of Liquid Crystal Droplets Dispersed in an Epoxy Matrix

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This paper describes light control films consisting of submicron liquid crystal droplets dispersed in epoxy matrices. These films, which can respond optically to both applied electric fields and temperature changes, are potentially useful for displays and light shutters.

The optical performance of these films depends on a variety of structural, electro-optical and thermal properties. This paper describes scanning electron microscope studies of film structure, measurements of voltage dependent film transmittance, contrast ratio and light scattering, and calorimetric studies of the cure process which governs microdroplet formation in the films.

Keywords: liquid crystal, droplets, light control, epoxy, dispersed, polymer matrix

INTRODUCTION

Thin films composed of liquid crystalline micro-droplets dispersed in solid matrices¹⁻³ are promising materials for electro-optic applications. These films can be made with two fundamentally different types of matrix material: (i) a porous substrate in which the micro-droplets are interconnected, as in a sponge,¹ or (ii) a polymeric continuum in which the micro-droplets are randomly fixed in position but are not connected to each other.^{2,3} We are interested in materials of the second class in which the liquid crystal droplets are *spontaneously dispersed* in the continuum³ during film formation rather than *encapsulated* in thin polymer shells that are subsequently bonded together by another polymer, the continuum.² Polymer-dispersed liquid

crystal (PDLC) films and their practical applications have recently been described by Doane and his collaborators at Kent State University;³ their films were made from epoxy-based matrix materials and standard liquid crystalline materials. In this paper we describe the properties of films prepared in our laboratory using similar, though not identical, epoxy materials and sample preparation techniques. In a companion paper⁴ we present a similar study on films made from a new class of matrix materials, namely, ultraviolet curable adhesives.

In this paper we describe some aspects of (1) the micro-structure of the epoxy-based films as revealed by scanning electron microscopy (SEM); (2) the electro-optic behavior of the films as revealed by transmittance, brightness, and light scattering measurements; and (3) thermal properties of the films determined by differential scanning calorimetry.

OPERATING PRINCIPLES

PDLC films are potentially useful as electro-optic devices because they can be switched electrically from a light scattering "off-state" to a highly transparent "on-state." They can also be switched by heating them to the isotropic state; this operating mode will not be discussed further in this paper.

Multiple Light Scattering in the Off-State

The polymer matrix material is optically isotropic and has refractive index n_p ; the liquid crystalline material within the microdroplets is optically uniaxial and is characterized by an ordinary refractive index n_o and an extraordinary refractive index n_e . In the off-state (no applied voltage), the polymer-liquid crystal interaction at each microdroplet boundary determines the configuration of the liquid crystal director within the droplet; in general, this configuration is not uniform within each droplet or from droplet to droplet.³ As a result, light rays incident on the droplets probe a range of refractive index values between n_o and n_e . Since $n_o \neq n_e$, these indices cannot all be equal to the polymer refractive index n_p and incoming light is scattered by the microdroplets. The SEM photograph of Figure 1 shows that the diameters of the liquid crystal microdroplets are comparable to the wavelength of visible light ($\sim 1 \mu m$ or less); since these diameters are small compared with the film thickness (typically $\sim 30 \mu m$), a light ray will be scattered many times before emerging from the film. Because of this strong *multiple* scattering, the film appears milky

white in the off-state. The degree of off-state scattering will depend on both the size and the number density of the liquid crystalline microdroplets. SEM studies like those discussed below suggest that these quantities can be controlled by proper choice of materials and by the procedures used to prepare the films.

Refractive Index Matching in the On-State

Upon application of an electric field of sufficient magnitude to overcome the interactions at the droplet boundaries, the liquid crystal directors within each droplet become uniformly oriented along the direction of the applied field. Under these conditions, normally incident light probes essentially the ordinary refractive index of the liquid crystal alone. If $n_o \approx n_p$, the film will be essentially transparent. Removal of the applied electric field makes the film revert to its off-state described above. Clearly, in order to achieve high on-state transmittance at all operating temperatures, one has to ensure that $n_o \approx n_p$ over the entire operating temperature range. Proper choice of both the liquid crystal and the polymer matrix material plays a crucial role in this index matching problem.

SAMPLES

The PDLC films used in our experiments were prepared essentially as described in Reference 3. A mixture containing the desired proportions of liquid crystal, epoxy resin, and curing agent was first prepared. The liquid crystals used in our films were Schiff bases, cyanobiphenyl derivatives, or mixtures of these materials. We used a standard resin material, the product of the condensation of bisphenol A and epichlorohydrin. Finally, as the curing agent, we used a standard mercaptan-based hardener. The components were vigorously mixed together for about 30 s; the mixture was then allowed to cure in a manner consistent with the type of measurement to be performed.

Samples for Optical Studies

Each sample consisted of a PDLC film cured between two flat glass plates which had previously been coated with a thin transparent layer of conducting indium-tin-oxide (ITO). Film thickness, typically 27–30 μm , was controlled by glass microsphere spacers.[†] Portions of the

[†]Duke Scientific Corp., Palo Alto, CA.

ITO layers which were intentionally not covered during sample preparation served as electrode contacts for applying voltage across the PDLC films. The quality of the samples was judged initially by simple visual inspection of their electro-optic characteristics. In the absence of applied voltage (off-state), all PDLC films appeared milky white. Only films which switched to a uniformly transparent on-state when sufficient voltage ($25\text{--}100\text{ }V_{RMS}$ at 100 Hz) was applied to the electrodes were considered good samples and used for further electro-optical studies.

Samples for Structure Analysis and Calorimetry

Scanning electron microscopy (SEM) is potentially the most powerful technique for studying the structure of PDLC films. Samples for SEM studies were prepared by placing a drop of the uncured PDLC mixture directly on an aluminum stub and letting it cure *in situ*. The cured sample was cut to reveal a fresh cross section of its internal structure. The cut had to appear flat over a distance of several tens of micrometers in order to yield good photographs. The exposed cross section was then vacuum desiccated for at least one hour to remove the liquid crystal fluid from its surface; finally, a thin conducting layer of a gold-palladium alloy was vacuum-sputtered onto the cut section. This sample preparation technique generates SEM samples that reveal the liquid crystalline droplets as empty, cross-sectioned cavities that were once filled with the liquid crystalline material.

Photomicrographs showing details of the PDLC film cross sections were recorded using an International Scientific Instruments Model ISI-SX-30 SEM unit. One should note that, since the SEM samples are bulk samples, they are much thicker than those used for the optical measurements. The PDLC structure that they reveal appears, nevertheless, identical to that obtained from SEM samples intentionally prepared with thicknesses similar to those of the samples used in the optical studies.

Samples for calorimetric studies were prepared in similar fashion except, of course, they were not alloy-coated.

FILM STRUCTURE

Figure 1 shows an SEM photograph obtained from a chemically cured sample consisting of a liquid crystalline mixture dispersed in an epoxy-based matrix. It reveals several important features: the droplets of

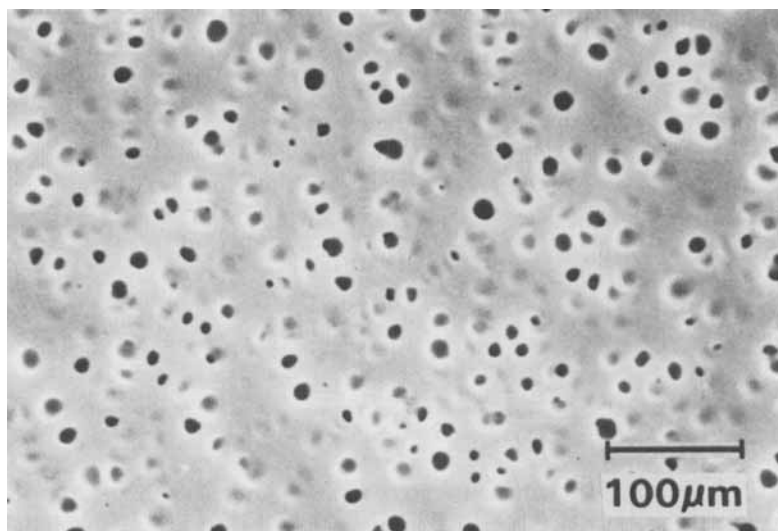


FIGURE 1 SEM photomicrograph of a cross section through a polymer-dispersed liquid crystal sample.

liquid crystalline material are (1) *uniformly* dispersed within the polymer matrix (2) with nearly spherical shape and (3) an average diameter of $\sim 1 \mu\text{m}$; furthermore, (4) the droplets are not interconnected and (5) few coalescence events can be detected in any given photograph.

ELECTRO-OPTIC PROPERTIES

Transmittance vs. Voltage

Figure 2 shows a typical transmittance vs. voltage curve for a PDLC film. The frequency of the applied sinusoidal voltage was 100 Hz . The transmittance was measured with a Perkin-Elmer Lambda-5 UV/visible spectrophotometer at a wavelength of 555 nm . The total transmittance range is from 2% to 76%. Transmittance has reached 90% of its maximum value with $24 V_{\text{RMS}}$ applied to the film.

The transmittance curves for increasing and decreasing voltage differ slightly. We have not studied this hysteresis in detail; it may be the result of charging effects. We have verified that the transmittance curves shown in Figure 2 are reproduced upon repeated cycling of the voltage from 0 to $50 V_{\text{RMS}}$.

The transmittance vs. voltage curves show no sharp voltage thresh-

old for the onset of transmittance. The voltage range over which the transmittance increases from 10% to 90% extends from about 10 to 24 V_{RMS} for this film and varies significantly from film to film. The shape of the transmittance vs. voltage curves should depend on liquid crystal material parameters such as dielectric and elastic constants, which are known to influence the electro-optic behavior of conventional nematic liquid crystal devices.⁵ In addition, we expect that liquid crystal droplet size and film thickness will also be important in determining voltage-dependent film transmittance. We plan to explore these areas in future studies. At this stage of development, it is not clear whether PDLC films will be useful in multiplexed displays.

Transmittance vs. Wavelength

In Figure 3 the transmittance of the same film whose voltage dependent transmittance has just been discussed is shown as a function of wavelength for both the on-state ($V = 50 V_{RMS}$) and the off-state. These curves illustrate the transmittance behavior generally observed for films containing no absorbing dyes in the liquid crystal. Transmittance generally increases with wavelength in both the on- and off-states. For the few samples for which we have measured transmittance at wavelengths above 900 nm, this increase persists to beyond 1.5

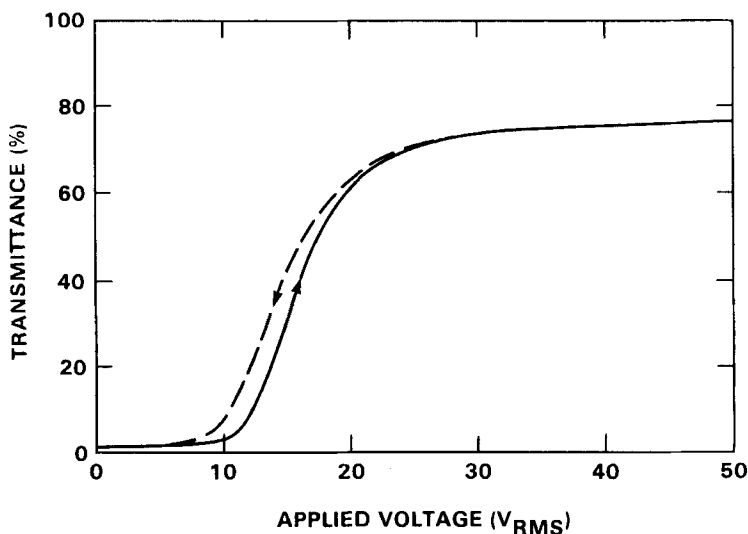


FIGURE 2 Transmittance vs. voltage for a polymer-dispersed liquid crystal film. Arrows distinguish the curves for increasing or decreasing voltage.

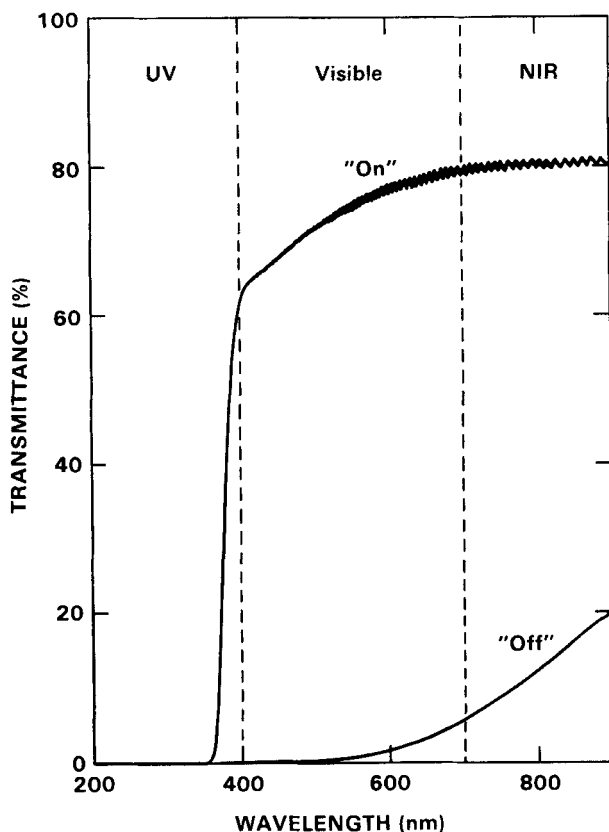


FIGURE 3 Transmittance vs. wavelength for the polymer-dispersed liquid crystal film of Figure 2. The upper trace corresponds to the on-state ($V = 50 V_{RMS}$) and the lower trace to the off-state ($V = 0$).

μm in the on-state and to beyond $2 \mu m$ in the off-state. Comparison of the transmittance curves in the figure with those of an ITO-coated glass slide shows that the sharp decrease in transmittance below $400 nm$ is shifted to longer wavelengths by the PDLC film. The oscillations in the on-state transmittance curve are interference fringes caused by multiple reflections at the film/ITO interfaces; these oscillations occur only in films with very uniform thickness. The presence of these fringes correlates well with visual observation of the uniformity of transmittance across the film as voltage is increased.

Contrast Ratio

Contrast ratio is almost universally accepted as a figure of merit for electro-optic displays; however, there is neither a universally accepted

definition of contrast ratio nor a standardized procedure for determining it experimentally. Contrast ratios of displays have been determined with collimated or diffuse monochromatic or broadband illumination; some broadband measurements have included the effect of the spectral response of the human eye while others have not.⁶⁻¹² For nonscattering, passive systems which change the intensity but not the direction of the incident illumination, all these contrast ratios can be expected to provide similar, albeit not identical, measures of system performance. However, PDLC films are passive systems which scatter the incident illumination; consequently, contrast ratios of these films depend strongly on the procedures used to determine them, as we shall show.

To illustrate this, we have determined contrast ratios of PDLC films by two different methods. The first is based on photometric measurements of film brightness in the on- and off-states using diffuse illumination. Light from two tungsten-halogen projector bulbs was passed through a pair of transparent diffusers and further diffused by multiple reflections between two matte white screens before illuminating the sample. Baffles prevented any direct light from the bulbs from reaching the sample. Light transmitted through the sample was measured with a photometer with a $\frac{1}{4}^\circ$ field of view.[†] We verified by direct measurement that the brightness readings were independent of distance for photometer-sample separations between 300 and 1500 mm, as they should be. Over this distance range, the sample area contributing to the measurements was small compared to the total sample area (about 600 mm²) but large compared to any imperfections in the samples.

Since the PDLC films are passive elements, it is convenient to use normalized brightness values L_v^{on}/L_v^0 and L_v^{off}/L_v^0 where L_v^{on} and L_v^{off} are the measured film brightness (luminance) values in the on- and off-states, respectively[‡] and L_v^0 is the brightness measured by the photometer with the sample removed from the system. In our measurements L_v^0 was ≈ 3 fL. Film contrast ratio (*CR*) may be defined as:

$$CR = \frac{L_v^{on}/L_v^0}{L_v^{off}/L_v^0} \quad (1)$$

[†]Spectra Spotmeter, Photo Research, Inc., Burbank, CA.

[‡]The subscript *v* indicates that brightness is a photometric or visual quantity which includes the effect of the spectral response of the human eye.

Normalized brightness values in the on- and off-states and the contrast ratios derived from them are tabulated for several typical PDLC samples in Table I.

The second procedure we used to determine contrast ratio is based on measurements of the spectral transmittance of the films in their on- and off-states (*cf* Figure 3). If the spectral distribution of the illumination reaching the sample is known, spectral transmittance data can be used to determine the photopic transmittance and the photopic contrast ratio, i.e., the transmittance and contrast ratio which would be perceived by an observer. The percent photopic or visual transmittance of the sample over the wavelength range from λ_1 to λ_2 is given by:

$$T_v = \frac{\int_{\lambda_1}^{\lambda_2} S(\lambda)T(\lambda)\bar{y}(\lambda)d\lambda}{\int_{\lambda_1}^{\lambda_2} S(\lambda)\bar{y}(\lambda)d\lambda} \quad (2)$$

where $S(\lambda)$ is the spectral irradiance produced by the source at the sample, $T(\lambda)$ is the spectral transmittance of the sample, and $\bar{y}(\lambda)$ is the spectral response of the human eye.¹³

The contrast ratio can be obtained from:

$$CR = \frac{T_v^{on}}{T_v^{off}} \quad (3)$$

where T_v^{on} and T_v^{off} denote, respectively, the wavelength-integrated transmittances of the sample in the on- and off-states.

For comparison with the contrast values obtained from our photometric brightness measurements, we used for $S(\lambda)$ in Eq. (2) the relative spectral irradiance $S_A(\lambda)$ of CIE Standard Source A.¹³ Since

TABLE I
Transmittances and contrast ratios of some PDLC films

Sample Number		#2484	#2461	#2253	#2465
Brightness (Normalized)	L_v^{on}/L_v^0 (%)	75.4	74.7	78.0	82.5
	L_v^{off}/L_v^0 (%)	23.9	25.0	26.9	33.8
	$CR = L_v^{on}/L_v^{off}$	3.15	2.99	2.90	2.44
Transmittance (Illuminant A)	T_v^{on} (%)	69.2	56.2	76.6	79.6
	T_v^{off} (%)	0.40	0.80	1.70	3.50
	$CR = T_v^{on}/T_v^{off}$	173.0	140.5	45.1	22.7

$S_A(\lambda)$ is the (normalized) radiant exitance¹³ of a blackbody at temperature $T = 2855.6$ K, Illuminant A transmittance should closely simulate the transmittance of a sample illuminated by a tungsten lamp. Wavelength-integrated Illuminant A transmittances of the same samples used for brightness measurements and the contrast ratios derived from them are summarized in Table I.

Inspection of this table shows that the contrast ratios determined from brightness measurements with diffuse illumination are approximately 3 for all the samples measured, whereas contrast ratios determined from transmittance measurements varied from 22.7 to 173 depending on the sample. These differences can be explained by considering the basic operation of the films and the geometries of the two measurements.

In the off-state, the flux of light energy incident onto the sample from a given direction is redistributed over the entire range of forward and backward scattering directions because of the strong multiple scattering described earlier.

In the brightness measurements, this scattering produces two competing effects. The photometer accepts only light propagating within a small cone about its optical axis. Much of the light which would have been collected by the photometer in the absence of a sample is scattered out of the acceptance cone of the photometer. This tends to reduce off-state brightness and increase contrast ratio. Because of the diffuse illumination, however, light impinges on the sample from many directions and a fraction of the light from each direction is scattered into the acceptance cone of the photometer. This can significantly increase the off-state brightness measured by the photometer, thereby decreasing contrast ratio.

In the transmittance measurements, light impinges on the sample only from a small range of incident angles and the spectrometer measures the fraction of this light which continues to propagate within this narrow angular range after passing through the sample. Because of the strong off-state scattering, much of the incident light is scattered out of this range. The narrow cone of sample illumination limits the directions from which light can be scattered into the cone of transmitted light accepted by the spectrometer. The strong scattering and narrow illumination cone combine to produce a very low off-state transmittance which increases contrast ratio.

Film behavior in the on-state also contributes to differences in contrast ratios determined from brightness and transmittance measurements. In the on-state, the molecules within the liquid crystal microdroplets are reoriented by applied voltage so that their long

axes are predominantly pointed along the direction of the applied electric field, i.e., perpendicular to the film.[†] Light propagation along the long molecular axis is governed only by the ordinary index of refraction of the liquid crystal, which can be made very close to the refractive index of the surrounding polymer by proper choice of materials. The small index mismatch at the polymer-droplet interfaces means that little or no light is scattered. This index-matching condition can be nearly satisfied for illumination confined to within a small cone about the sample normal, as in the transmittance measurements. Therefore, on-state transmittance can be very high. This high on-state transmittance and the small off-state transmittance discussed above result in a very large contrast ratio.

In the brightness measurements with diffuse illumination, only a fraction of the incident light propagates normal to the sample. For other propagation directions, the liquid-crystal refractive index becomes increasingly different from the ordinary index as the angle of incidence increases. Therefore, obliquely incident light is scattered, the degree of scattering increasing with increasing angle of incidence. Thus, in the on-state, the photometer measures the small fraction of the diffuse incident light which impinges on the sample within a small cone about the sample normal and which undergoes little scattering, plus the fraction of obliquely incident light which is scattered into this cone as in the off-state. The net result is an on-state brightness which, in many samples, is only a few times larger than the brightness in the off-state. The small brightness difference results in a small contrast ratio.

The ratios of Table I support these ideas. The data also demonstrate that contrast ratio is improved primarily by decreasing the brightness or transmittance in the off-state.

Angular Dependence of Light Scattering

From the above discussion it is clear that knowledge and control of the angular dependence of light scattering by PDLC films will be important for optimizing their electro-optic performance. It will also be important for designing proper lighting for displays using these films. We have begun measurements of angular dependent light scattering and report here some preliminary results.

In our experiments, light from the central 5 mm diameter of a chopped, spatially-filtered, collimated HeNe laser beam ($\lambda = 632.8$

[†]The liquid crystal has a positive dielectric anisotropy.

nm) was normally incident on the PDLC sample. A collecting lens imaged the sample film plane onto a photodiode detector whose output was monitored with a lock-in amplifier tuned to the 1 kHz chopping frequency. An aperture in the focal plane of this lens insured that only light scattered within a cone of 0.5° half angle about the optical axis of the detection system would be collected by the photodetector. The entire detection system (lens, focal plane aperture and photodetector) could be rotated about a point directly below the sample film plane so that we could measure the scattered light as a function of scattering angle θ over the range $-170^\circ \leq \theta \leq 170^\circ$. For each angle of incidence the scattered power received by the detector was recorded every 1° for $-45^\circ \leq \theta \leq 45^\circ$ and every 5° for scattering angles outside this range.

The angular dependence of the flux scattered by a typical PDLC film is illustrated in Figure 4. The ordinate on each curve is the power received by the photodetector at each scattering angle normalized to the incident laser power. This ordinate is directly proportional to the differential scattering cross section.

The scattered flux received by the photodetector is strongly peaked in the forward direction. The forward scattering peak is stronger in the on-state than in the off-state; this is expected since, in the on-state, the sample is essentially transparent and very little light is scattered out of the incident beam.

A quantitative description of the seven decade variation in the magnitude of the differential scattering cross section is not possible without a precise theoretical description of the scattering of light by particles composed of anisotropic materials. Such a theory has not yet been developed. We can, however, qualitatively account for some of the observed angular dependence and for the positions of the minima at $\theta = \pm 90^\circ$ by recalling the structure of the PDLC film. The glass and epoxy matrix material both have refractive indices of ~ 1.52 ; therefore, scattered light leaving the sample will be refracted when it enters the surrounding air. From Snell's Law we find that an angular range $\theta_2 - \theta_1$ in air is related to an angular range $\theta_{p2} - \theta_{p1}$ inside the polymer by:

$$\theta_2 - \theta_1 = \sin^{-1}(n_p \cdot \sin \theta_{p2}) - \sin^{-1}(n_p \cdot \sin \theta_{p1}). \quad (4)$$

This means, for example, that light scattered in the 1° angular range $0.5^\circ \leq \theta_p \leq 1.5^\circ$ is spread out by refraction into the 1.5° angular range $0.75^\circ \leq \theta \leq 2.25^\circ$ whereas light scattered in the 1° angular range $39^\circ \leq \theta_p \leq 40^\circ$ is spread out by refraction into the 3.9° angular

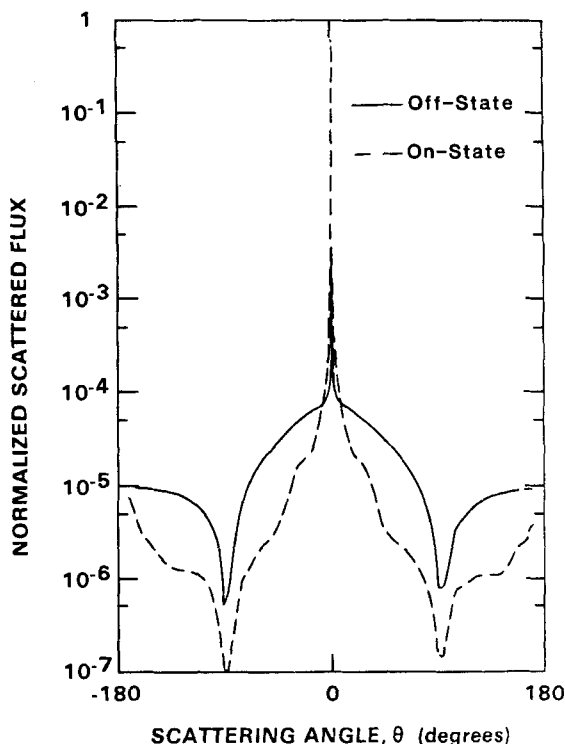


FIGURE 4 Angular dependence of light scattering from a typical polymer-dispersed liquid crystal film. The ordinate is the scattered flux measured by the photodetector per unit incident laser flux vs. scattering angle θ for normally incident light; it is directly proportional to the differential scattering cross section.

range $70.7^\circ \leq \theta \leq 74.6^\circ$. Therefore, even if the angular distribution of scattered light were uniform within the polymer, it would be highly nonuniform when measured outside the sample in air and the light scattered into a fixed small solid angle in air would decrease monotonically as the scattering angle increased from 0° to 90° . If the light scattering distribution within the polymer is already peaked in the forward direction, this peaking will be enhanced in the angular distribution measured in air.

Additional insight into the decrease in differential cross section and, in particular, the sharp minima at $\theta = \pm 90^\circ$ can be gained by thinking of the illuminated sample area as a source of "diffuse" light. It is well known¹⁴ that, for such a source, the flux emitted in a given direction depends on the projected area of the source in that direction.

The projected area of our “source” decreases monotonically to zero as the scattering angle $\theta \rightarrow 90^\circ$.

The symmetry of the scattering about the forward direction, which is evident in Figure 4, can be understood in terms of the molecular orientation within the liquid crystal droplets as a function of applied electric field. At zero field the average droplet directors are randomly oriented and there is no preferred direction within the film. Furthermore, all refraction of scattered light should be symmetric about the normal to the film at normal incidence. Therefore, for normally incident light, we can expect the differential scattering cross section in the off-state to be symmetric about the forward direction. As the field increases, the molecules within each droplet attempt to align themselves along the applied field. In a strong field this alignment is achieved throughout most of the droplet. Therefore, the director distribution within each droplet should be cylindrically symmetric about the normal to the film and the differential cross section in the on-state should also be symmetric about the forward direction for normally incident light.

We can exploit this symmetry in the angular distribution of the scattered light to compute by integration the total flux scattered into the forward and backward hemispheres. We find that the forward:backward ratio is $\sim 4:1$ in the off-state and $\sim 27:1$ in the on-state. This means that, in applications where PDLC films are to be used to control the transmission of energy rather than merely to control image visibility, it will be necessary either to increase significantly the fraction of backscattered radiation or to add absorbing materials to the films.

CALORIMETRIC RESULTS

Differential scanning calorimetry (DSC) has proved to be a particularly useful tool for studying the formation and phase behavior of PDLC's. As indicated elsewhere,⁴ DSC measurements of the nematic–isotropic transition enthalpies ΔH_{NI} of both cured and uncured matrix/liquid crystal mixtures strongly support the view that the liquid crystal microdroplets are formed as a result of a polymerization-induced phase separation (PIPS) process; that is, as polymerization proceeds, the solubility of liquid crystal in the growing polymer decreases, leading to at least a partial separation of the two phases.

Evidence that the separation is only partial is also provided by ΔH_{NI} measurements. For a fully cured, epoxy-based PDLC contain-

ing 37.2 vol % p-n-heptocyanobiphenyl (7CB), we measured ΔH_{NI} to be 0.23 cal/gm whereas, for pure 7CB, $\Delta H_{NI} = 0.83$ cal/gm (0.230 Kcal/mol).¹⁵ For complete phase separation, we would expect (on the basis of simple density and volume considerations) the transition enthalpy of the PDLC to be reduced to 0.27 cal/gm. Therefore, only about 85% ($0.23 \times 100/0.27$) of the liquid crystal has phase separated from the polymer matrix. The liquid crystal remaining in the matrix acts as a plasticizer, as is evident from the 9 K depression of the glass transition temperature (Figure 5). Furthermore, an appreciable amount of monomer remains dissolved in the liquid crystal, resulting in a depression of the nematic–isotropic transition temperature T_{NI} from 316 K to 313 K. The amount of impurity in the liquid crystal microdroplets cannot be estimated from the Van't Hoff equation for temperature depression since the basic assumptions underlying the equation are not satisfied.

DSC can also be used to determine the isothermal cure kinetics of the PDLC system by heating an uncured sample rapidly to the desired

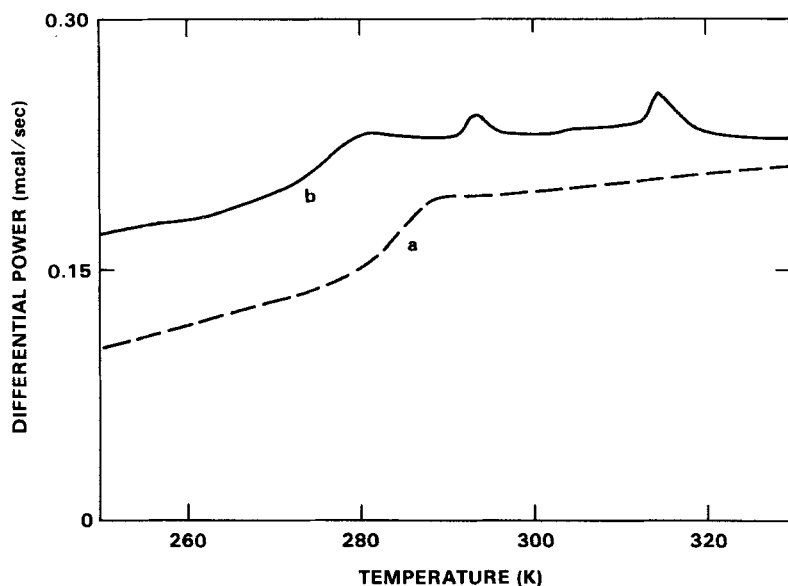


FIGURE 5 Differential scanning calorimetry (DSC) traces of: a) a cured pure epoxy matrix material and b) a PDLC containing 37.2 vol % 7CB in the epoxy. The reduction in the glass transition temperature from ~ 284 K to ~ 275 K is readily apparent. The peak at 313 K (curve b) is due to the nematic–isotropic transition of the PDLC. The smaller lower temperature peak may be associated with some residual melting.

cure temperature and monitoring the time dependence of the heat evolved during the cure at that temperature. Some preliminary results are given in Figure 6, which shows that the presence of liquid crystal both slows polymerization[†] and "smooths" the process from two sequential steps to essentially a single step process.

SUMMARY

In this paper we have described some structural, electro-optic, and thermal properties of polymer-dispersed liquid crystal (PDLC) films in which chemically cured epoxies were used as the matrix materials. These films are a promising new technology for light control.

Structurally, the films contain unconnected microdroplets of liquid crystalline material which are uniformly dispersed in the polymer matrix. Typical droplet diameters are $\sim 1 \mu\text{m}$ or less. Both droplet

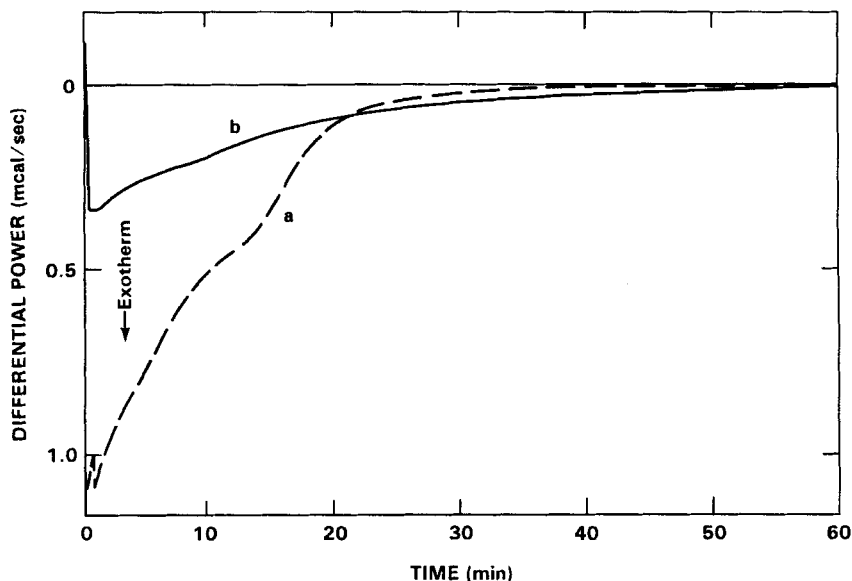


FIGURE 6 DSC measurements of heat evolved during isothermal cure at 350 K: a) pure polymer and b) polymer containing 30 vol % liquid crystal (British Drug House mixture E7). The sample masses in the two cases are equal to within 3%.

[†]The rate constant at 350 K is decreased by about 12% from 1.25×10^{-3} to $1.1 \times 10^{-3} \text{ sec}^{-1}$.

size and number density can be controlled by proper choice of materials and fabrication procedures.

The PDLC films appear milky white in the absence of applied voltage because of strong *multiple* light scattering by the micro-droplets. When sufficient voltage (25–100 V_{RMS}) is applied across the films, they become transparent, provided the ordinary refractive index of the liquid crystal within the droplets is sufficiently close to the index of the polymer matrix material. On-state transmittances above 75% and off-state transmittances below 2% (determined from spectrophotometric measurements at 555 nm) have been achieved in these films. Wavelength-integrated contrast ratios for incandescent illumination have been computed from spectral transmittance data; they range from ~20 to ~175 depending on the film. Contrast ratios determined from direct measurements of photometric brightness are substantially lower—about 3 for all the films we studied. These differences have been explained by analyzing the illumination and collection geometries in the transmittance and brightness measurements, together with the multiple scattering of light by the films. These results underscore the need to standardize procedures for determining contrast ratios of these new electro-optic materials.

Calorimetric studies support the view that PDLC formation proceeds via a polymerization-induced phase separation (PIPS) process, but indicate that the separation is only partial in the systems studied thus far. Some liquid crystal remains in the polymer matrix, acting as a plasticizer, while some polymer precursor is retained in the liquid crystal and reduces the nematic–isotropic transition temperature. Calorimetric measurements of PDLC cure kinetics also indicate that the liquid crystal tends to retard and “smooth” the cure process.

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