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Effect of polymer matrix glass transition temperature on polymer dispersed liquid crystal electro-optics

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We have studied the electro-optic properties as a function of temperature of a polymer dispersed liquid crystal film composed of E7 dispersed as droplets in a polyvinylformal (PVFM) matrix. The drive voltage and turn-off time change abruptly as the temperature is raised above the glass transition temperature (T_g) of the PVFM matrix. There is essentially no hysteresis below, but significant hysteresis above T_g . These temperature effects are completely reversible. The rapid change in electro-optic properties cannot be entirely explained by changes in the polymer dielectric properties or droplet shape. Freedericksz measurements show no abrupt change in the surface anchoring energy at T_g , which may be responsible for the changes observed in the electro-optic response.

The electro-optics of polymer dispersed liquid crystal (PDLC) light shutters are influenced by a number of parameters including the type of polymer and liquid crystal used, the film thickness, the droplet shape, size and density, and the dielectric properties of the polymer and liquid crystal.^{1,2} Recent work on the dielectric response of PDLC films has demonstrated that the driving voltage can be dramatically increased by conductive shielding of the applied field.^{3,4} For a PDLC composed of E7 dispersed in a polymethylmethacrylate matrix, conductive shielding is typically observed at driving frequencies below 100 Hz. We purified the components in this system to remove ionic impurities and reduce the shielding. Contrary to our expectations, although the shielding was reduced, the driving voltage increased. Differential scanning calorimetry showed that the polymer matrix glass transition temperature (T_g) had been raised above the operating temperature of the sample as a result of the purification. We therefore postulated that the increase in the matrix T_g resulted in the increase in switching voltage, presumably through a modification of the surface interaction between the liquid crystal and the polymer. To test this hypothesis, we have studied the electro-optic characteristics of a PDLC system in the vicinity of the matrix T_g .

PDLC shutters were made using the eutectic liquid crystal mixture, E7 (EM chemicals), dissolved with polyvinylformal, PVFM (Aldrich), in a common solvent by the standard solvent induced phase separation method.⁵ The resulting solution was poured on a conducting glass substrate and the solvent allowed to evaporate. We added 20 μm spacers to control film thickness and heated the PDLC material above the softening point. A second substrate was added with pressure to contact the spacers. We then cooled the film to room temperature at a prescribed rate to control droplet size.

Conducting leads were attached to the front and back substrate of the PDLC shutter using conductive paint and a 5 min epoxy adhesive. The shutter was placed in a Metler FP 80 heating stage to control temperature to $\pm 0.1^\circ\text{C}$. The collimated beam from a HeNe laser was passed

through the heating stage and sample. The transmitted intensity was monitored with a silicon diode photodetector. The output of a gated pulse/function generator was amplified and used to drive the PDLC shutter. The drive signal and the response of the silicon diode were monitored with an oscilloscope. The driving voltage, turn-off time, and hysteresis of the PDLC shutters were measured as a function of temperature.

Freedericksz cells consisted of 1/4-in. thick conducting glass substrates coated with a thin layer of PVFM with 20% (by weight) E7 added as a plasticizer to model the composition of the PDLC matrix. The cells were rubbed to achieve parallel alignment and filled with E7. The capacitance and optical retardation of the cells were measured as a function of applied voltage and temperature. From these results the anchoring strength was calculated as a function of temperature by the method of Yokoyama and van Sprang.⁶

Differential scanning calorimetry of a PDLC composed of PVFM/E7 in a weight ratio of 1:2 reveals a T_g for the matrix at 35°C . The voltage required to turn the cell 90% on, V_{90} , and the turn-off time, τ_{off} , of this shutter are shown as a function of temperature in Fig. 1. The V_{90} and τ_{off} change gradually below and rapidly above T_g . The abrupt change in the V_{90} and τ_{off} response at T_g is completely reversible. A similar effect is observed for a PVFM/E7 shutter with a weight ratio of 1:1 ($T_g = 30^\circ\text{C}$) and for a PVFM/E43 shutter with a weight ratio of 1:2 ($T_g = 29^\circ\text{C}$).

We also measured the hysteresis of the PVFM/E7 PDLC shutter as a function of temperature. Figure 2 shows the hysteresis as a function of temperature for the PVFM samples. Below T_g the hysteresis is minimal [Fig. 2(a)], while above T_g substantial hysteresis is observed [Fig. 2(b)].

Several factors may contribute to the change in the electro-optic properties at T_g . Ionic conduction is typically enhanced above T_g because the dramatic decrease in viscosity leads to space-charge accumulation that modifies the field in a droplet. To determine the impact of this effect, the

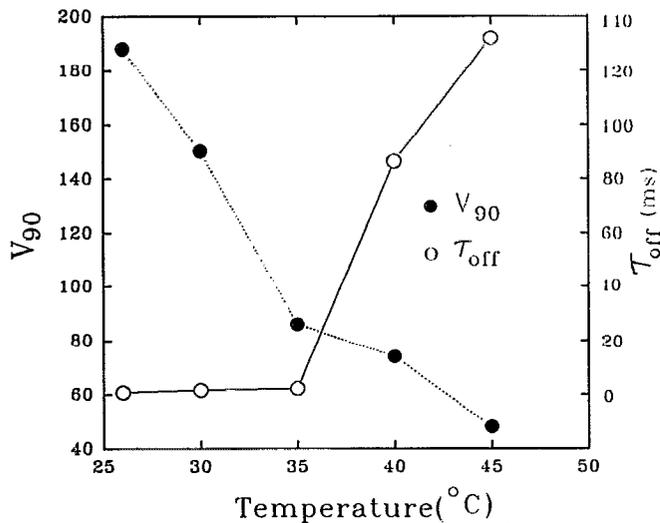


FIG. 1. Electro-optic response of E7/PVFM PDLC (1:2 weight ratio) as a function of temperature: $\times = V_{90}$, $\bullet = \tau_{off}$.

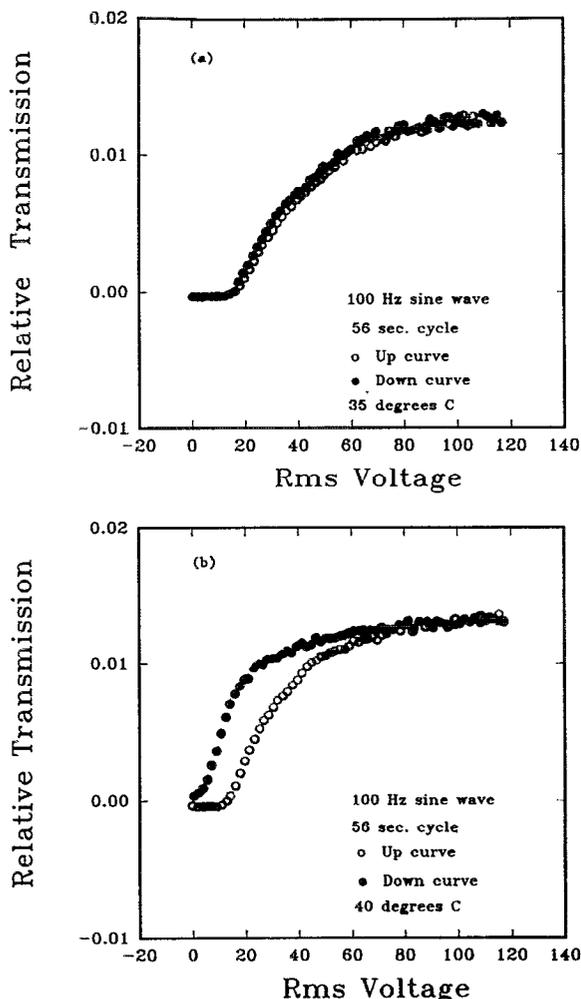


FIG. 2. Hysteresis of E7/PVFM PDLC measured with a ramped 1 kHz sine wave measured at (A) 35°C and at (B) 40°C.

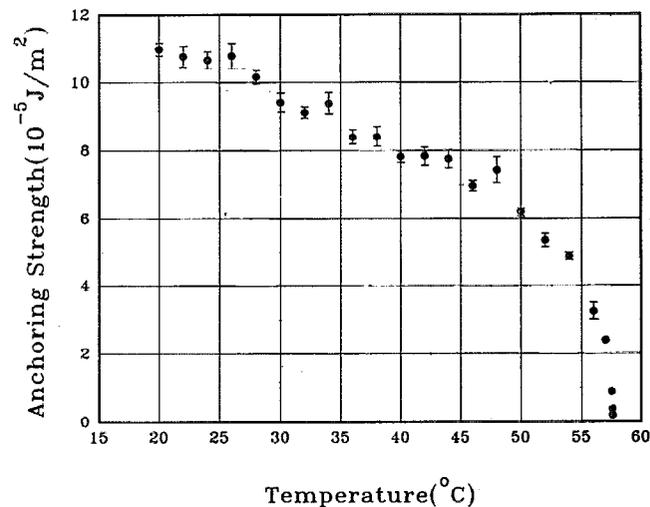


FIG. 3. Anchoring strength of E7 at a PVFM surface measured as a function of temperature by the method of Yokoyama and van Sprang.

dielectric response of the PVFM/E7 shutter was measured as a function of frequency and temperature. Above 500 Hz, we observed no evidence of any space-charge accumulation either above or below T_g . Since the abrupt change in V_{90} was evident even with 5 kHz drive signals, shielding effects were ruled out as a possible cause.

The V_{90} and τ_{off} could also be affected by changes in the droplet shape. The increased polymer flexibility might allow the droplets to relax from an elliptical to a more spherical shape and thereby reduce V_{90} and increase τ_{off} . This relaxation could result from the relief of stored up strain in the polymer; however, the variations are totally reversible, eliminating this possibility. Another possible explanation is that the density of the matrix changes abruptly at T_g . The thermal expansivity of the matrix is expected to change at T_g but no abrupt change in density is predicted. We measured the refractive index as a function of temperature of PVFM containing 20% E7. Changes in density are reflected as changes in the refractive index; however, no abrupt change in the refractive index is observed at T_g .

We have concluded from these studies that neither changes in dielectric properties nor changes in droplet shape can fully explain the changes in V_{90} and τ_{off} at T_g . We have therefore made Fredericksz measurements of the anchoring energy of E7 at a PVFM surface as a function of temperature. Preliminary results show no clear effect of the glass transition on the anchoring strength of E7 at the PVFM interface (Fig. 3). The results are not conclusive; however, the surface structure may be quite different in a PDLC than in the planar cell used to make the anchoring measurements.

Our investigations have shown that abrupt changes in the electro-optic response of PDLC films composed of E7 dispersed in a PVFM matrix occur at the glass transition temperature of the matrix. These effects cannot be explained by variations in the dielectric properties or droplet shape. We postulate that changes of the liquid crystal/polymer interface at the glass transition of the polymer

may be responsible for the observed electro-optic behavior. However, preliminary measurements of the anchoring strength as a function of temperature do not show any abrupt change at the matrix T_g .

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