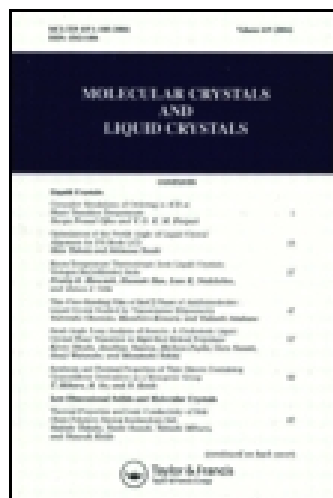


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# A Study of Hysteresis and Bistability in a Polymer Stabilised Nematic Liquid Crystal Using Paramagnetic Resonance and Electro-Optical Studies

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We observed hysteresis and bistability in a nematic liquid crystal mixture (E7) stabilised with an ultraviolet (UV) curable resin (Masterbond UV 10) in a weight ratio of 9:1. When the mixture is photocured at 90°C, for times between 0 and 60 min, the nematic clearing point is found to increase from 50°C to the value observed for pure E7. The degree of polymerization increases with longer cure time, leaving less GV10 input to depress the clearing point. Using electron paramagnetic resonance (EPR) spectroscopy, we observed a two phase system in the nematic spectra which is much more distinct when the cure is performed well below the clearing temperature, indicating decreased compatibility. The spectra also indicate little long range alignment as the sample is heated through the nematic range, but the spectra do indicate order as the sample is then cooled, yielding a bi-stable system. One possible explanation for this behaviour is that surface energy is overcome by thermal and magnetic energy as the sample is heated, allowing the magnetic field to align the sample. Typically, the anchoring energy of a liquid crystal to a polymer surface approaches zero as the temperature increases to near, but below, the clearing point. The EPR observations are verified by optical transmission studies.

*Keywords:* Liquid crystals, EPR, hysteresis.

## 1. INTRODUCTION

There has been an effort to understand the properties of polymer dispersed liquid crystal displays (PDLC)<sup>1–6</sup> and more recently, polymer stabilised cholesteric displays (PSCT).<sup>7–10</sup> Generally, these studies have been to measure the electro-optical properties and microscope textures of various displays. Previously,<sup>11</sup> we demonstrated the usefulness of electron paramagnetic resonance (EPR) studies of dissolved spin probes to study PDLCs. Using this technique we are able to extract information concerning the molecular dynamics and ordering in the polymer, liquid crystal, and interfacial regions of the PDLC. Electron paramagnetic resonance is a powerful technique that allows us to examine the materials on a microscopic scale. In this work we apply EPR to study polymer stabilised textures. We also apply microscopic texture observations and electro-optic studies, in addition to EPR in a preliminary study of a polymer stabilised nematic liquid crystal. The effects of polymer properties (degree of

polymerization and temperature at which the polymer was formed and the thermal history of the sample are studied. These studies indicate the existence of two stable configurations.

## 2. EXPERIMENTAL

The EPR samples consisted of the liquid crystal, E7 and an ultraviolet curable epoxy resin Master Bond UV10 (Master Bond Corporation). The Master Bond UV10 is clear formulation with a curved refractive index of 1.52, developed for liquid crystal device applications. A small amount of the spin probe cholestane (COL) was also added to the mixture. Cholestane is a cigar shaped molecule (aspect ratio approximately 4.8) that has nearly axial  $g$ - and hyperfine tensors. The anisotropy of the hyperfine tensor make it possible to detect the ordering of the probe<sup>11,12</sup> which is indicated by a contraction of the EPR spectra.

The EPR spectra were observed using an IBM X-band spectrometer with a variable temperature controller accessory. The magnetic field was monitored by a Hall probe that had been previously calibrated near  $g = 2$  (0.34 tesla) using an NMR magnetometer. The spectrometer frequency was measured using a Hewlett Packard microwave frequency counter. Data were gathered and processed using an IBM clone with EPR software developed for this purpose. The observed spectra were composite signals coming from both the polymer and liquid crystal regions, making it difficult to accurately ascertain the zero crossing points of the liquid crystal spectra which in turn are used to determine hyperfine splitting and hence the ordering of the liquid crystal.<sup>11,12</sup>

The phase behaviour of the sample was observed using a Leitz Laborlux 12 Pol polarizing microscope equipped with a Mettler FP 82 hot stage and a Mettler FP 80 central processor. Electro-optic transmission studies were performed on samples (E7/Master Bond UV10 (9:1)) held between conducting glass plates separated by 15  $\mu\text{m}$  spacers.

## 3. RESULTS

The nematic to isotropic clearing temperature ( $T_{\text{NI}}$ ) was detected using texture observations via an optical microscope. At 90°C, the E7/UV10 sample was subjected to uv irradiation for times of 0, 10, 20, 40 and 60 min, with  $T_{\text{NI}}$  observations of 50.3, 54.3, 58.2, 60 and 60.5°C respectively. The last temperature is nearly equal to the  $T_{\text{NI}}$  reported for pure E7. These data are plotted in Figure 1. The EPR spectra, observed at 19°C, from samples cured for times greater than 10 min appear quite similar. The same is true for spectral variations as the temperature is varied. The nematic to isotropic transition is clearly detected in the EPR spectra. Apparently the unpolymerized UV10 behaves as an impurity depressing  $T_{\text{NI}}$ . Polymerization induces phase separation, thereby decreasing the concentration of UV10 dissolved in E7. Noting that there is only 0.5°C difference in the values of  $T_{\text{NI}}$  for 40 and 60 mins of irradiation time, we conclude that nearly all of the UV10 was polymerized by 40

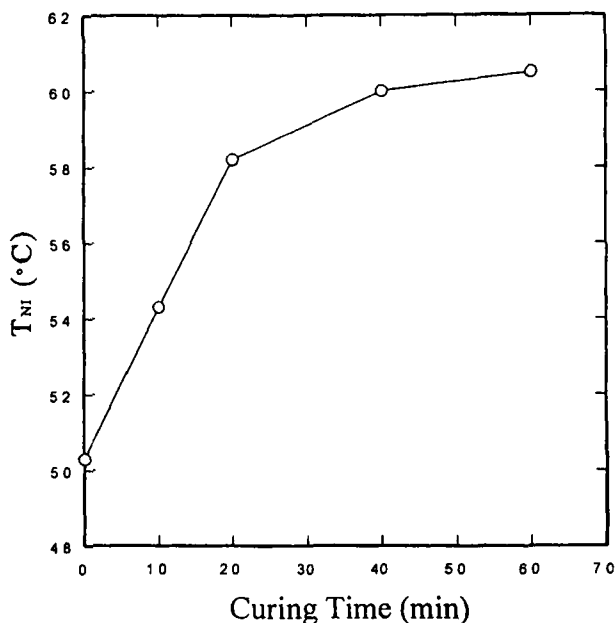


FIGURE 1 The nematic to isotropic transition temperature,  $T_{NI}$ , for E7/Master Bond UV10 (9:1) Samples cured at 90°C for different curing times.

minutes. For irradiation times of 10 min. or less, a substantial amount of UV10 remains dissolved in the liquid crystal which disturbs the structure. This is reflected in the EPR spectra.

In a second set of experiments, the sample temperature during irradiation was varied between room temperature and 90 °C. The value of the  $T_{NI}$  in the cured sample was unaffected by the temperature of cure. EPR spectra from at least two distinct phases were observed. When the curing temperature was below  $T_{NI}$ , the peaks in the spectra attributable to the liquid crystal phase are quite a bit stronger. While no distinct break occurs at  $T_{NI}$ , the composite spectra do indicate that samples cured at temperatures below  $T_{NI}$  are less compatible than those cured above  $T_{NI}$ . Previous research showed that smaller liquid crystal domains result with higher cure temperatures.<sup>13</sup> The smaller domains increase the surface to volume ratio and therefore the relative importance of surface anchoring. The increase in surface anchoring of the liquid crystal molecules to the polymer results in random alignment of the liquid crystal, increasing the width of the liquid crystal peaks in the EPR spectra. Some larger liquid crystal domains are still present. Therefore, some aligned liquid crystal remains.

The actual spectra observed depend upon the thermal history of the sample. Starting with a sample cooled from the isotropic with no fields present, one observes an EPR spectrum of fairly large width, indicative of a poorly aligned sample. As the temperature increases towards the clearing point, a temperature is reached at which the spectrum contracts. At this point the surface anchoring energy has decreased to the point where the liquid crystal can align with the magnetic field of the spectrometer. As the sample is

further heated above  $T_{NI}$  an isotropic EPR spectrum is observed. EPR spectra are then gathered as the temperature is decreased, indicating that liquid crystal order is present. EPR spectra taken during this heating and cooling experiment are shown in Figure 2. The heating and cooling spectra are clearly different. This hysteresis is further illustrated in Figure 3, where the heating data (open circles) indicate large splittings characteristic of a poorly aligned sample, and the cooling data (closed circles) indicate smaller splittings characteristic of an aligned sample. If the sample is left outside of the magnetic field at room temperature for long periods of time it retains its alignment (verified for 11 hours). Conversely, if the sample is heated to the isotropic phase and cooled outside of the field, it returns to the poorly aligned state. These experiments demonstrate the bistability of the sample.

Bistability and hysteresis are confirmed by electro-optic studies. A sample cell that is 15  $\mu\text{m}$  thick contains a 9:1 UV cured mixture of E7/Master Bond. The transmission is measured as the amplitude of an applied 2000 Hz signal is varied. The results are plotted in Figure 4 where the open circles are the data for increasing voltage and the solid circles are the data for decreasing voltage. The hysteresis between the two sets of data is clearly observed. As expected, data corresponding to decreasing voltage display higher transmission since the sample is aligned by the electric field. The temperature dependent response is also studied where a constant 5.5 V, 2000 Hz voltage is applied to an initially poorly aligned sample, is heated to the isotropic, and then cooled. The

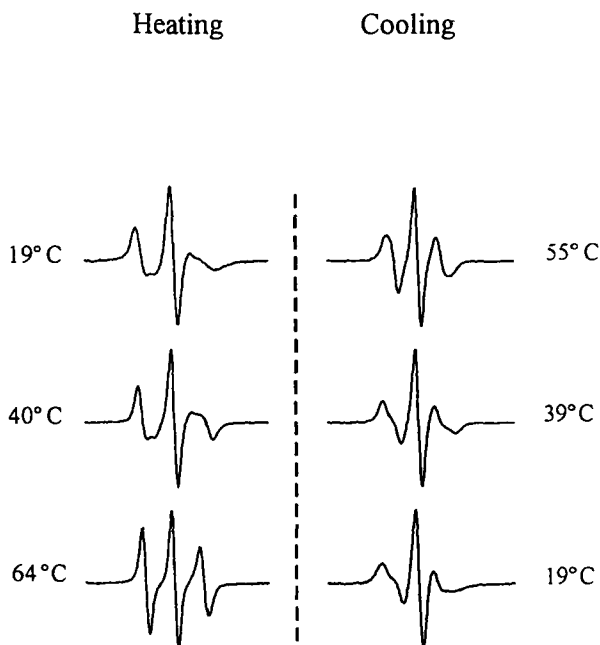


FIGURE 2 EPR spectra from COL dissolved in E7/Master Bond UV10 (9:1) versus temperature. The sample is initially disordered. It is then heated to the isotropic phase and then cooled back to room temperature. The heating and cooling spectra are clearly different illustrating the sample hysteresis. Full width = 100 Gauss.

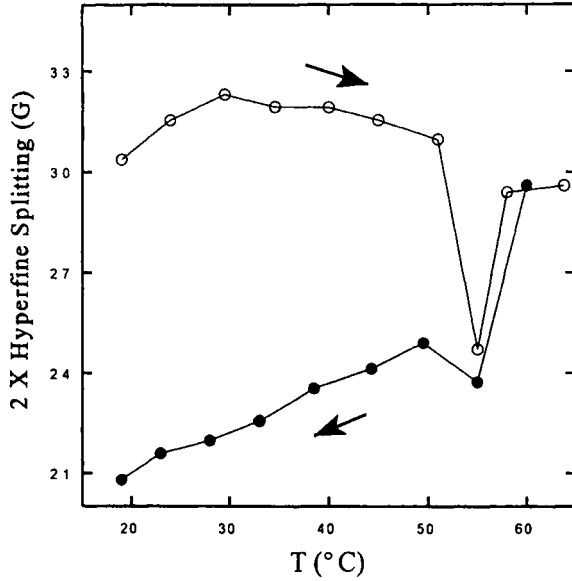


FIGURE 3 Spectral splittings versus temperature taken from the data of Figure 2. The heating curve spectral splitting (open circles) data are characteristic of a poorly aligned sample and the cooling spectral splitting (closed circles) data are characteristic of an aligned sample.

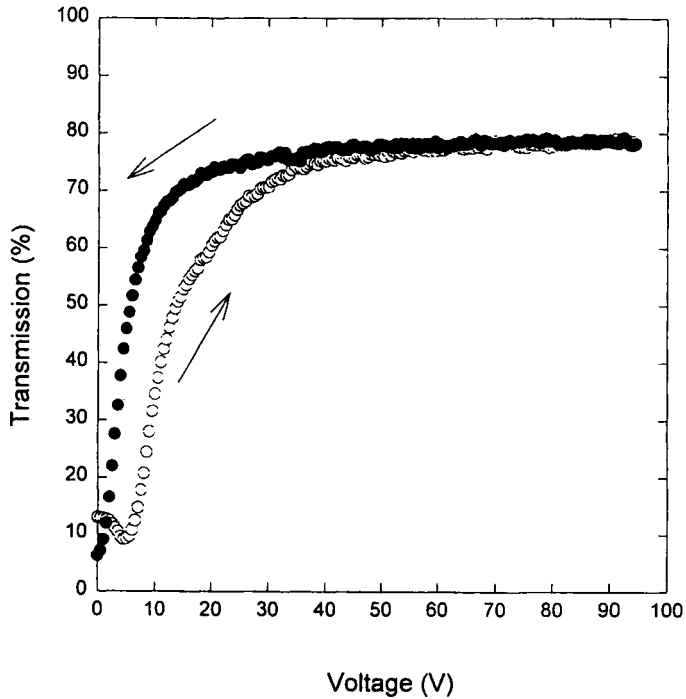


FIGURE 4 Light transmission versus applied voltage for increasing (open circles) and decreasing (closed circles) voltage. These electro-optical data also illustrate hysteresis, the larger electric fields order the sample.

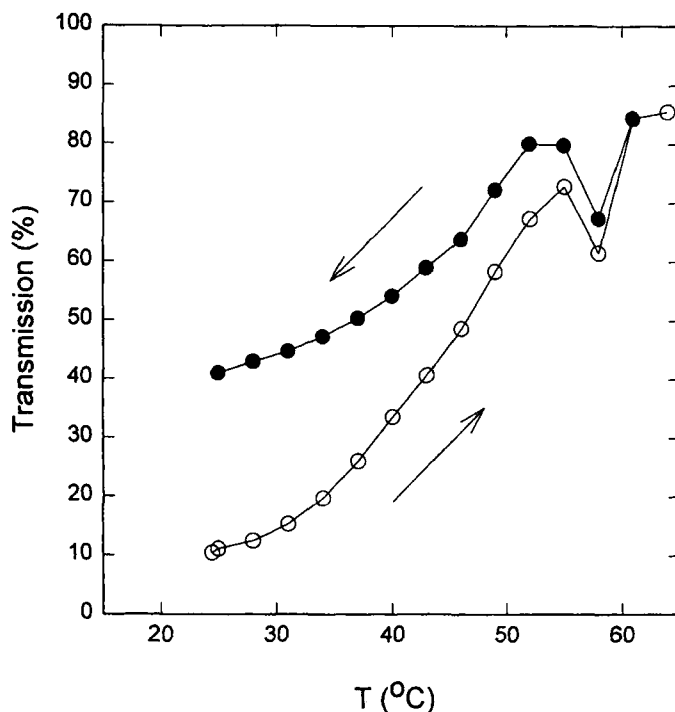


FIGURE 5 Light transmission versus temperature for a sample with a constant applied 5.5 v. signal. The heating curve (open circles) and the cooling curve (closed circles) are clearly different; both represent stable states.

cooling data show a higher transmission than the heating data since the sample is aligned by the field. These data are illustrated in Figure 5 where the hysteresis is again clearly seen. Both the aligned and the poorly aligned states are stable in agreement with the EPR data.

#### 4. DISCUSSION

We have demonstrated the existence of two stable states and the ability to switch between them. This suggests the possibility of constructing a display. The hysteresis experiments were performed using samples cured in the isotropic (90 °C) and nematic (25 °C) phases and we have observed very little difference. However, samples cured for 60 minutes show a greater difference in the poorly aligned to aligned EPR spectral splitting than do samples cured for 10 minutes. The existence of the UV10 impurity somewhat mitigates the hysteresis. We have demonstrated the existence of two stable states, one with random alignment of the director throughout the sample, and one with a uniformly aligned director. The difference between the two stable states lies in the



orientation of the liquid crystal director at the polymer interface. The EPR samples are bulk samples making it difficult to determine their optical properties; however, the aligned samples look lighter to the eye than poorly aligned samples. Corresponding electro-optical studies confirm these results.

The surface anchoring of the liquid crystal at room temperature is quite strong and an elevated temperature is required before the magnetic field of the spectrometer (.34 T) can align the liquid crystal. The anchoring is quite small<sup>5</sup> near the clearing point so it is no surprise that the anchoring can be overcome by the magnetic field at elevated temperature near  $T_{NI}$ . Conversely, for a liquid crystal, electrical interactions are typically stronger than magnetic interactions, so that elevated temperatures are not necessary to switch polymer stabilised displays.<sup>7-10</sup>

### Acknowledgement

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