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A method for the formation of polymer walls in liquid crystal/polymer mixtures

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We have investigated the formation of polymer walls for high polymer content liquid crystal (LC) formulations, using a patterned electric field to induce phase separation. The effect of this field on the phase separation temperature of a LC/monomer mixture is studied as a function of the photopolymerizable monomer concentration. The phase separation temperature increases with the patterned field strength. The application of a patterned field results in segregation of the LC molecules in the high electric field regions, i.e., pixels, whereas the monomers segregate in the low-field regions, i.e., interpixels. Subsequent photopolymerization results in the formation of polymer walls around the pixels. The structure of the polymer walls was investigated using scanning electron microscopy.

In recent years, cholesteric liquid crystal materials have been of great interest for reflective display applications. These materials have been utilized to prepare displays which have two stable states at zero field: a selectively reflective planar state and a weakly scattering focal conic state.1–3 The first bistable, polymer stabilized cholesteric texture (PSCT) devices involved a low concentration of photocurable monomers dispersed in the cholesteric liquid crystal mixture. Relatively high polymer content formulations have also been used to produce bistable reflective PSCT displays.4–6 These formulations have some potential advantages over the low, or no, polymer content formulations. Since the polymer concentration is high enough to provide a self-adhering and self-sustaining structure, flexible devices of large area can be fabricated. The Liquid Crystal Institute has successfully demonstrated a four-inch-square bistable reflective PSCT display with 320 by 320 pixels6 and a writing tablet, fabricated from high polymer content formulations using plastic substrates. However, the high polymer content formulations produce dense polymer networks that result in significant light scattering in the focal conic state. Light scattering reduces the color purity and brightness of reflected light in the planar state, and consequently, the contrast of a display.

In order to improve the brightness and contrast while maintaining the structural benefits of polymer networks, polymer walls have been formed in high polymer content PSCT displays.7 The formulations were composed of ultraviolet (UV) curable monomers and chiral nematic liquid crystals. The formation of polymer walls was achieved by irradiating selective areas of a cell with UV light through a photomask to induce phase separation by photopolymerization.8 This method was also used by researchers from Sharp in the formation of polymer walls for the fabrications of axially symmetric aligned microcells (ASM)9 and polymer matrix supertwisted nematic liquid crystal displays (PM-STN-LCDs).10 The polymer walls in the interpixel regions not only improve the electro-optic characteristics of PSCT displays, but also provide excellent pressure resistance preventing distortion of a display image.7,10

In this letter, we present a method for creation of patterned polymer walls in high polymer content formulations. We found that application of a patterned electric field during phase separation and subsequent blanket UV-irradiation results in formation of polymer walls in the interpixel regions of a cell. The effect of a patterned electric field on the phase separation temperature of a mixture formulation is investigated with different concentrations of an UV-curable monomer, using cross-polarized optical microscopy. Scanning electron microscopy (SEM) is employed to investigate the polymer wall structure.

A chiral nematic mixture (CNM) composed of CB15/CE2/E48 in a 21:21:58 weight ratio was used for the liquid crystal (LC) formulation. The CB15 and CE2 are single chiral components and E48 is a nematic liquid crystal. Various amounts (10–30% w/w) of Norland optical adhesive 65 (NOA65) as a photopolymerizable monomer were used to prepare mixture formulations with CNM. The substrates were glass plates coated with indium tin oxide (ITO) etched to form a line pattern. The widths of ITO lines and spacing between lines were approximately 300 and 25 μm, respectively. Two substrates were sandwiched to form a cell with a cross pattern of ITO electrode lines. The gap was controlled using 4.5 μm plastic sphere spacers. The cells were capillary filled at 100 °C where the CNM/NOA65 mixture formulation was in the isotropic state.

After filling, the cells were cooled down to room temperature at a rate of 0.5 °C/min to induce phase separation with and without an applied patterned electric field (ac). The phase separation temperature was observed and recorded during the cooling using a cross-polarized optical microscope in transmission mode. Upon cooling to room temperature the whole area of the resulting cell was exposed to UV light to fix the phase-separated morphology by curing the NOA65 monomers. The UV exposure was performed for 20 min using an Electro-Lite ELC 4000 unit of 25 mW/cm² intensity at 365 nm wavelength.

The phase separation temperatures, $T_{sep}$, of the CNM/monomer mixtures were investigated as a function of the...
patterned electric field strength. In these mixtures the phase separation generally occurs from an isotropic, homogeneous state to a heterogeneous state of the CNM rich phase and the monomer rich phase upon cooling. In the absence of the field, addition of the monomer to CNM resulted in a reduction of the $T_{sep}$ of the mixture. In particular, an increase in the monomer concentration from 10 to 30% (w/w) resulted in a decrease in $T_{sep}$ from 45 to 27 °C. The effect of the patterned field strength on $T_{sep}$ was shown in Fig. 1, as well as the transition temperature of the pure CNM from isotropic to anisotropic LC phase. The pure CNM had a transition temperature of 70 °C, independent of the applied field magnitude. However, fields as low as 1–2 V/μm were sufficient to change $T_{sep}$ of the CNM/monomer mixtures. An increase in the electric field strength resulted in an increase in the $T_{sep}$ of all mixtures. At field strengths above 6–7 V/μm, which is enough to homeotropically align the CNM, a gradual increase in $T_{sep}$ approaching the transition temperature of the pure CNM was observed.

Figure 2 shows transmission optical micrographs of the cells made from the mixture formulations with different concentrations of the monomer. Figures 2(a) and 2(b) show the structures obtained from a mixture containing 10% (w/w) monomer. The cells were cooled from 100 °C to room temperature and subsequently UV cured with no field and a field of 17.8 V/μm, respectively. Figure 2(a) shows that the structure obtained in the absence of a field consists of an interpenetrating polymer network in a continuous LC phase. The formation of this structure is attributed to temperature-induced phase separation. Application of a patterned field

![Figure 1](image1.png)

**FIG. 1.** Effect of a patterned electric field on (a) a transition temperature of the pure CNM from isotropic to anisotropic state and, on phase separation temperatures of (b) CNM/NOA65 (90/10), (c) CNM/NOA65 (80/20), and (d) CNM/NOA65 (70/30) mixture formulations.

![Figure 2](image2.png)

**FIG. 2.** Transmission optical micrographs of the cells made from (a) CNM/NOA65 (90/10) with no field, (b) CNM/NOA65 (90/10) with 17.8 V/μm, (c) CNM/NOA65 (80/20) with 17.8 V/μm, and (d) CNM/NOA65 (70/30) with 17.8 V/μm.
resulted in a significant change in the phase-separated morphology [Fig. 2(b)]. The CNM molecules segregated into the high-field regions to form electro-optically responding pixels. The monomers segregated into the low-field regions and formed polymer walls in the interpixel regions after photopolymerization. As a result, the pixels were rich in CNM molecules with droplet-like domains of polymers and the interpixels were rich in polymers with some embedded CNM molecules. Increasing the concentration of monomer, as shown in Figs. 2(c) and 2(d), resulted in expansion of the polymer domains into the pixel regions.

The above results demonstrate that the applied patterned field enhances phase separation of the CNM molecules and the monomers. This phase separation reduces the concentration of monomer in the CNM rich pixel regions. These domains, therefore, exhibit a phase transition temperature closer to that of the pure CNM.

The structure of the resulting polymer walls was investigated using scanning electron microscopy (SEM). To prepare samples for SEM, the UV-cured cells were immersed in hexane for a day and disassembled. The substrates were then rinsed with hexane to remove the liquid crystal. They were then dried and glued to aluminum SEM stubs using 5 min epoxy. The resulting stubs were placed in a vacuum oven for 1 h at 100 °C and then coated with Ag/Pt in a Hummer VI-A sputtering system. Figures 3(a) and 3(b) show SEM images of polymer networks derived from a mixture containing 10% (w/w) monomer with no applied field and a field of 17.8 V/μm, respectively. The results are consistent with the observations made from optical microscopy. The “honeycomb-type” polymer walls were predominantly formed in the interpixel regions. The walls have an approximate width of 25 μm and a height of 4.5 μm, consistent with the electrode line spacing and cell gap. The small voids in the walls were considered to contain CNM molecules that were dissolved in hexane during sample preparation. Increasing the concentration of the monomer, as shown in Figs. 3(c) and 3(d), resulted in an increase in the relative proportion of the polymer network in both the walls and pixel regions.

The results suggest that the separation of the liquid crystal and monomer results from Kelvin type force of the form:

\[
F = P \cdot \nabla E
\]

where \( P \) is the polarizability of the material and \( E \) is the field strength. Since the CNM has a larger dielectric constant than the monomers, it experiences a greater force from the fringing fields in the interpixel regions. The liquid crystal molecules, therefore, are forced to the high-field regions of the pixel area. The monomers are then left in the interpixel regions with low-field strengths. This suggests that the strength and gradient of the field determine the degree of separation between the liquid crystal and the monomer.

Furthermore, preliminary results with different ITO patterns, and thus fringing field strengths, have shown that a larger gradient in the field induces a greater separation between the LC and the monomers. We have also demonstrated formation of polymer walls using nematic mixtures and patterned electric fields. This indicates that this procedure may be used to produce polymer walls in conventional liquid crystal devices such as twisted nematic (TN) and super-twisted nematic (STN) displays.

In conclusion, we presented a method for formation of polymer walls using high polymer content LC formulations and a patterned electric field. Application of a patterned electric field during cooling induces phase separation of LC molecules and photopolymerizable monomers, with the LC molecules in the pixel regions and the monomers in the interpixel regions. Subsequent blanket UV irradiation resulted in polymerization of monomers to form polymer walls around the pixels. Currently, the mechanism and optimization of this polymer wall formation are being investigated.

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