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Study of the purifying affects of thermal annealing for polymer-wall liquid crystal cells

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The thermal annealing process was proposed to purify the pixel regions of a liquid crystal (LC) cell with polymer walls. This technique, based on thermal-induced phase separation, successfully evicts the residual monomers from the LC volume and significantly improves electro-optical properties of the polymer-wall LC devices. The influence of the annealing process on the purity of LC-rich domain and the electro-optic properties of a LC cell was explored with a series of experiments. According to the experimental results, the annealing technique is extremely prospective for constructing flexible polymer-wall LC display applications.

Keywords: polymer wall; phase separation; annealing; phase retardation

1. Introduction

In recent years, flexible liquid crystal devices (LCDs) using plastic substrates have been attracting great attention for applications, since they offer the advantages of lighter weight, thinner packaging, more flexibility, and lower manufacturing cost through roll-to-roll processing (*1–6*). However, the plastic substrates do not give firm mechanical support for the molecular alignment of liquid crystals (LCs) between them. To overcome these problems, several types of polymer walls and/or networks as supporting structures have been applied to enhance the optical and mechanical properties of LCDs. The polymer walls adhere to the surfaces of the two flexible substrates, supplying exceptional mechanical stability and keeping the cell gap constant even when the LCD is bent or curved. Such devices with polymer walls not only preserve the structural merits, but also avoid unwanted light scattering since the pixel regions contain relatively pure LCs. Therefore, the polymer walls in a LC layer are considered for the fabrication of flexible LCDs on flexible plastic substrates.

These micro-polymer walls contained in the LC cell are prepared by an anisotropic phase separation method, which applies a high patterned electric field to a mixture of LC and monomer during phase separation (*7*) or spatially modulated ultraviolet (UV) light intensity using a photomask (*8–10*). Photopolymerisation in the inter-pixel region induces phase separation of the polymer into these inter-pixel regions, and the polymer-wall structures are then formed. Nevertheless, complete segregation of the UV-curable material is still difficult to achieve, and therefore a second exposure of the UV material is critically required to eliminate the remaining monomers. Consequently, the fabricated polymer-wall LCD cannot avoid a considerable amount of light leakage through the wall boundary in the dark state. In addition, there are often some residual polymers in the pixel region, which always reduce the optical properties and increase the operating voltage of the device (*9, 10*). Due to polymer networks forming LC domains and probably misaligning the LC molecules, the exclusion of these networks within the pixel region becomes more vital. Moreover, the residual unpolymerised monomers in the pure LC-rich region may be considered as external impurities and can seriously degrade the electro-optical properties of the LCD. To enhance the LCD performance, a critical technique is appreciably required to obtain more complete separation of LC and polymer to improve the wall structure and increase the purity of the LC-rich region without sacrificing LC alignment.

Since the UV light curing conditions are not precisely controlled, some uncured monomers in the LC-rich region will always reside in the pixel region during the manufacturing process. These residual pre-polymers will inhibit the LC molecules realigned under the external electric field and then degrade the electro-optic properties of the LC cell. Under these considerations, a highly efficient technique to drive monomers out of the pixel region is a vital requisite. In this study, an annealing process was proposed to significantly squeeze the residual monomers out of the LC pixel regions and subsequently improve the

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electro-optic characteristics of the LC cell. This proposed purification technology is mainly based on the principle of temperature-induced phase separation (TIPS). According to the temperature difference, the phase separation of the LC and UV-cured monomer is induced. While the temperature is carefully controlled, greater coalescence of LC droplets can be obtained gradually so as to expel the remaining monomers progressively from the LC domains. Based on the experimental results of electro-optic measurements, the characteristics of a LC cell are found to be considerably improved by the annealing treatment in this work. These improvements were achieved due to the polymer layers that resided in the LC-pixel region and significantly increased the anchoring force at the polymer wall, were appreciably diminished by the proposed annealing process.

2. Sample preparation

The patterned polymer walls in the inter-pixel regions of a LC cell are commonly made by irradiating selective areas of a cell with UV light through a photomask to induce phase separation by photo-polymerisation (*8–10*), as shown in Figure 1. To fabricate the polymer walls within the cell gap between the electrodes of the LC cell, a mixed solution of the photo-curable monomers (Norland Optical Adhesive NOA65) and nematic LC (E7, Merck) was prepared previously with a weight ratio of 1:9. Then, the mixed pre-polymer/LC solution was injected into the empty cell with capillary action. To avoid the non-uniform injection caused by the viscosity difference between LC molecules and the monomer, the sample was heated at a temperature above the LC's clearing point during the mixture injection. Subsequently, the polymer wall was formed with UV light exposure by cross-linking the polymers through a photomask. At this moment, the monomer concentration was reducing with the UV-induced polymerisation, and the polymer then aggregated in the unmasked areas and was separated from the nematic LC. As a result, molecular-aligned polymer walls in the interpixel regions were formed, and the LC was squeezed out of the irradiated regions (i.e. segregated into the unexposed regions) to form electro-optically responding pixels.

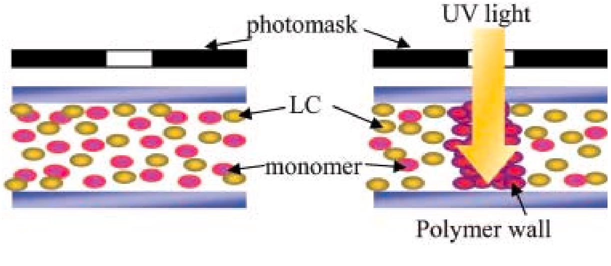


Figure 1. Formation of the polymer-wall structure by the photo-polymerisation-induced phase separation of the LC/monomer.

However, complete segregation of the UV-curable monomer is difficult to achieve, and removal of the remaining UV-curable material is critically required with the second exposure of UV light (*9–11*). Although a second exposure could address the residual monomer, it would solidify the residual monomer with a polymer network in the LC domain. The dispersed polymer networks anchor the LC molecules, spatially change the threshold voltage, and scatter light. Therefore, the fabricated polymer-wall LCD could not stop a considerable amount of light leakage through the wall boundary in the dark state, and some polymers residing in the unexposed region always reduce the optical properties and increase the operating voltage of a LCD (*9*). To overcome this significant problem, a technique to expel the remained monomers from the pixel regions is a vital requisite for developing the flexible LCDs.

In this work, a thermal annealing process based on the principle of TIPS is proposed to significantly squeeze the residual monomers out of the LC pixel regions and improve the purity of the LC-rich regions, as demonstrated in Figure 2. Due to some residual monomers residing in the pixel region (shown in Figure 2(a)) after formation of the polymer walls, an annealing process is sequentially executed. LC samples are heated beyond the clear point to become isotropic at first and then slowly cooled at a controlled rate of 0.2°C/min to room temperature. When the temperature is cooled from the clear point of the LC/monomer mixture, phase separation into LC-rich domains occurs, which causes the LC to phase separate into droplets as shown in Figure 2(c). At this time, the LC domains initiate nucleation and start to grow. Gradually, larger and more coalescing LC droplets appear with decreasing temperature, as shown in Figures 2(d)–(g). As a result, the remaining monomers are progressively driven towards the boundaries between the polymer walls and pixel regions, and high-purity LC domains can be successfully achieved.

In general, the nucleation and growth of LC droplets in the solution decreases the bulk of the free energy of these droplets and the solution, but the free energy of the surface of the growing LC droplets increases. The phase separation of the LC and pre-polymer molecules progresses with the competition between the free energy of the bulk and the surface. Hence, the growing LC droplets coalesce together to

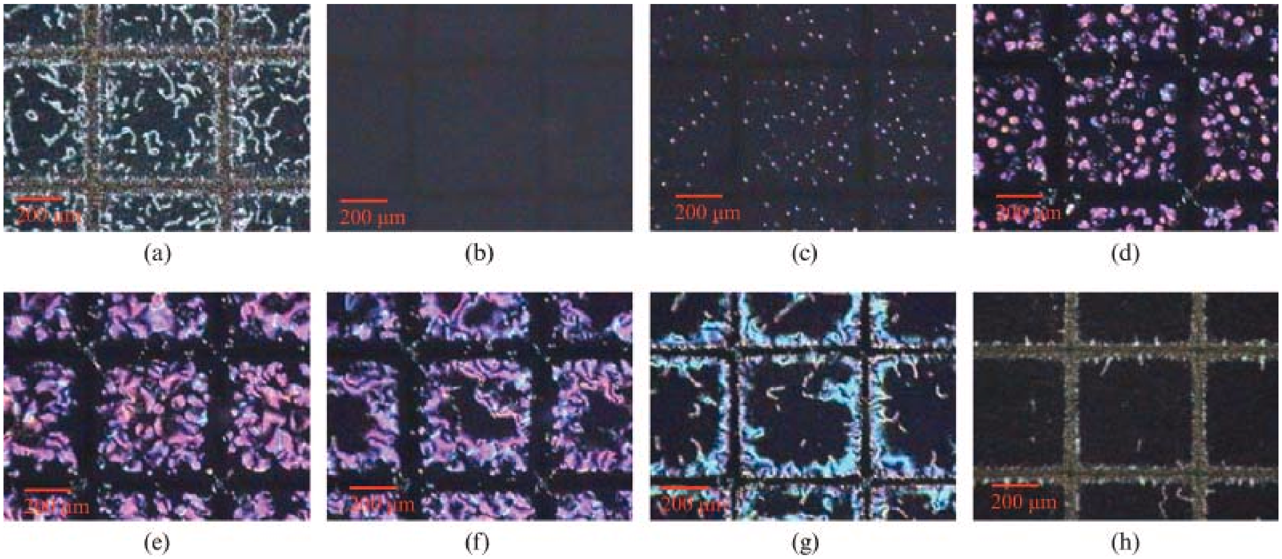
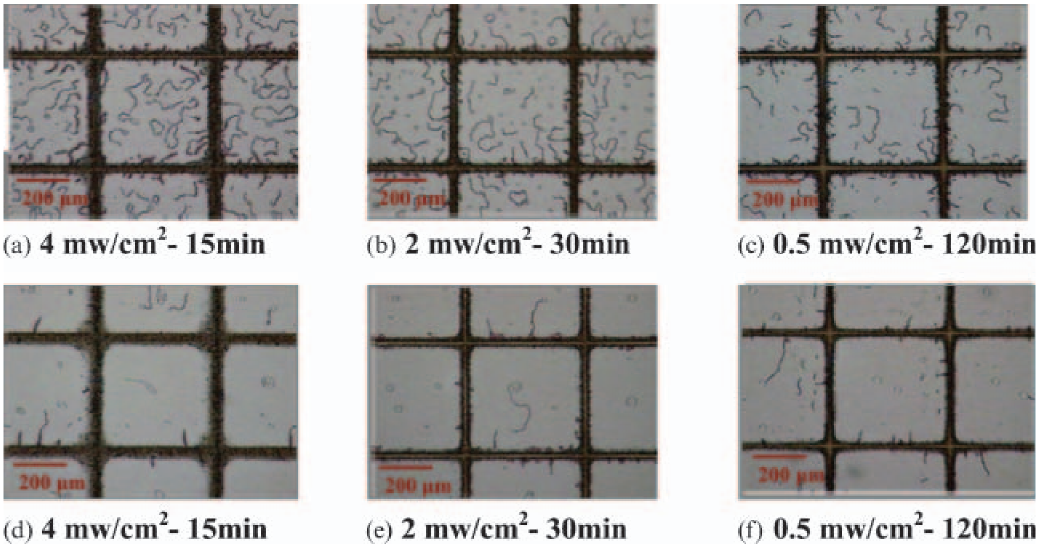


Figure 2. The process of the annealing treatment to purify the polymer-wall LC cell, based on the thermal-induced phase separation, successfully evicts the residual monomers from the LC volume. The phase change of the LC/monomer solution thermally induced during the annealing process was observed. (a) Initial LC sample. (b) LC sample at isotropic state. (c)–(g) Cooling the sample from the clear point, LC droplets nucleated in the solution and the growing LC droplets coalesced to expel the residual monomers from the LC domain. (h) Purified sample.

decrease the surface free energy of the LC droplets and gradually impel the residual monomers towards the boundaries between the polymer walls and pixel regions. After complete phase separation of the LC and monomers was achieved, a second exposure of the UV light was applied to solidify the remaining UV-curable material near the polymer-wall boundaries. Therefore, high pureness of the LC domains can be successfully realised.

3. Results and discussion

The transmission optical micrographs of the homogeneous LC cells with polymer walls were observed for different UV light intensity, as shown in Figure 3. The results indicate that the polymer walls have been successfully formed and confined to a narrow strip in the centre of the inter-pixel regions, while the LCs tended to remain in the pixel regions of the cell. However, some residual monomers, which will



(a) **4 mw/cm^2- 15min** (b) **2 mw/cm^2- 30min** (c) **0.5 mw/cm^2- 120min**

(d) **4 mw/cm^2- 15min** (e) **2 mw/cm^2- 30min** (f) **0.5 mw/cm^2- 120min**

Figure 3. Polarising microscope photographs of the phase separation structure formed at various exposure conditions. (a)–(c) Before annealing. (d)–(f) After annealing.

significantly influence the electro-optic behaviour of the polymer-wall LCDs, were evidently found in the pixel region, as shown in Figures 3(a)–(c). To ameliorate the electro-optic performance of a LCD, the thermal annealing process was applied in this work. By means of cooling the heated LC/prepolymer solution, the phase separation of the LC/prepolymer progressed with the coalescence of growing LC droplets. Moreover, the monomers were gradually squeezed out of the LC-rich regions and towards the boundaries of the polymer walls, so that the purity of the LC pixel region can be notably improved, as shown in Figures 3(d)–(f).

The influence of the annealing treatment on the electro-optic behaviour of LC cells was evaluated by the voltage-dependent phase retardation measurement (*12*). Figure 4 shows that the impact of the annealing treatment on the voltage-dependent phase changes the characteristics of LC cells exposed by UV light exposure at an intensity of $4\,\mathrm{mW\,cm^{-2}}$ for 20 min. According to the $\Delta P(V)$ $(=P(0)-P(V))$ curves of the cells, the electro-optic characteristics of the polymer-wall LC cells were all similar to those previously observed in the pure LC cell without polymer structure (*12*). Based on the experimental results of Figure 4, the maximum voltage-induced phase difference ΔP of the LC cell without annealing treatment was found to be less than that of an annealed LC cell. This is because some residual monomers resided in the pixel regions, which anchored LC molecules, and therefore the LC molecules cannot be reoriented so as to be completely parallel to the electric field.

Table 1 also provides a summary of the voltage-independent response time of LC cells exposed to UV light at an intensity of $4\,\mathrm{mW\,cm^{-2}}$ and an exposure time of 20 min. According to the experimental results demonstrated in Table 1, we found that the annealing treatment can significantly lessen the rise and fall times of a LC cell, especially for a lower driving voltage. As a result of fewer polymer networks remaining in the pixel region and a decreasing anchoring force at the polymer wall by virtue of the annealing process, a slight abatement of response time can be achieved. Therefore, the thermal annealing treatment plays a critical role in the optimisation of the polymer-wall formation in future development of flexible displays.

Table 1. Comparisons of the voltage-dependent response time of LC cells with/without the annealing treatment.

Voltage (V)	**2**	**4**	**6**	**7**
T_r (ms) (non-annealing)	**70**	**12**	**5**	**3**
T_r (ms) (annealing)	61	11	4	3
T_f (ms) (non-annealing)	**84**	**88**	**91**	**92**
T_f (annealing)	76	80	81	83

In addition, the impact of the annealing process on the voltage-dependent transmission of LC cells was also probed, as demonstrated in Figure 5. At $V=0$, we found that the light transmission of the LC cell without the annealing treatment is less than that of the annealed cell. Due to residual polymer networks remaining in the pixel regions of the un-annealed cell, the LC directors inside the domains are bound by the polymer network, and some LC domains are randomly oriented so that a weak scattering of light is present in the voltage-off state. Based on the experimental results, the residual monomers are found to be effectively diminished by the proposed process; the light transmission of a LC cell increases and the light leakage in the dark state is

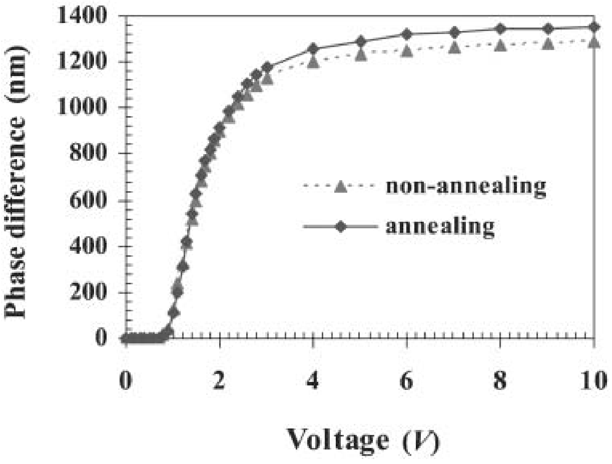


Figure 4. The influence of the annealing process on the voltage-dependence phase retardation difference of LC cells exposed to UV light with an intensity of $4\,\mathrm{mW\,cm^{-2}}$ for 20 min.

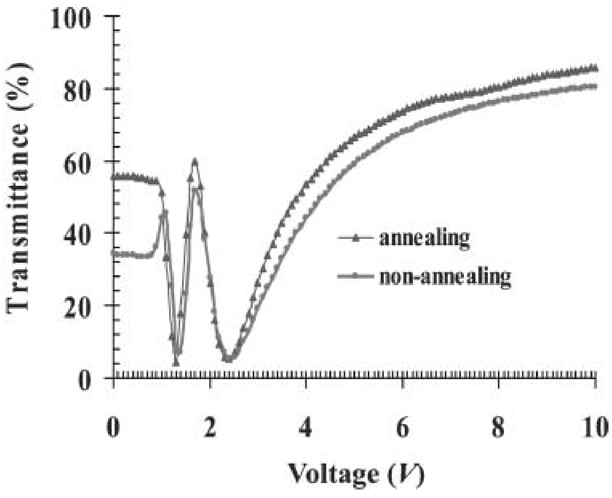


Figure 5. The voltage-dependent transmission characteristics of LC cells formed with/without annealing treatments.

also appreciably diminished. Therefore, the contrast ratio of a LC cell is significantly improved by the thermal annealing. As a result, we claim that the proposed annealing process can successfully purify the LC domains, and afterwards the electro-optic behaviour of a LC cell can be effectively improved.

4. Conclusion

We have experimentally demonstrated that an annealing technique based on thermal-induced phase separation successfully depurates the LC-rich regions and appreciably overcomes the problem of residual monomers inherently residing in the pixel region. The process can prevent any incomplete optical phase retardation and the slower response time of the LC cell caused by the dispersed polymer network in the LC domain. The proposed annealing technique facilitates the purity of the LC cell-containing polymer-wall structure and will be especially useful for the development of plastic LCDs in the future.

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