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Characterisation of polymer wall formation in nematic liquid crystal devices

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A phase-sensitive measurement technique is proposed to characterise polymer wall formation in a nematic liquid crystal cell. The impact of photopolymerisable monomer concentration and curing time on the electro-optical properties of polymer-wall LC cells was studied. The experimental results indicate that optimum curing conditions for constructing the polymer wall in an LC cell can be easily achieved by means of the proposed method. The structure of the polymer walls was also investigated using scanning electron microscopy and a polarising optical microscope.

Keywords: polymer wall; liquid-crystal phase separation; phase-sensitive measurement

1. Introduction

Recently, flexible liquid crystal devices (LCDs) using plastic substrates have attracted considerable attention because they offer the advantages of lighter weight, thinner packaging, more flexibility and, through continuous roll-to-roll processing, lower manufacturing cost than other similar available devices (*1, 2*). However, the plastic substrates do not give a firm mechanical support for the molecular alignment of LCs between them. To overcome these problems, several types of polymer walls and/or networks as supporting structures have been proposed and applied to enhance the optical and mechanical properties of LCDs. Polymer walls are particularly useful in plastic substrates for improving the mechanical properties of a wide variety of displays by providing a pressure-resistant, self-adhering and self-sustaining film.

More recently, attention has been focused on designing and making the polymer confined to "walls" surrounding the pixels (*2–7*) of the LCDs. To fabricate these micropolymer walls, an anisotropic phase separation method, using a mixture of LC and monomer by means of applying a highly patterned electric field to a solution during phase separation (*7*), or a spatially modulated UV intensity using a photomask (*2–6*) is applied. The patterned electric field method requires rather high fields of 10–15 $\mathrm{V\,\mu m^{-1}}$ during wall formation. Such fields may be unsuitable for displays with active matrix addressing. The second method, which applies the photopolymerisation of UV-curable materials contained in a LC cell with a photomask to block UV light from the pixel regions of the cell, is very simple. However, complete segregation of the UV curable material is still hard to achieve, and it requires removing the residual UV-curable material with the second UV exposure. Thus, the fabricated polymer-wall LC device could not avoid a considerable amount of leakage light through the wall boundary in the dark state, and some residual polymers in the LC pixel region always reduce optical properties and increase operating voltage of the device (*2*). To optimise display performance, effective and accurate ways to examine the photopolymerisation degree and eliminate polymer networks within the pixel region become more vital.

Scanning electron microscopy (SEM) and polarising optical microscopy (POM) are commonly employed to investigate the formation of the polymer wall structure. However, these methods cannot precisely determine whether the photopolymerisation process of the UV-curable monomers is complete. To prepare the sample for SEM, which is an indirect, destructive and complex measurement, requires disassembling the LC cell. Thus, a simple, novel and accurate technique to determine the optimum curing conditions for fabricating the polymer walls in LC cells is of critical importance. In this study, a phase-sensitive optical heterodyne technique (*8*) is proposed to evaluate whether some residual monomers exist in an unexposed region. The proposed technique combines both the common-path optical heterodyne interferometer and the differential phase detection scheme. Owing to the designed common-path configuration, the phase retardation of the LC cell can be accurately measured in terms of the phase difference of the optical heterodyne signal. This method, free from background noise and with higher stability and accuracy of measurement than conventional

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measurement techniques (*5–8*), can be successfully achieved with relatively straightforward and non-destructive measurement procedures.

Because the dispersed polymer networks reside in the pixel region, they anchor the LC molecules and significantly influence their orientation (*2*). The measurement of the voltage-dependent phase difference was very helpful in evaluating the effects of the remaining monomer or polymer network on the distribution of LC directors and further assessing the degree of photopolymerisation by the proposed technique. Based on the experimental results, the threshold voltage and the maximum voltage-dependent phase difference of the LC cell with polymer walls were found to be appreciably influenced by the UV curing conditions and the mixture ratio, and slightly different from the pure LC cell.

2. Background theory

Formation of polymer wall cells

Polymer walls in the inter-pixel regions of a LC cell are achieved by irradiating selective areas of a cell with UV light through a photomask to induce phase separation by photopolymerisation, as shown in Figure 1 a. First, an LC cell is filled with LC and UV curable monomer, and then UV light is exposed through a photomask. The monomer molecules that flow into the irradiated areas by thermal diffusion or thermal convection are photopolymerised by the UV light, as shown in Figure 1 b. Polymer aggregates in the unmasked areas and is separated from LC, because it does not dissolve in the solution. Thus, polymer walls in the inter-pixel regions are formed, and LC molecules are squeezed out of the irradiated regions to form electro-optically responding pixels.

During the manufacturing process, when the UV curing conditions are not precisely controlled, some uncured monomers in the LC-rich region will reside in the pixel region. These residual pre-polymers slightly inhibit the LC molecules realigned under an external electric field and then degrade the electro-optical properties of the LC cell. The more residual monomers remain in the pixel regions the greater the deviation in the electro-optical behaviour of the LC cell from one with no polymer walls (i.e. pure LC cell). To optimise the performance of the polymer-wall cell, a method to accurately and simply explore the degree of photopolymerisation and the purity of the pixel region in situ is vitally significant.

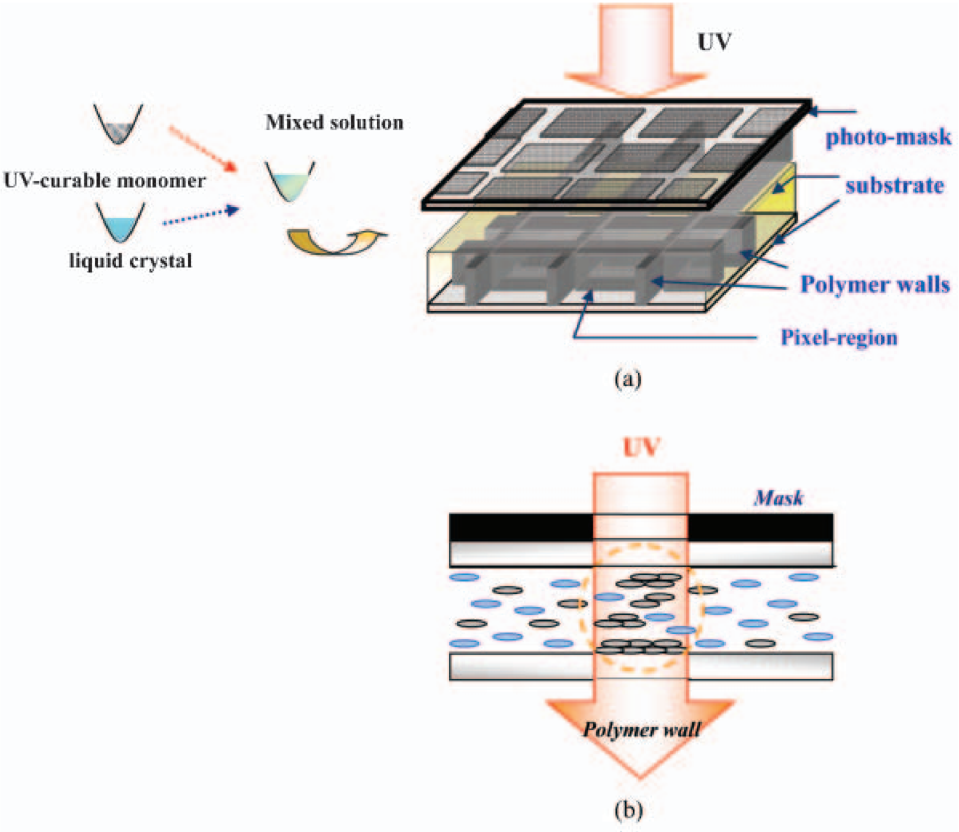


Figure 1. Fabrication method of polymer walls using a photomask. Photopolymerization in the inter-pixel region induces phase separation of polymer into these inter-pixel regions.

Voltage-dependent phase retardation of LC cell

Since LC molecules act as a uniaxial medium and exhibit a birefringence effect, the two orthogonal linearly polarised light waves through the LC medium propagate at different speeds. Consequently, a phase difference between these two orthogonal waves occurs after travelling through the LC material. As the applied voltage is smaller than the threshold voltage, the LC molecules are undisturbed and are all aligned almost parallel to the surface of the ITO glass substrate, so that the maximum phase retardation, $R_{\max} = \left(n_e^{eff} - n_o\right)d$, of the homogeneously-aligned NLC cell is reached. Here, $n_e^{eff} = \frac{n_e n_o}{\sqrt{n_e^2 \sin^2 \varphi_{\mathrm{p}} + n_e^2 \cos^2 \varphi_{\mathrm{p}}}}$ and φ_{p} is the pretilt angle. When the external voltage is beyond a critical value, the LC directors begin to realign in the direction of the electric field so that the phase retardation of the orthogonally polarised waves is gradually reduced with increasing voltage and finally reaches a steady state.

Since the remaining monomer or polymer network in the pixel region slightly inhibits the orientation of the LC molecules reoriented under the external electric field, it considerably influences the electro-optical characteristics of a cell. More residual monomers residing in the pixel region will impede the LC molecules much more, tilted in the electric field direction and diminish the phase difference. As a result, by comparing the measured voltage-dependent phase differences, the polymer wall formation and the purity of a cell can be simply and accurately determined in real time.

3. Experimental

To fabricate the polymer wall within the parallel-aligned LC cell, a mixed solution of LC and UV-curable monomers was prepared in advance. Two amounts (10 and 20% w/w) of monomers (NOA65; Norland Products, Inc.) were used to prepare mixture formulations with NLC RDP94289 (DIC Inc.). The birefringence of the RDP94289 material was n_e=1.621 and n_o=1.495 at wavelength λ=589 nm. The cell gap was controlled with a 9.3 µm spacer and the cells were capillary filled with the RDP94289/NOA65 mixture formulation. After filling, a photomask with a linewidth of 25 µm and a 500 µm interval pattern was placed on top of the glass substrates, and the whole area of a cell was exposed to UV light. In the present experiment, the UV exposure intensity was fixed at 4 mW cm^{-2} with a wavelength of 365 nm.

To explore the microstructure of the resulting polymer walls and the LC alignment of the resulting cells, POM and SEM measurements were applied, respectively. The UV-cured cells for SEM were disassembled and immersed in hexane for one day. The substrates were then rinsed with hexane to remove the LC. In addition, the voltage-dependent phase retardation of an LC cell was probed with the proposed technique, as shown in Figure 2, in which light is transmitted at normal incidence to the cell. To obtain the influence of UV-curing conditions on the electro-optical properties of the LC cell, the relationship between the applied voltage and phase retardation had to be obtained first. A square wave from 0 to 10 V with 1 kHz was applied to the LC cell, and the voltage-dependent phase retardation, *R–V*, of the LC cell was established.

4. Results and discussion

Microscopic observations

The transmission optical micrographs of the homogeneous LC cells containing 10 wt % monomers were observed for different UV exposure times, as shown in Figure 3. The results indicate that polymer walls have been successfully formed. The polymer was confined to a narrow strip in the centre of the inter-pixel regions, whereas the LC tended to remain in the pixel regions of the cell. Good brightness of the pixels in the absence of the field showed good LC alignment, along with good segregation of LC and polymer. If the UV exposure time was insufficient, the polymer wall structure was not completely formed, as shown with the dashed circle in Figure 3 a. The sample with a longer curing time, on the contrary, exhibited a well-defined wall structure, which indicates that the polymer is

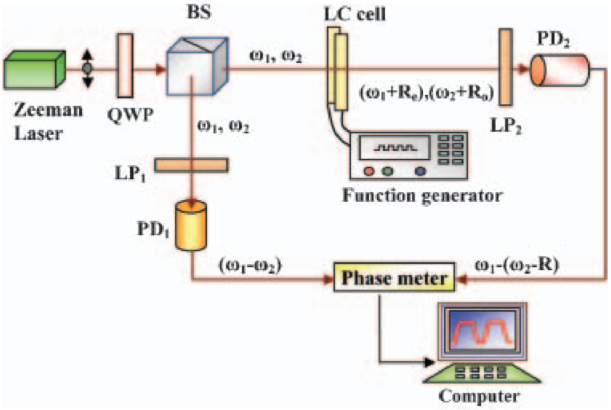


Figure 2. Experimental set-up for probing the phase retardation of a polymer wall LC cell as a function of applied voltage. Schematic diagram of the Zeeman dual-frequency laser interferometer system: BS – beam splitter; LP$_{1,2}$ – polarizer; PD$_{1,2}$ – photodiodes; QWP – quarter waveplate.

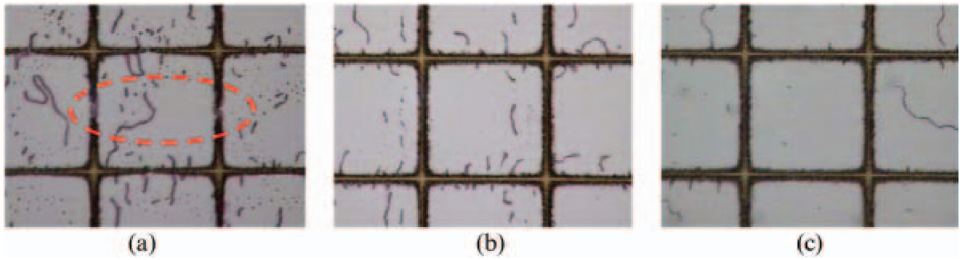
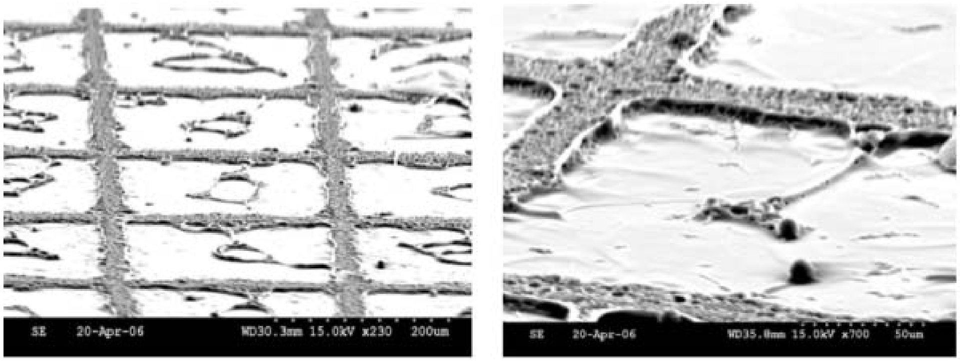


Figure 3. Polarizing micrographs of the parallel-aligned LC cells with polymer walls, containing 10% NOA65 and 90% LC (RDP94289) for different times of UV light irradiation through a photomask: (a) 40 min, (b) 60 min, (c) 120 min.

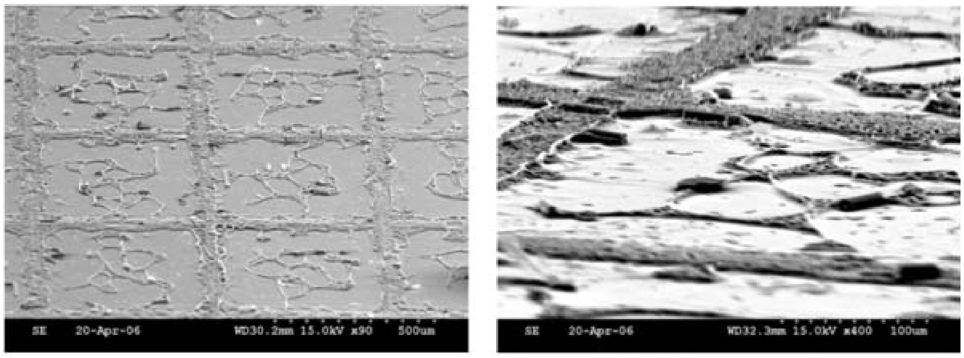
segregated in the wall region almost completely due to the phase separation. Figure 3 also shows a bit of mottling or grainy texture within the pixels, which was not present in the pure LC cell and is probably caused by the residual monomers.

Figures 4 a and 4 b show SEM images of the polymer derived from a mixture containing 10% and 20% monomers, respectively. According to microscopic observations of polymer wall structure, the "honeycomb" polymer walls were predominantly formed in the inter-pixel regions. The small voids in the walls were considered to apparently contain LC molecules that were dissolved in hexane during sample preparation. The experiments also showed that the fine polymer fibres spread out three-dimensionally, and increasing the monomer concentration resulted in an increase in the relative proportion of the polymer network in both the walls and pixel regions, as shown in Figure 4. The results are consistent with the observations made using optical microscopy.

The light transmitted through the cell under different applied voltages was also observed using POM, as shown in Figure 5. The darkness in the pixel



(a) 10 % NOA65



(b) 20 % NOA65

Figure 4. SEM images of polymer walls and polymer networks derived from a mixture containing (a) 10% and (b) 20% (w/w) NOA65 monomers.

regions in the ON state increased with increasing voltage. But comparing a pure LC cell without polymer, these darkness levels were only slightly diminished by the addition of polymer within the pixels. It appears that the polymer had a minimal effect on the LC alignment. Therefore, to obtain a complete wall structure without sacrificing LC alignment, a method becomes critically imperative during wall formation to directly probe whether complete separation of LC and polymer has been achieved. Unfortunately, SEM measurements cannot offer the advantages of rapidity and simplicity (absolutely no sample preparation), and is destructive for tested sample, so that it can not be directly and purely applied to probe polymer wall formation.

The electro-optic characteristics of LC cells

The microscopic observations (POM/SEM) cannot precisely evaluate whether complete phase separation of LC/monomer mixture is achieved to form the polymer walls. A phase-sensitive technique was applied to probe the electro-optical response of the polymer-wall LC cells influenced by the degree of photopolymerisation. The voltage-dependent phase change $\Delta R = |R(V) - R(0)|$ of the LC cells with and without polymer walls was obtained by measuring the phase difference of the two beat signals in the heterodyne interferometer system. Figure 6 shows the curing time dependence of the voltage-dependent phase characteristics of NLC cells with different monomer concentrations. The electro-optical characteristics of the LC cells for different exposure times were similar to those observed in the cell without polymer. If the curing time was not enough to complete the photopolymerisation reaction, the voltage-dependent phase change, ΔR curve, deviated significantly form that of the pure LC cell, e.g. for the 10% NOA65 cell with a 40 min exposure time. Based on the experimental results of Figure 6a, some residual monomers should remain in the pixel regions and further degrade the performance of the LC cell for less curing time. The electro-optical responses of tested cells with polymer walls were found to be closer to those of the pure LC cell with increasing UV exposure time. To achieve complete phase separation of LC/monomer mixture in a cell, longer curing time was critically required. According to the experimental results, the curing times required to obtain almost complete photopolymerisation were 60 min and 120 min for 10% and 20% NOA65 cells, respectively. Above these complete-curing times, the electro-optical characteristics were found to reach saturation.

In addition, according to $\Delta R(V)$ curves of the curing time 40 min for 10% and 20% NOA65 cells, the curve of the 20%NOA65 cell was closer to that of a pure LC cell than one of 10% NOA65. This is because the higher density of UV-curable monomer makes the initial photopolymerisation faster, so that the polymerisation rate of 20% NOA65 cells was initially faster than that of 10% NOA65 cells, as expected. But to achieve complete photopolymerisation, a longer time to achieve higher separation quality is necessitated for higher monomer concentration, so that 120 min curing time to complete the phase separation for 20% NOA65 was necessary. The higher monomer concentration may result in greater expansion of the polymer domains into the pixel regions, thus anchoring the LC molecules and preventing them from completely reorienting parallel to the electric field. The maximum voltage-induced phase difference of an LC cell decreased for higher monomer concentration, as demonstrated in Figures 6a and 6b. These experimental results correspond well to the statements demonstrated in Figure 3.

Table 1 provides a summary of the electro-optical response of the LC cells. Based on the experimental results shown in Table 1, the threshold voltage and response time of LC cells with 10% and 20% NOA65 concentrations showed similar behaviour, except for a slight increase of threshold voltage and response time in the cell with higher monomer concentration. These slight increases of threshold voltage and response time were due to dense polymer networks remaining in the pixel region and increased anchoring force at the polymer wall. Even though the wall

Figure 5. Light transmitted through a LC cell at 0V (a), 2V (b), 3V (c), and 7V (d).

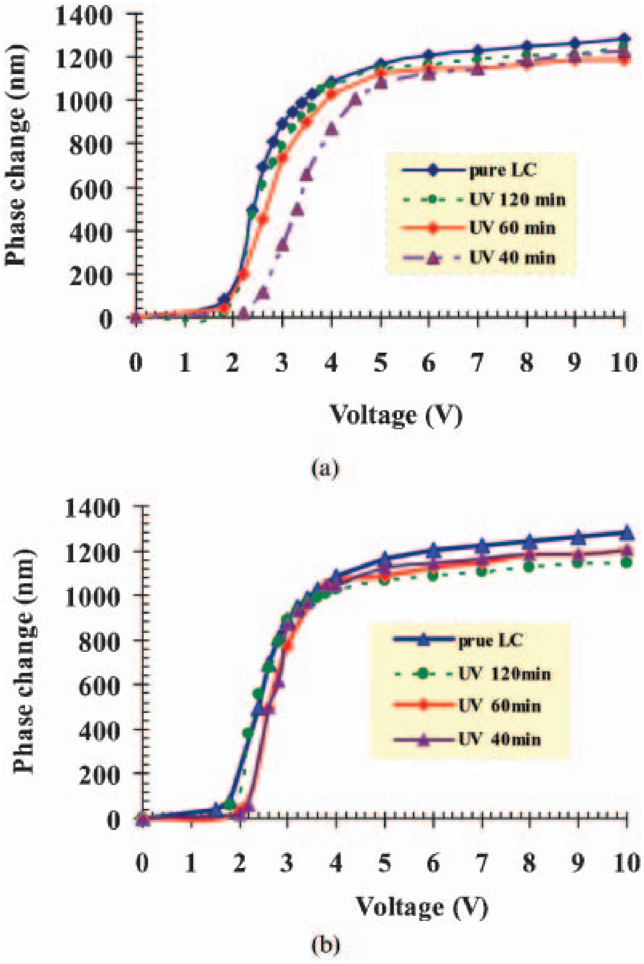


Figure 6. Phase change vs. voltage curves measured for different curing times under different monomer concentrations: (a) 10% NOA65; (b) 20% NOA65.

structure was more complete with increasing NOA65 percentage to provide a self-adhering and self-sustaining structure, the electro-optical performance of the polymer-wall cell degraded somewhat, such as decreasing the maximum phase difference, as well as increasing the threshold voltage and response time. Therefore, optimisation of polymer wall formation plays a critical role and is currently being investigated.

Although the structure of polymer walls can be measured with POM and SEM, the influence of some residual monomer in the un-exposed region on the performance of an LC cell and the completeness of the photopolymerisation induced phase separation cannot be accurately and easily measured. In contrast, the proposed phase-sensitive method can not only evaluate the electro-optical properties of LC molecules (*8*), but also be successfully applied to assess the degree of

Table 1. Electro-optical response of LC cells with and without polymer walls. The response time of the LC cell was measured at an applied voltage 7 V.

LC cell	Exposure time	V_{th}/V	t_{rise}/ms	t_{full}/ms
Pure LC material		1.75	10.2	43.5
	40 min	2.3	11.9	58.7
LC/NOA65 (9/1)	60 min	1.8	10.7	50.6
	120 min	1.75	10.4	44.8
	40 min	2.2	14	53.2
LC/NOA65 (8/2)	60 min	2.2	12.6	48.9
	120 min	1.8	11.1	47.6

photopolymerisation of UV-curable monomers in detail. Benefiting from the designed common-path optical configuration and the phase-sensitive measurement, the environmental disturbance and surface reflection were also considerably diminished. Thus, the optimisation of the polymer wall formation in a cell can be easily investigated with the proposed technique, which is relatively fast, highly accurate and simple.

5. Conclusions

A novel and simple technique for characterising polymer wall formation in a LC cell has been proposed with phase-sensitive measurement. The impacts of UV exposure time and monomer concentration on the electro-optical properties of a cell have been demonstrated. Due to the inherent polymer networks remaining in the pixel region break up the LC domains, the electro-optical response was found to degrade slightly in this study. Comparing the voltage-dependence phase difference curves of different tested cells with that of a pure LC cell, the completeness of polymerisation-induced phase separation could be easily determined.

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