

# Formation of High-Performance Polymer Walls in a Liquid Crystal Cell by Phase Separation of Fluorinated Polymer Mixture

Jong-In Baek<sup>\*\*</sup>, Jong-Ha Shin<sup>\*\*</sup>, Min-Cheol Oh<sup>\*</sup>, Jae-Chang Kim<sup>\*</sup>, and Tae-Hoon Yoon<sup>\*</sup>

## Abstract

In this paper, we report the fabrication of high quality polymer walls by using a monomer containing fluorine (F-monomer). Polymer walls with no phase retardation were fabricated by using photo-polymerization induced anisotropic phase separation of the mixture composed of liquid crystal (LC) and F-monomer. Thanks to the immiscibility of fluoride, we could form high quality polymer walls with no light leakage. We measured electro-optic characteristics of a twisted-nematic (TN) LC cell whose polymer walls were fabricated by using the F-monomer, and the measurements were compared with that fabricated by using the monomer without fluorine.

**Keywords** : liquid crystal display, polymer wall, phase separation, pixel isolation, fluorinated polymer, flexible display

## 1. Introduction

Recently, LCDs have become more important because of rapid increase in the scope of applications. Among various flat panel displays, LCDs have the most superior characteristics such as thinness, light weight, and low power consumption. Although LCDs are generally fabricated on glass substrates, they are thick, heavy, and easy to break. Especially, because mobile devices are always exposed to various shocks, glass substrates may not be the best choice for preserving the devices safely. Thus, plastic substrates have been considered as substitutes of the glass substrates [1-3]. Plastic substrates are flexible, light, and stronger against the external shock than glass substrates. However, the flexibility of plastic LCDs is not always advantageous. Since the operation of LCDs is based on the polarization state control of the incident light by the electro-optic effect, the distorted cell-gap of a bent cell may make it difficult to display the desired information clearly. To solve this problem, fabrication of the wall structure inside of an LC

cell has been studied [4-8].

There are two ways to form the wall structure in LC cells. One is to form the wall structure before injecting LC into the cell [4] and the other is to use the anisotropic phase separation by photo-polymerization of the LC/monomer mixture [5-8]. Although the former may provide walls with high quality, they may make it difficult to inject LC molecules uniformly to a large-sized panel. So fabrication of polymer walls using the phase separation method is recommended if clear phase separation can be obtained while maintaining the initial alignment of LC molecules.

Once we can form high quality polymer walls in a LC cell, their application need not be limited to the enhancement of the intrinsic strength or the maintenance of the cell-gap in flexible displays. There have been reports on the applications of polymer walls to various LCD modes, such as the bend aligned LC cell [11], wide viewing angle LCD modes [12,13], and the enhancement of the memory retention time in bistable LC devices [14]. The main obstacles involved in the widespread use of the OCB mode have been the non-uniform bend transition and the additional bias voltage to keep the initial bend state. To solve this problem, the bend alignment of a LC cell by using polymer walls has been proposed, by which we can also eliminate the non-uniform bend transition and the bias voltage. In the axially symmetric aligned microcell [12] or locked super-homeotropic mode [13], the effect of polymer walls on the LC alignment results in the multi-domain structure

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<sup>\*</sup> Member, KIDS; <sup>\*\*</sup> Student Member, KIDS.

Corresponding Author : Jong-In Baek

Department of Electronics Engineering, Pusan National University, Busan 609-735, Korea.

E-mail : jongin100@pusan.ac.kr Tel : +051 510-1700 Fax : +051 515-5190

enabling the intrinsic wide-viewing-angle LC modes to be realized. In bistable LC devices, pixels isolated by polymer walls can maintain each memory state for much longer time [14].

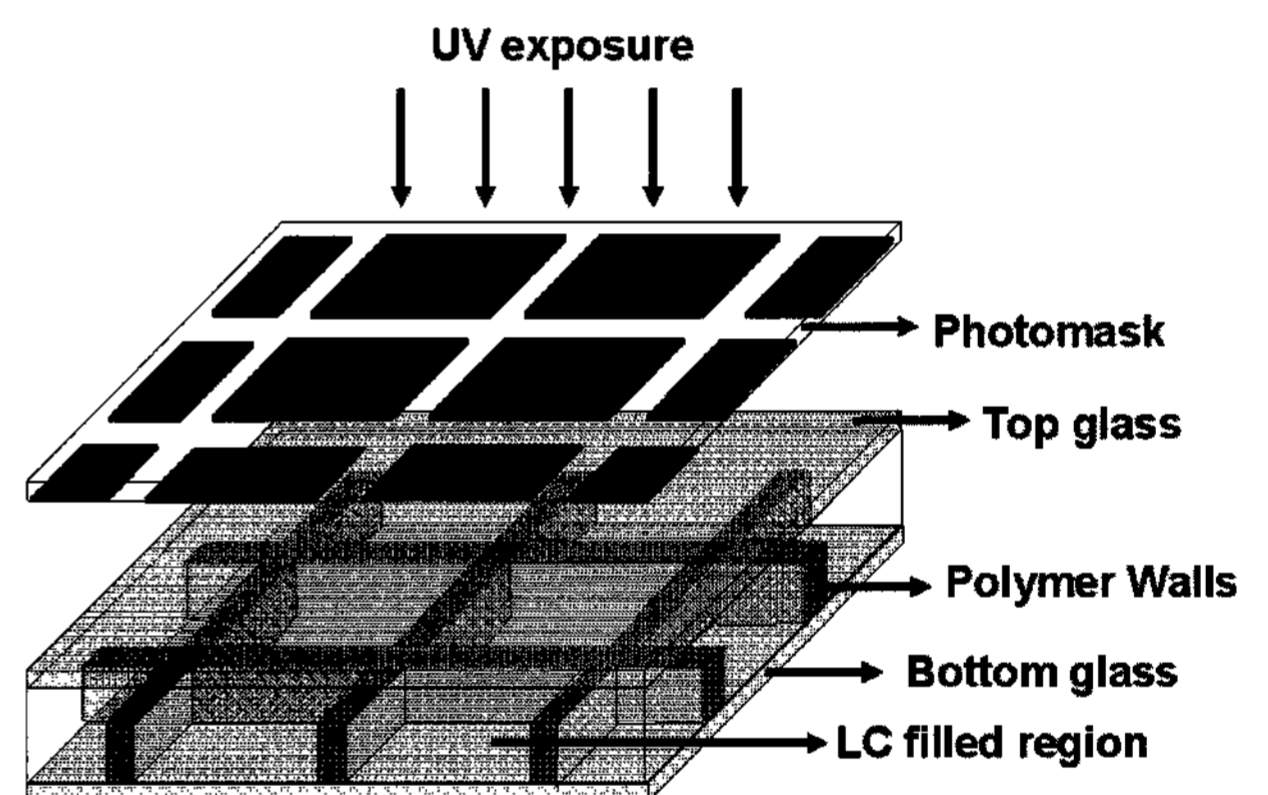
In this paper, we discuss about the fabrication of high quality polymer walls without phase retardation by using the monomer containing fluorine. It is well known that, when the Teflon®, one of the fluorides, is coated on the surface of a frying pan, no eggs adhere to it. The anti-adhesive property that prevents eggs from sticking onto the pan may be applied to anisotropic phase separation of the initial LC/polymer mixture for the fabrication of polymer walls. We can expect that the anti-adhesive property of fluorides will aid the photo-polymerization process for the fabrication of polymer walls.

In this study, a UV-curable perfluorinated acrylate material, a fluorinated polymer, was used. It was developed originally to be used as a low-loss polymer material for optical waveguide devices, because the fluorinated material provides low optical absorption for 1300 and 1550 nm wavelength regions [15,16]. As expected, we were able to form high quality polymer walls with the aid of the fluorine. We measured the electro-optic characteristics of a TN LC cell whose polymer walls were fabricated by using the F-monomer, which were compared with those of a cell fabricated by using the monomer without fluorine.

## 2. Fabrication Method

The fabrication process of polymer walls by phase separation in a LC cell is as follows. First, homogeneous alignment material SE-3140 (Nissan) was spin-coated on both indium-tin-oxide (ITO) coated substrates. The cellgap between the two substrates was fixed to 2.3  $\mu\text{m}$  by silica spacers at the Gooch-Tarry first maximum condition for the TN mode [17]. Rubbing directions of the two substrates were made to be perpendicular to each other in order to confirm the reliable alignment on each substrate by fabricating a TN cell with polymer walls. Before preparing empty cells, we mixed the F-monomer and LC with the ratio of 15:85 in wt %. MLC-6265-100 (Merck) was used as the liquid crystal material. For comparison, we also made polymer walls by using the monomer without fluorine, Norland optical adhesion 68 (NOA68). Furthermore, all the cell fabrication process with the F-monomer

reported in this paper was conducted under the optimized condition for NOA68. The LC/monomer mixture was injected into prepared empty cells by capillary action. To avoid non-uniform injection due to the difference in viscosity between LC molecules and the monomer, the cells were heated to a temperature above the clearing point when the mixture was injected. Then, mixture-filled cells were exposed to the UV light through a photo-mask for 40 minutes at a temperature of 100°C above the clearing point. Each pixel area of 300  $\mu\text{m} \times 300 \mu\text{m}$  was blocked by a photo-mask, while wall areas with the width of 30  $\mu\text{m}$  were exposed to the UV source for polymerization of the monomer. The overall process to form polymer walls in a liquid crystal cell is shown in Fig. 1. A Xenon lamp (Oriel) was used as the UV source for the exposure. It has maximum intensity at the wavelength of 365 nm. We fixed its electric power to 200 W.



**Fig. 1.** Overall structure for the formation of polymer walls in a liquid crystal cell by using photo-polymerization induced anisotropic phase separation of the LC/monomer mixture.

To verify the immiscibility of the fluorinated polymer from the LC material, we examined the liquid contact angles of each material prior to experiments. The contact angle was measured with water and the LC solution when they are dropped on the film surface made of cross-linked UV-curable polymers such as NOA 68 and the fluorinated polymer. As summarized in Table 1, the fluorinated polymer exhibited higher contact angles compared to NOA65 and NOA68 for both cases of water and LC. From the larger contact angle of LC on fluorinated polymer, we could confirm that the LC is almost immiscible with the fluorinated polymer.

**Table 1.** Contact angles measured by dropping water and the liquid crystal on the substrates coated with different polymer materials, NOA65, NOA68, and the fluorinated polymer

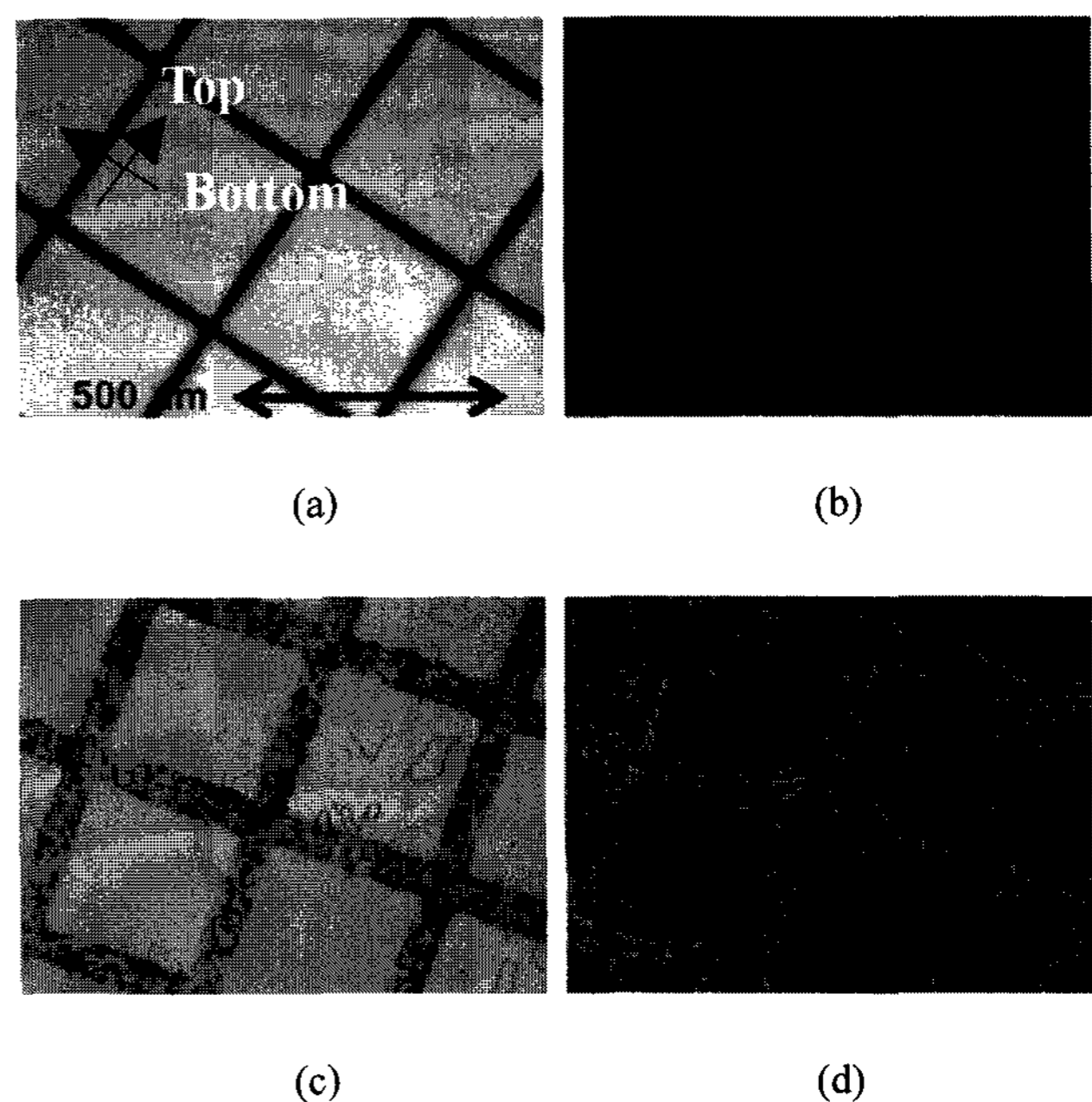
	Water	Liquid Crystal
NOA65	65.9	17.1
NOA68	68.1	27.0
Fluorinated polymer	106.7	44.5

### 3. Results and Discussion

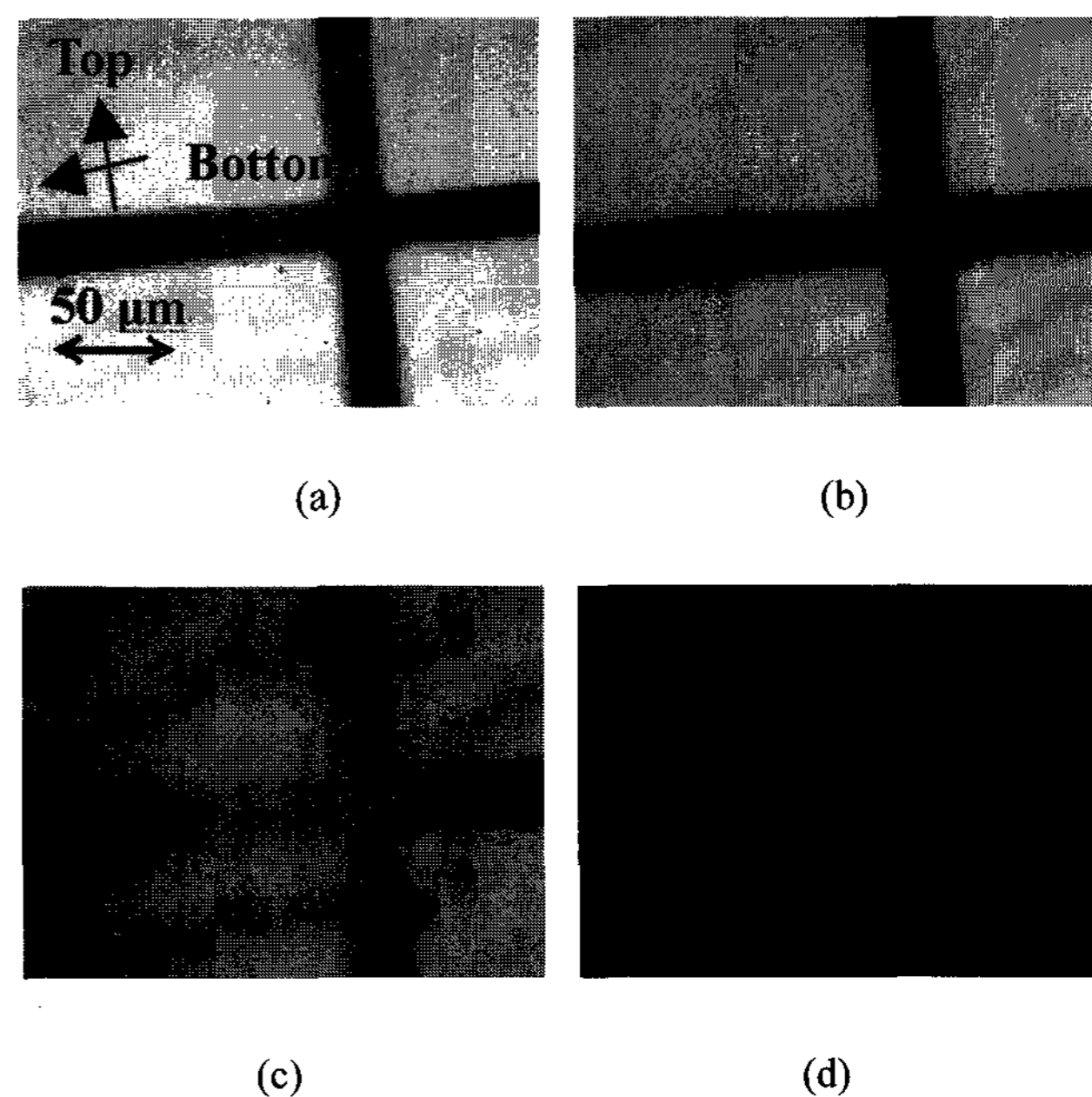
Fig. 2 shows the fabricated LC cells with polymer walls between crossed polarizers observed through a microscope. As the LC director on both substrates of cells are matched by rubbing with the transmission axis of each polarizer, fabricated TN cells show a bright state without an applied electric field. This confirms that LC alignment is preserved even after the polymer walls are formed. An LC cell fabricated with the F-monomer shows very black wall areas and clear distinction between wall areas and pixel areas, as shown in Fig. 2(a). The very black state of wall areas under the crossed polarizers may be attributed to zero-retardation of polymer walls. In the photo-polymerization process using a photo-mask, phase separation of the initial mixture is important in both pixel and wall areas. Thanks to the anti-adhesive property of the F-polymer, we could successfully achieve phase separation for fabrication of polymer walls. Strong attraction of F-polymer molecules between themselves pushed all the LC molecules to pixel areas during the photo-polymerization so that high quality polymer walls and isolated pixels were obtained at the same time.

For comparison, an LC cell fabricated with NOA68 under the same condition is also shown in Fig. 2(c). This time, the wall areas show a coloured bright state, which may be due to the retardation effect of the remaining LC molecules within the polymer wall structure. The dark state of an LC cell fabricated with the F-monomer is also superior to that fabricated with NOA68, as shown in Figs. 2(b) and 2(d). The very dark state can be observed in an LC cell fabricated by using the F-polymer, while there is the light leakage in a cell fabricated by using the monomer without fluorine.

Next, we closely examined boundaries between pixels and walls as we increased the amplitude of the applied voltages. As can be seen in Fig. 3, the transition to the dark state begins at the pixel-wall interfaces. It is believed that pixel/wall interfaces help



**Fig. 2.** Micrographs of TN LC cells whose polymer walls are fabricated by using the F-monomer (a) at 0 V, (b) at 5 V, and NOA68 (c) at 0 V, (d) at 5 V. Crossed white arrows in (a) indicate the rubbing direction of each substrate and the transmission axes of crossed polarizers.

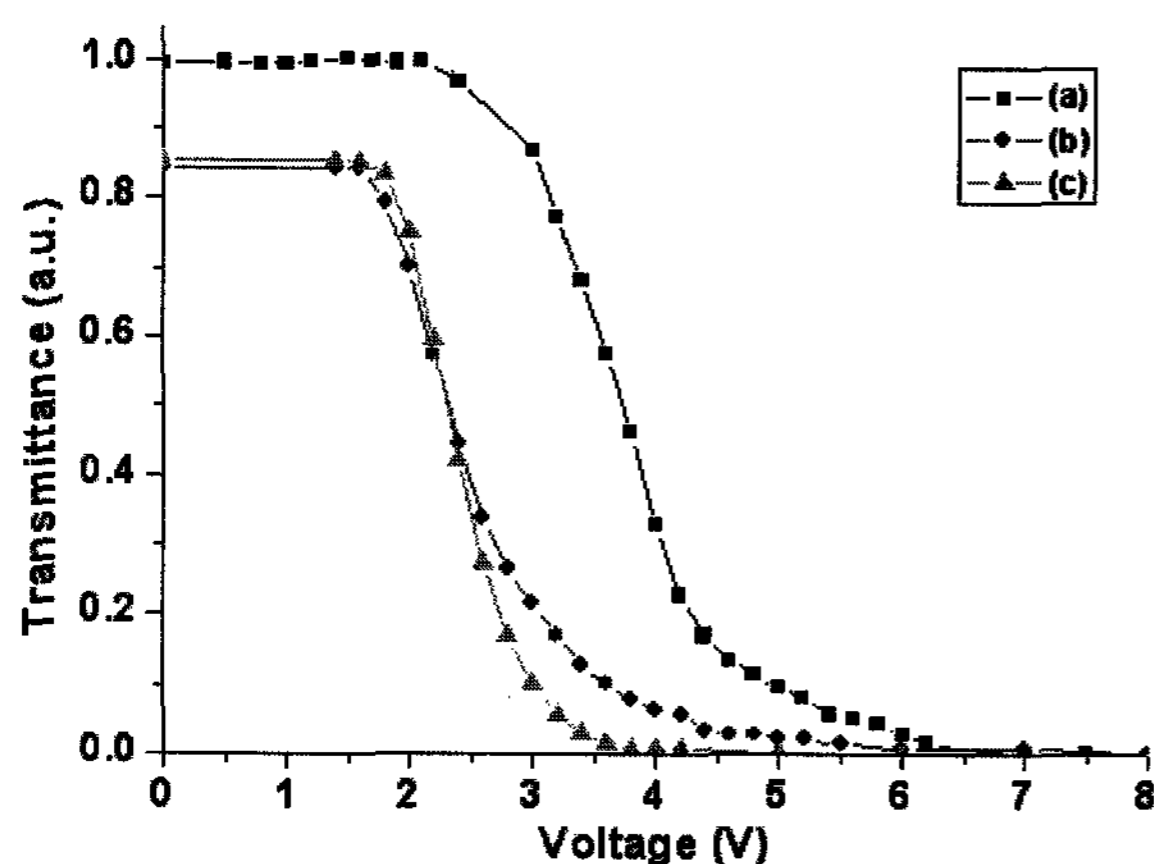


**Fig. 3.** Micrographs of a TN LC cell whose polymer walls are fabricated by using the F-monomer at (a) 0 V, (b) 2.6 V, (c) 4.1 V, and (d) 4.5 V. Crossed black arrows in (a) indicate the rubbing direction of each substrate and the transmission axes of crossed polarizers.

the easier alignment of LC molecules near the interfaces along the applied vertical electric field. Electro-optic

characteristics of TN cells with and without polymer walls are shown in Fig. 4. The threshold voltages of an LC cell with polymer walls are lower, which also may be attributed to the effect of pixel-wall interfaces that helps LC molecules near the interfaces to align along the applied vertical electric field. Fig. 4 also shows that an LC cell fabricated with the F-monomer reaches zero transmittance at a lower voltage than that fabricated with NOA68. This suggests that it is possible to operate the device at high contrast and at a lower voltage hence reducing power consumption level.

Response times between the dark and the bright states were also measured by applying 1 kHz square-wave pulse of 5 V to the cell. As LC cells were fabricated in the TN mode, they show normally white state between crossed polarizers. Turn-on time of a TN cell with polymer walls was about 2 ms, which is much faster than that of a TN cell without walls, i.e., 4 ms. This fast turn-on time of a TN cell with polymer walls also may be aided by pixel-wall interfaces that aid the vertical alignment of LC molecules near the walls. On the other hand, the relaxation time was much longer in an LC cell with polymer walls than that of without them, i.e., 5 ms. An LC cell fabricated with NOA68 was slower, i.e., 16 ms, than that fabricated with the F-monomer, i.e., 12 ms. Slower relaxation of LC cells with polymer walls may be attributed to the disturbance by pixel-wall interfaces. Pixel-wall interfaces aid the alignment of LC molecules near the interfaces along the vertical field direction, while they impede the relaxation to



**Fig. 4.** Voltage-dependent optical transmission curves of a TN LC cell. (a) without polymer walls, (b) with polymer walls fabricated by using NOA68, (c) with polymer walls fabricated by using the F-monomer.

the homogeneous alignment. The lower transmittance of cells with polymer walls is attributed to the polymer walls that decrease the area for the light transmission.

#### 4. Conclusion

We formed polymer walls with no retardation by using the F-monomer in LC cells. Thanks to the superior immiscibility of fluorides, we were able to successfully fabricate high quality polymer walls by anisotropic phase separation of the initial mixture by photo-polymerization. LC Cells formed by using the F-monomer showed very dark wall areas. The boundaries between the pixels and walls of an LC cell formed by using the F-polymer were much sharper than those of a cell formed by using the monomer without fluorine.

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