Formation of Polymer-Wall-Stabilized 
Bend-Mode Liquid Crystal Cells

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We propose a novel pi-cell with polymer walls that can be stabilized in a bent configuration, using the polymerization-induced phase separation of liquid crystals from a cross-linked polymer formed through free-radical photo-polymerization. The polymer walls were formed using an ultraviolet (UV)-curable multifunctional monomer, which was exposed to non-uniform UV-illumination through a photomask while maintaining a constant concentration of liquid crystal in the micro-celled structures. When a mixed solution of the liquid crystal and a UV-curable monomer held between two substrates was subjected to an electric field and partially irradiated with UV light, the monomer polymerized to form walls that were vertical with respect to the substrate. Consequently, the bend-alignment of the liquid crystal was stabilized by both the interfaces with the polymer walls and the alignment layers on substrates. 

Keywords: liquid crystal device, pi-cell, bend alignment, photopolymer, polymerization-induced phase separation, polymer wall.

1. Introduction

Liquid crystal devices are currently being studied for use in a number of new electro-optic applications due to their low operation voltage, low power consumption, compact size and low fabrication cost. In particular, thin-film-transistor liquid-crystal-displays are widely utilized in information displays such as notebook computers, monitors and televisions, because they have excellent resolution quality. Because of the inherently high viscosity of the liquid crystal directors, the electro-optic response of nematic liquid crystals is inevitably slow. Conventional liquid-crystal devices, such as homogeneous cells and twisted-nematic cells, exhibit a back-flow effect that gives rise to "optical bounce" during the relaxation process, which increases the decay time.[1,2] Extensive research efforts have been devoted to the study of liquid-crystal materials to induce a faster response speed.

The "pi-cell"[1,3] or "optically-compensated bend mode"[2,4] has an exceptionally fast electro-optical response. In the pi-cell, the pre-tilt angles in the top and bottom substrates lie in opposite directions. The opposing pre-tilt angles lead to a fast response time for pi-cells. The bend configuration director profile in the voltage-on state eliminates the back-flow effect and therefore results in a fast relaxation time.[1,2] However, the bend configuration in a pi-cell is unstable at low driving field. In these devices, a more stable splayed configuration appears first, and a long warm-up period is needed to transform the LC device from the splayed state to the bend state. This becomes problematic in display applications, where the
conversion of the inter-pixel LC molecules from the splayed to the bend configuration is accompanied by disclination generation. Two methods have been proposed to solve the problem. The first is a nucleation method that utilizes a starting point for the splay-to-bend transition that incorporates spacers and a high-tilt region within each pixel from the outset.[5-7] Although the stability of the configuration of the bends indeed improves in the nucleation region, it requires an initialization process to convert from the splayed to the bend configuration and an operating bias voltage to maintain the bends in a stable state. The second method is to add a small fraction of polymeric chains into the liquid crystal to stabilize the bend configuration.[8] Unfortunately, this approach decreases the optical qualities, such as the contrast ratio and the brightness of the device, owing to light being scattered due to the index mismatch between the liquid crystal and the polymer.

To overcome these problems, we propose a novel pi-cell with polymer walls that can stabilize the configuration of the bends in the initial stages. This “bend-cell” was fabricated using photopolymerization-induced phase separation.[9] A mixed-solution of UV-curable monomer and liquid crystal sandwiched between two substrates was subjected to an electric field and a partially non-uniform illumination process with UV light. The monomer became polymerized, forming walls that were vertical with respect to the substrate. Consequently, the bend-alignment of the cells was stabilized by both the interfaces with the polymer walls and the alignment layers on the substrates. In this paper, we describe a novel pi-cell with polymer walls formed from a UV-curable multifunctional monomer that is able to stabilize the state of the bends. We used optical microscopy to study the liquid crystal/polymer composite structure of these new cells, which were formed under various polymerization conditions, and the mechanism for the formation of the polymer walls was investigated.

2. Fabrication

We used a mixture that phase-separated into polymer-rich and liquid crystal-rich regions below the phase separation temperature, and which formed a homogeneous solution at elevated temperatures. In this study, a photopolymerization-induced phase separation method was used to prepare pi-cells with polymer walls from a liquid crystal mixture (JB-5002××, supplied by Chisso Corp.) and a UV-curable prepolymer material (NOA73, supplied by Norland Products Inc.). JB-5002×× is a nematic mixture that exhibits positive dielectric anisotropy (Δε = 9.0, ε⊥ = 4.2), high birefringence (Δn = 0.203, nω = 1.515), the same elastic constants of splay and bend (K11 = K22 = 13.4), a low viscosity constant of 30.6 mPa·s at 20°C, and a nematic-isotropic transition temperature of 83.4°C. NOA73 is an acrylate multifunctional monomer that will cure when exposed to UV light with a wavelength of between 350-380nm.

Figure 1 shows the process that we used to fabricate our device. Firstly, homogeneous mixtures of 90 wt% of JB-5002×× and 10 wt% of NOA73 were introduced into the thin gap between two glass substrates, which were coated with indium-tin-oxide (ITO) electrodes. The dimensions of the gap were set by inserting

Fig. 1. Fabrication process for a bend-mode cell stabilized by polymer-walls.
5μm plastic spacers. The substrates that we used in this cell were coated with polyimide alignment layers (SE7759, supplied by Nissan Chemical Industries, Ltd.) that were rubbed in parallel directions, producing a pre-tilt angle of about 7 degrees for the liquid crystal molecules after the rubbing process. The cells were capillary-filled at 100°C, a temperature at which the formulation mixture was in the isotropic phase. The phase separation temperature of the liquid crystal/monomer (90/10) formulation was 68°C, as observed during the cooling using a cross-polarizing optical microscope in transmission mode.

After filling, the homogeneous mixtures in the cells were cooled down to 40°C to induce phase separation. The phase separation that occurs in the mixture goes from an isotropic, homogeneous state to a heterogeneous state upon cooling, including a nematic-rich phase and a monomer-rich phase. A 20V, 120Hz square wave AC voltage was applied to the cells to change the alignment of the liquid crystal molecules from the splayed to the bend state. Finally, 365nm wavelength ultraviolet (UV) light with an intensity of 40 mW/cm² was used to irradiate the nematic/monomer solution for 30 minutes through an external photomask with a linewidth of 25μm and a 500μm interval pattern in order to form the polymer walls by polymerizing the monomers floating in the UV exposed areas.

3. Results and Discussion
3.1 Polymer Wall Structure

When polymer walls are formed in liquid crystals they affect the orientation of the liquid crystal material. They are used to stabilize desirable liquid crystal configurations and to control the electro-optical properties of liquid crystal devices. In order to optimize the electro-optic performance, it is important to understand the morphology of the polymer walls.

A confocal laser microscope (VK-8510, supplied by KEYENCE Corp.) was used to examine the morphology of the polymer walls, because there were various factors that we were uncertain about. Laser microscope images delineate two-dimensional distributions of reflective light intensity from objects. These microscopes have the advantage of only capturing images in the focal plane, which allows us to yield high-resolution images due to the elimination of the out-of-focal-plane images that are the origin of deterioration in resolution. To prepare a sample for microscopic measurement, a UV-cured cell was immersed in methanol for one hour and then disassembled. The substrate was then rinsed with methanol to remove the liquid crystal and dried for a further one hour. Figure 2 shows laser microscope images of a selection of polymer walls derived from a mixture containing 10 wt% of monomer at a temperature of 40°C. Solid and well-defined walls with sharp, smooth boundaries can be obtained by optimization of the temperature for phase separation. The small voids in the walls were considered to contain liquid crystal molecules that were dissolved in methanol during the sample preparation. The polymer walls were predominantly formed in the interpixel regions, which were arranged in a square grid, having an approximate width of

![Fig. 2. Polymer morphology observed with a confocal laser scanning microscope. Micrographs of polymer morphology labeled (a) and (b) show images using objective lenses with magnifications of ×10 and ×100, respectively.](image-url)
25\,\mu m and an interval of 500\,\mu m, consistent with the photomask pattern. A micro-sized polymer-particle is confirmed near the wall in Fig. 2(b). This assumes that the free radicals that were diffused from the high UV-intensity region and/or the residual monomer were polymerized in the non-UV-irradiation region.

3.2 Observation of the Splay-to-Bend Transition

We observed the configuration of the changes in the liquid crystal molecules during the splay-to-bend transition for pi-cells with and without the polymer walls. Figure 3 shows photographs of a pi-cell without polymer walls that was fabricated using zero concentration of the monomer, which was placed between two crossed polarizers. As the applied voltage increases, the liquid crystal directors go through the splayed and then the bend configurations. At lower voltages, the splayed state has lower free energy than that of the bent state. Therefore, the splay state is more stable than the bent state, as shown in Fig. 3(a). From calculating the Gibbs free energies of the bent and splayed configurations at a pre-tilt angle of 7\,^\circ, based on Frank's elastic theory[10], the voltage at which the bent and splayed configurations have equal free energy is defined as the critical voltage ($V_{cr}$), which is 2.1 V in this case. By applying a voltage higher than $V_{cr}$, the free energy of the bent state becomes lower than that of the splayed state. Thus, a voltage higher than $V_{cr}$ must be applied to change from the splayed to the bent alignment, which is known to also depend on both the applied voltage and the length of time for which this voltage is applied. Figure 3(b) is a photograph of the transition process at 5V with a 120Hz square wave, and shows that the splay-to-bend transition above $V_{cr}$ occurs in two steps: (1) nucleation of a region with the bent state and (2) the spread of the bent state region. We measured the transition time from the splayed to the bent alignment in detail in order to clarify the dominant factors affecting

![Fig. 3](image)

Fig. 3. Appearance of a pi-cell without polymer walls that was fabricated using zero concentration of the monomer placed between crossed polarizers aligned at 45\,^\circ to the liquid crystal surface alignment direction. (a), (b), and (c) show the splayed state at zero voltage, the splay(gray)-to-bend(black) transition process at 5V, and the bend state at 5V, respectively.

![Fig. 4](image)

Fig. 4. Optical micrographs of a pi-cell with polymer walls placed between crossed polarizers aligned at 45\,^\circ to the liquid crystal surface alignment direction at drive voltages of (a) 0 volt, (b) 2.1 volt, (c) 4 volt, and (d) 6 volt.
the transition of a cell. A time of over 300 seconds at an applied voltage of 3V followed by 4 seconds at 10V was needed for the configuration over all of the area of the cell could make the transition from the splayed to the bent states.

In order to study the effect of the alignment of the liquid crystal in the inter-pixel regions located in the square grid constituted by the polymer walls, we used a polarizing optical microscope (ECLIPSE E600POL, supplied by Nikon Corp.) to observe the alignment structure in the cells. Figure 4 shows the results of various measurement voltages, ranging from 0V to 6V, that were applied to a fabricated cell with polymer walls placed between crossed polarizers that were aligned at 45° to the liquid crystal surface alignment direction. The splay-to-bend transition process cannot be observed in the fabricated cells under any applied voltage. We also confirmed continuous half tones reproducible without disclination generation as shown in Fig. 4(b), 4(c), and 4(d). After the voltage was turned off, the liquid crystal throughout the cells remained in the bent configuration. However, a 180°-twisted configuration of the liquid crystal was observed in the initial state of the cell at zero applied voltage (Fig. 4(a)). In this case, the transition time for the initial state to convert from the twisted to the bent states is fairly fast, because the energy barrier between the bent and the twisted configurations, as calculated from the Gibbs free energy, is slight below $V_{cr}$. There are no twisted domains observable when the applied voltage is above $V_{cr}$.

3.3 Bend-Stabilization Models

According to the above observation results, it is confirmed that the liquid crystal configuration of the pi-cells is strongly dependent on the polymer walls. We now propose a model for the formation of the polymer walls and how the bend-configuration is stabilized by the polymer-walls.

In polymer-walled cells formed by polymerization-induced phase separation, spatial variations in the structure can be achieved when non-uniform polymerization conditions are introduced. The distribution of the polymer walls is due to the local phase separation process, which is different from conventional polymer-dispersed liquid crystal (PDLC). Polymer diffusion and phase separation processes are involved in the formation of these polymer walls.

The formation of polymer walls is achieved by irradiating selected areas of a cell with UV light through a photomask to induce phase separation by polymerization, as shown in Fig. 5. The monomer molecules are then polymerized and the polymer separates from the nematic component. In the irradiated region, more free radicals are produced, and the monomers become polymerized to form polymers. The consumption of monomers in these regions lowers their chemical potential.
This induces the monomers to diffuse from the low to the high intensity regions. On the other hand, the liquid crystal molecules diffuse from the high to low intensity regions to balance the chemical potential. As a result, the liquid crystal is squeezed out of high intensity regions. Thus, alternating polymer-rich and liquid crystal-rich regions are formed, depending on the photomask pattern. We believe that a phenomenological diffusion model can be used to describe the kinetics of the wall formation in the liquid crystal cell.

During the polymerization process we can control the configuration of the mixture of monomer and liquid crystal by applying an external electric field. The polymer walls that are formed in the bent state by applying a voltage above the critical voltage are assumed to maintain the bend configuration after the removal of the voltage, as shown in Fig. 5. Because this device is composed of a large number of micro-celled structures, and owing to its closed structure, the bend configuration is stabilized by both the interfaces with the polymer walls and the conventional surface alignment layers, and so the structure remained, even after we turned off the voltage.

4. Conclusions

In this study, we have proposed a novel pi-cell using in-situ fabricated polymer walls. This cell was formed by a local photopolymerization-induced phase separation process using non-uniform UV irradiation and by separating the formation of the liquid crystal region and the polymer region by applying an electric field to control the liquid crystal alignment during the phase separation. In a pi-cell containing such polymer walls, the configuration of the bends was stabilized by a three-dimensional alignment based on both interfaces of the polymer walls and the alignment layers on the substrates. The final device exhibits great potential for many applications, since there is no need for an initialization voltage to cause the splay-to-bend transition and no operating bias voltage is required to maintain the bends. The polymer walls formed in the pi-cell not only improve the electro-optic characteristics of the device, but also afford excellent pressure resistance, preventing distortion of the display. Currently, the detailed mechanism and optimization of this method of polymer wall formation are being investigated.

References