Chemical Physics Publications   Department of Chemical Physics

11-3-2003

Formation and Localization of Internal Polymer Columnar Structures in Liquid Crystal Cells

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Recommended Citation

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Internal polymer columnar structures in liquid crystal (LC) cells have been produced using the method of thermally-induced phase separation of LC/prepolymer solution and solidified by photopolymerization. These polymer columns adhere to both substrates and enhance control of the LC cell spacing and mechanical stability. The existence and profile of the polymer columns were investigated by optical and scanning electron microscopy techniques. Supertwisted nematic LC cells with polymer columnar structures have been constructed using this method and their electro-optical characteristics measured. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1623325]

Liquid crystal displays (LCDs) fabricated using plastic substrates have many advantages over traditional LCDs built with glass substrates, such as being lightweight and immune from breakage, and have the flexibility necessary for portable devices. Two of the biggest challenges related to the fabrication of flexible devices are spacing (or, cell-gap) control and resistance to mechanical stress. Traditionally, glass or plastic beads or fibers have been used to maintain a uniform cell gap in LCDs.[1] But in cells built with flexible plastic substrates, the spacers tend to move around and aggregate especially when the cell gap is temporarily increased by mechanical deformation, thus causing loss of control of the spacing.

Many researchers have built internal polymer structures, such as polymer walls, in LC cells to enhance the mechanical and optical properties of LCDs.[2–5] In general, there are two fabrication methods by which to build polymer walls. One method relies on application of a ''patterned'' electric field to cause phase separation followed by UV irradiation to polymerize the segregated polymer regions.[4,5] The second method employs photomasks to block UV from the pixel region and only induces phase separation of the polymer into interpixel regions.[2,3] The polymer wall structures in LC cells provide good cell-gap control, resistance to pressure, and prevent distortion of the displayed image. However, the use and precise placement of photomask or patterned electrodes and the high electric field (10–15 V/μm)[5,6] make these methods cumbersome and costly for manufacturing.

In this letter, we present a method that yields an internal polymer structure with great ease in fabrication. We found that the thermally-induced phase separation of a mixture of LC and prepolymer resulted in the formation of prepolymer columns dispersed in a uniformly aligned LC host. Subsequent irradiation of UV light polymerizes the prepolymer columns and fixes their location and shape, and causes them to adhere to the two substrates with which they are in contact. These internal polymer columnar structures serve to stabilize the cell gap and enhance the mechanical stability of LC devices, especially in the case of plastic LC devices, which are built with flexible plastic substrates. The existence and profile of polymer columns formed in supertwist nematic (STN) LC cells with different concentrations of prepolymer were investigated using polarizing optical microscopy and scanning electron microscopy. The electro-optical properties of STN LC cells with internal polymer columnar structures were also investigated.

The empty cells used in our experiment were constructed of indium–tin-oxide (ITO) coated glass substrates spin coated with the polyimide KJ-01 (shown in Fig. 1), synthesized at Kent State University. This polyimide (PI) KJ-01 was specially synthesized with cyano-biphenyl side chains which greatly enhanced its interaction with LC molecules and resulted in good wetting and uniform alignment of the LC on the PI surfaces after phase separation of the LC and prepolymer. The PI coated substrates were first soft baked at
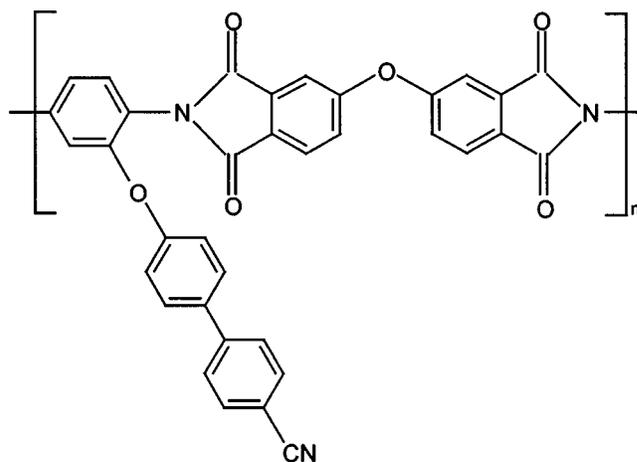

FIG. 1. Chemical structure of polyimide KJ-01.

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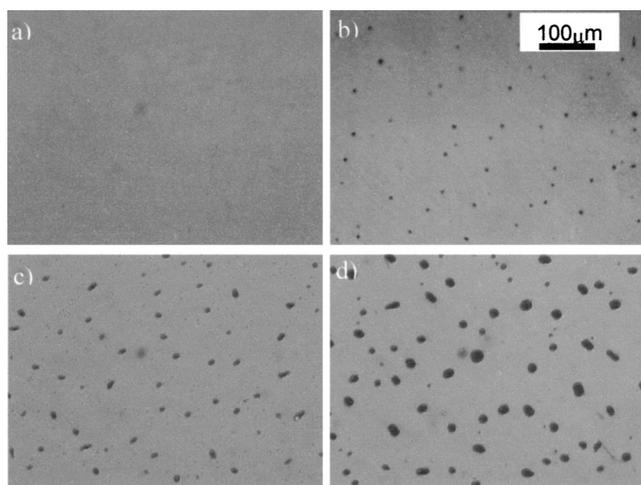
FIG. 2. Microscopic texture of cells made from mixtures which contain chiral nematic liquid crystal ZLI5400/100 and (a) 0% polymer, (b) 7 wt % NOA77, (c) 10 wt % NOA77, and (d) 15 wt % NOA77.

90 °C for 5 min to evaporate the solvent. They were hard baked at 180 °C for 1 h to complete the imidization reaction and form polyimide. The substrates then were unidirectionally rubbed with a velvet cloth. The rubbing directions of two substrates formed a left-handed twist angle of 200°. The cell gap was maintained at 5 μm with glass fiber spacers.

We used an UV curable optical adhesive (NOA77, Norland Products) as the prepolymer, and mixed it with the nematic LC (ZLI5400/100, Merck Inc.) in ratios of 7:93, 10:90, and 15:85 by weight, respectively. The NOA77 adhesive adheres well to glass as well as to plastic substrates. A left-handed chiral agent (S811, also from Merck Inc.) was dissolved in the LC in a concentration of 0.6 wt % to induce the desired twist. The mixtures were well stirred at 80 °C, which is 5 °C over the clear point of the LC. Then the mixtures were placed into empty cells at 80 °C by capillary action. At this temperature, the liquid crystal and prepolymer formed a homogeneous, isotropic solution. The cells were cooled at a rate of 2 °C/min using a Mettler FP-82HT hot stage. The sample cell with 10 wt % prepolymer loading was observed under a polarizing microscope during cooling. When the temperature fell below 68 °C, the isotropic mixture started to phase separate into two regions of birefringent nematic (LC-rich) regions and isotropic (prepolymer-rich) regions. The nematic domains grew continuously as the phase separation of LC phase from the solution continued with the cooling.

By the time the cell reached room temperature (~25 °C), microscopic isotropic prepolymer-rich droplets were nearly uniform and randomly dispersed in the aligned chiral nematic LC host and touched both of the substrates. The cells were then treated with UV irradiation (~1 mW/cm^2) for 10 min. The prepolymer droplets were polymerized and formed solid polymer columns.

The resultant cells were examined under a polarizing optical microscope. Figures 2(b)–2(d) show the microscopic texture of the cells filled with mixtures containing 7, 10, and 15 wt % NOA77 prepolymer. As a reference, Fig. 2(a) shows the microscopic texture of a standard 200° twist STN LC cell made with the conventional method using ZLI5400-100+0.6 wt % chiral S811 with no prepolymer. The black dots visible in Figs. 2(b)–2(d) are polymer columns uniformly dispersed in the LC volume. The average size of these columns in the cell with 7 wt % polymer is ~5–10 μm. When the polymer concentration was increased to 15 wt %, average size of the polymer columns increased to around 20–30 μm. The presence of polymer columns did not give rise to any disclination lines. The LC was aligned uniformly even in the vicinity of the polymer columns.

The presence of polymer columns and their shape profile were further investigated using scanning electron microscopy (SEM). To prepare samples for SEM, a cell made with the mixture containing 7 wt % prepolymer was opened. The substrates were rinsed with hexane for 3 min in order to remove the liquid crystal and then dried. A thin (~60 Å) over layer of gold was then deposited. Figure 3(a) shows SEM images of the solidified polymer columns attached to the substrate. The size of these polymer columns is estimated to fall between 5 and 10 μm. The SEM results are consistent with the optical microscopic observations.

The physical mechanism responsible for the formation of columns is similar to that modeled by Taylor and co-workers,[7] except that the rates of diffusion for prepolymer and LC molecules in the present case are different. Prepolymer molecules that come into contact with singularities on the surfaces or the bead spacers are pinned at these nucleation sites. A reduction in temperature causes the LC and prepolymer to become immiscible. The phase separation process in these mixtures is via nucleation and growth process along the binodal decomposition curve and there is an energy barrier against phase separation. External energy is required to overcome the barrier to initiate phase separation.[8] The
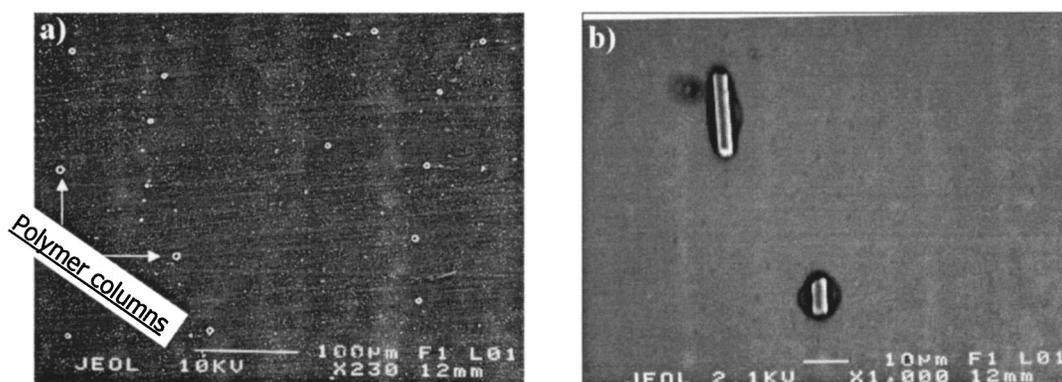

FIG. 3. SEM images of polymer columns obtained from LC cells that contained 7 wt % polymer and (b) polymer columns localized by spacers.
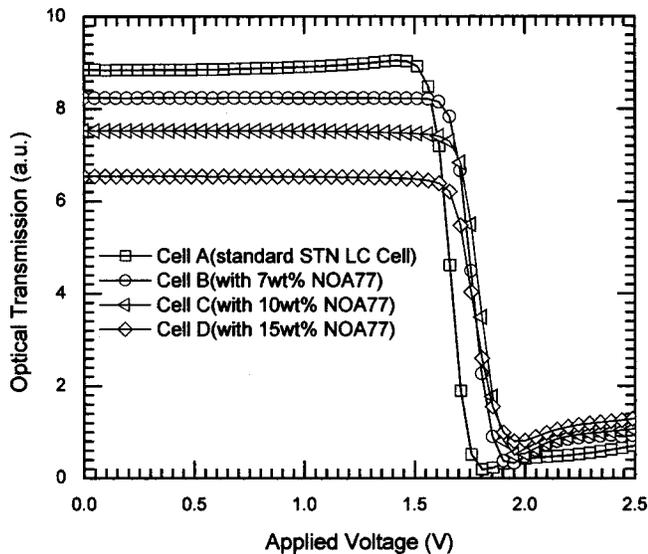
FIG. 4. Transmission vs voltage applied to a standard STN cell (without polymer) and polymer column STN cells made from mixtures containing 7, 10, and 15 wt % prepolymer NOA77.

spacers and other pinning sites act as nucleation sites and provide external energy to initiate phase separation. Prepolymer molecules collected in small volumes near the pinning sites and near the spacers. The spacers are eventually enveloped by the prepolymer due to the stronger interaction between the glass fiber surface and prepolymer molecules than that between glass fibers and the liquid crystal. When the volume collected near a point singularity becomes large enough (i.e., comparable to the cell thickness), it bridges the two substrates and takes on a column-like appearance. The location and shape of these polymer columns are fixed upon UV exposure by cross-linking reaction.

The SEM investigation also showed that some of the polymer mass was localized by glass fiber spacers [Fig. 3(b)]. Spacers are found to be surrounded by polymer and bonded to the sites of their initial positions. This structure provides the benefit of keeping the spacers from moving around and maintaining the cell thickness. This result also indicates the possibility of controlling the density, distribution, and localization of polymer columns via distribution of the spacers.

Figure 4 compares the voltage dependence of optical transmission of a standard STN-LC cell and three STN LC cells with polymer columns structures with different prepolymer contents. The twist angles are all 200° left handed. All the sample cells with polymer columns structure exhibit good electro-optical properties, with steep transmittance–voltage $(T-V)$ curves close to 1.1. The steepness of the $T-V$ curve was defined as V_{sat}/V_{th}, where V_{sat} is the satu-

ration driving voltage, and V_{th} is the threshold voltage. According to the ''iron law of multiplexing,'' maximum multiplexibility of 100:1 can be achieved in these cells using Alt and Pleshko addressing.[9] The field-off state of the cells with polymer columns is less bright than the standard cell with the LC alone, and the higher the polymer content, the less bright the field-off state. Also, optical leakage in the field-on state is a bit higher than that of the standard cell. This is to be expected since polymer columns are optically isotropic and nonoperable under the electrical field. The cell brightness and mechanical resistance property will need to be balanced by optimizing the density, size, and distribution of polymer columns for practical devices.

A comparison of different cells (Fig. 4) also shows that the driving voltage of the cells with polymer columns increased by ~0.2 V compared to the standard STN cell. Besides those polymer columns that are in contact with both substrates, there is still a small amount of prepolymer that forms tiny polymer beads (smaller than the cell gap) or a polymer network that is dispersed throughout the LC medium. These tiny polymer beads should show a noticeable voltage drop due to their smaller dielectric constant (for NOA77, $\epsilon_p = 3.3$) than those of LC ZLI5400-100 ($\epsilon_\perp = 4.6$, $\epsilon_\parallel = 14.5$, for 20 °C, 1 kHz).

In conclusion, we have presented a method to form and localize polymer columns in LC cells using thermally-induced phase separation of a LC/prepolymer mixture followed by a photopolymerization step. The polymer columns extend from one substrate to another and adhere to both of the substrates, thus enhancing the LC cell spacing control and mechanical ruggedness. We also demonstrated that STN LC cells with polymer column structures exhibited good electro-optical characteristics with steepness of 1.1. This technique can be used for fabricating LC devices in other configurations, such as twist nematic, electrically controlled birefringence, in-plane switching, and ferroelectric LCs.

[1] R. Culley and K. Surtani, U.S. Patent No. 4,501,471 (filed 1995).
[2] N. Yamada, S. Kohzaki, F. Funada, and K. Awane, SID Digest of Technical Papers 26, 575 (1995).
[3] T. Shinomiya, K. Fujimori, S. Yamagishi, K. Nishiguchi, S. Kozaki, Y. Ishii, F. Funada, and K. Awane, Asia Display, p. 255 (1995).
[4] Y. Kim, J. Francl, B. Taheri, and J. L. West, Appl. Phys. Lett. 72, 2253 (1998).
[5] G. R. Magyar, J. L. West, B. Taheri, Y. Kim, and V. Bodnar, SID Digest of Technical Papers 30, 664 (1999).
[6] V. Bodnar, J. Francl, B. Taheri, and J. L. West, Journal of SID 6/4, 227 (1998).
[7] T. Qian, J.-H. Kim, S. Kumar, and P. L. Taylor, Phys. Rev. E 61, 4007 (2000).
[8] P. S. Drzaic, Liquid Crystal Dispersions (World Scientific, Singapore, 1995).
[9] T. J. Scheffer, SID Seminar Lecture Notes S-7, May, 1986 (unpublished).