

## Phase separated composite films of liquid crystals

VALERY VORFLUSEV, JAE-HOON KIM and SATYENDRA KUMAR

Department of Physics, Kent State University, Kent, OH 44242, USA

Email: satyen@xray.kent.edu

**Abstract.** Phase separation of liquid crystals from a solution with polymers has long been studied and used to prepare polymer stabilized and polymer dispersed structures. They are formed by spatially isotropic phase separation. A new mode, in which the phase separation proceeds anisotropically, has recently been discovered. Known as phase separated composite films (PSCOF), the resultant structures are made of adjacent parallel layers of liquid crystal and solidified polymer. PSCOFs have been made with nematic, ferroelectric (FLC), and antiferroelectric (AFLC) liquid crystals. Liquid crystals in PSCOFs exhibit electro-optical properties not observed in devices prepared by conventional methods, polymer dispersion, or polymer stabilization methods. Devices incorporating FLCs possess grey scale and switch 100 times faster at low fields than conventional surface stabilized devices. This method makes it possible to prepare very flexible devices and devices with liquid crystal film thickness comparable to optical wavelengths with great ease.

**Keywords.** Phase separation; composite films; liquid crystal electro-optics.

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### 1. Introduction

Conventional electro-optical devices based on liquid crystals (LC) are prepared by sandwiching LC between two glass substrates with alignment layers to facilitate alignment of the LC's optical axis in a predetermined configuration. In recent years, dispersions of microscopic liquid crystal droplets in a polymer matrix have been developed [1–4]. Polymer dispersed liquid crystal (PDLC) devices operate in the scattering mode, where an electric field is used not to change the birefringence but the extent of light scattered by LC droplets due to a mismatch of refractive indices at the droplet boundary. PDLC structures are a result of isotropic and relatively fast phase separation. Here, we report a method of preparing LC based electro-optic devices using anisotropic phase separation of LC from its solution with a prepolymer [5]. The rate of phase separation is controlled and deliberately kept low to allow the system to undergo a complete phase separation in to regions of LC and solid polymer. This phase separated composite film (PSCOF) method can, in general, be used to prepare multi-layer structures either parallel or perpendicular to substrates. In the simplest case, it yields adjacent uniform layers of the LC and polymer. The configuration of the optic axis in the LC layer can be controlled with an alignment layer on the substrate closest to the LC layer. The operation of such PSCOF devices relies on changes in the direction of optic axis in response to an applied electric field, as in conventional displays.

## 2. Preparation of PSCOF structures

The method used to prepare PSCOF structures is essentially the same as that used for building PDLC devices. One starts with a pair of substrates coated with transparent electrodes of indium–tin oxide (ITO). One of the substrates is spin-coated with an alignment layer of a commonly used polymer, such as polyimide (PI) or poly-vinyl alcohol (PVA), which is rubbed. The other substrate is left untreated. They are separated by glass rod or bead spacers of diameter  $d$  commonly used in the LC display industry. We used commercially available photocurable prepolymer (Norland) NOA-65 and liquid crystals. The prepolymer and the LC are mixed in the ratio 60 : 40 and introduced in to the cell by capillary action at a temperature well above the clearing point of the LC.

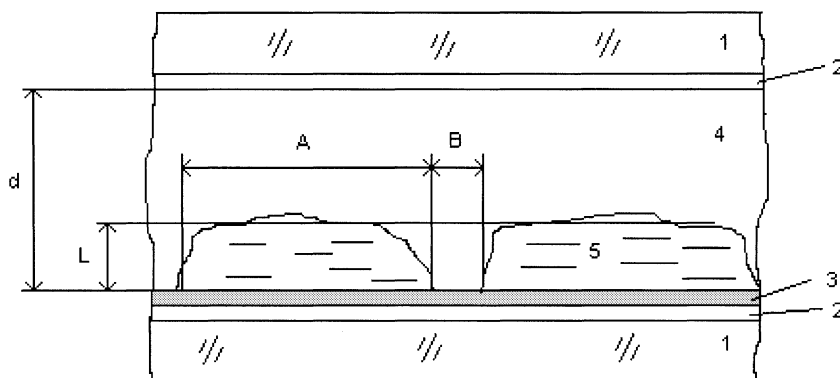
Phase separation is initiated by exposing the cell to UV light ( $\lambda = 350$  nm) through the substrate without the PVA alignment layer. The source of UV light is a Xenon (Oriental model 6269) lamp operated at 200 W of electrical power. The cell is exposed to a collimated beam of UV for approximately 5 min. To determine the internal structure of devices obtained in this manner, several cells were opened and washed with a solvent to remove the LC and then observed under a scanning electron microscope (SEM). As is evident from figure 1, phase separation results in a solidified film of polymer on the substrate close to the UV source and a liquid crystal film between the polymer film and the second substrate.

The LC (nematic, FLC, or AFLC) acquires a homogeneous alignment due to the influence of the rubbed alignment layer on the adjacent substrate. The LC and polymer films are uniform except in regions where the polymer-LC interface bonds to the opposite

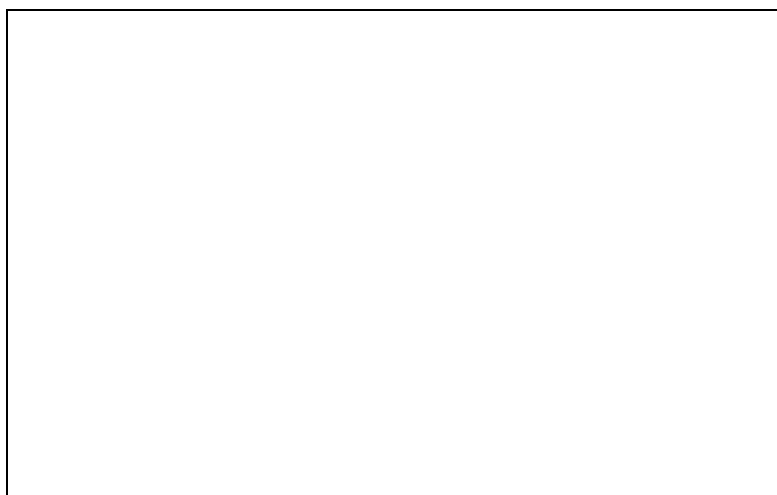


**Figure 1.** Polymer film on a glass substrate inside a PSCOF cell. B marks areas that were bonded to the upper substrate.

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**Figure 2.** Schematic presentation of the PSCOF structure. Here, areas A and B represent the lateral dimension of LC regions and the size of the regions where polymer film bonds to the second substrate.  $d$  and  $L$  are the cell gap and the thickness of LC film. 1, 2, 3, 4, and 5 are glass substrates, conducting film ITO, alignment layer, polymer and LC regions, respectively.



**Figure 3.** PSCOF film of Chisso-2004 in  $3\ \mu\text{m}$  cell. The small and large black dots are polymer B areas ( $\sim 1\ \mu\text{m}$ ) and spacers, respectively.

substrate at sites such as marked by areas B in figures 1 and 2. These bonding sites are affected by the concentration and chemical nature of the LC compound, the alignment layer, the rate of phase separation, and the cell thickness  $d$ . The process can be optimized to reduce the average size (to  $\sim 1\ \mu\text{m}$ , figure 3) and control the number of these bonding sites resulting in an almost perfectly uniform LC film.

Measurements on PSCOF cells, prepared with different concentrations of nematic liquid crystal E7 and prepolymer NOA-65, show that the thickness of the LC layer depends directly on the amount of LC in the mixture and that only a small amount of LC is trapped in the polymer film. Light scattered by the trapped LC is found to be negligible.

The mechanism responsible for the formation of PSCOF is similar to the anisotropic polymerization [6]. Because the absorption of the UV light is predominantly by the LC molecules in the solution, an intensity gradient is produced in the sample. Consequently, NOA-65 molecules first undergo polymerization near the substrate closest to the UV source and LC molecules are expelled from the polymerized volume forcing them to move away from the source. Droplet formation is inhibited because of relatively slow rate of phase separation and fast diffusion of the relatively small LC molecules. Consequently, the phase separated liquid crystal moves closer to the second substrate towards the region of lower UV intensity.

The presence of a PVA alignment layer on the substrate in contact with LC enhances the formation of uniform layers. In its presence, a PSCOF structure (parallel layer morphology) is obtainable at higher UV intensities (i.e., faster phase separation) for a range (1–5  $\mu\text{m}$ ) of cell thicknesses that we have studied. This suggests that the LC material wets the PVA alignment layer and easily spreads over it. The LC molecules near the alignment layer respond to its anchoring potential and align parallel to the rubbing direction. The volume of aligned LC grows during the phase separation process. Oriented LC molecules determine the microscopic structure of the polymer-LC interface which becomes compatible with their alignment. Although the use of one alignment layer can normally produce only homogeneously aligned cells, we have successfully prepared twisted nematic devices [4] by adding a chiral dopant to induce a twisted structure.

### **3. Advantages of the PSCOF method**

The PSCOF technology, because of its simple fabrication process and unique internal structure, provides a number of advantages as discussed below.

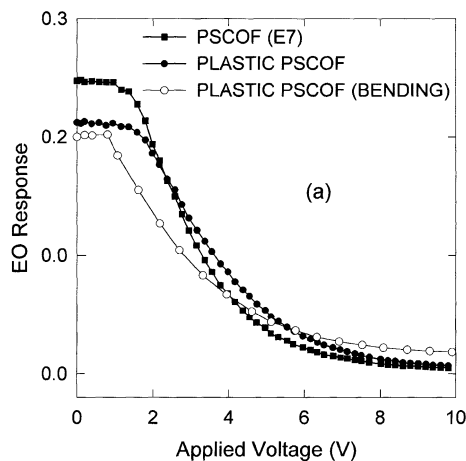
#### *3.1 Easy control of cell thickness*

LC films of practically any thickness can be prepared without the use of spacers of that size. Thin cells can be prepared using spacers of larger size which are easily available, have smaller size distribution, and cost less. The concentration can be varied to obtain precisely the desired thickness. This enables one to precisely fine tune the optical path length of the device. Furthermore, cells prepared with the PSCOF method tend to be very uniform. Devices with uniform and homogeneously aligned nematic LC film of thicknesses as small as 0.8  $\mu\text{m}$  ( $\sim 200$  molecules) have been successfully prepared using 3  $\mu\text{m}$  spacers. Still thinner films are possible.

#### *3.2 Mechanical ruggedness*

The polymer-LC interface in PSCOF binds to the substrate adjacent to the LC at a large number of randomly distributed but microscopic points thus providing it rigidity and strength and thereby decreasing the sensitivity to external mechanical deformations without compromising performance. Such mechanical deformations are known to render the SSFLC devices [7] impractical and have been one of the major obstacles to their commercialization. Under a large local pressure, such cells exhibit temporary changes in thickness. Their thickness reverts back to the original value within 5–15 sec after the pressure is released.

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**Figure 4.** (a) Transmission characteristics of a glass PSCOF cell, a 5 cm long flexible plastic substrate PSCOF cell, and the plastic cell bent in the middle by 1 cm, as shown in (b). Both cells were filled with nematic E7.

### 3.3 Flexibility

Because of the internal structure, where the two substrates are bonded to each other by the LC-polymer interface as discussed above, the PSCOF method lends itself to preparation of cells that are very flexible. Measurements on 5 cm long cells, deformed in the middle by 1 cm to form an arc, reveal no internal changes in the director configuration. Apparently, PSCOF devices are ideally suited for flexible display [8]. Figure 4(a) shows the characteristics of a PSCOF cell with glass substrates along with flexible substrates without and with 40% bending (figure 4(b)). The small change upon bending is due to the fact that the cell's optic axis is now on a curved substrate. The characteristic returns to that of unbent state when the pressure is released. We have made similar cells with nematic and (quite remarkably) ferroelectric LCs, all able to withstand the mechanical deformation.

### 3.4 Ideal method for active matrix LC devices

Only one alignment layer is required to align the LC in PSCOF devices. During the phase separation process, the LC imprints its own anchoring conditions compatible

with the alignment dictated by the rubbed surface. We have prepared TN and STN devices with alignment layer by adding a small amount of cholesteric material to induce appropriate twist.

All of the results presented here are obtained on PSCOF cells with only one alignment layer. In active matrix devices, the substrate with thin-film-transistors (TFT) can be selected to be the one without alignment layer, thus *eliminating the need for mechanical rubbing* which damages the TFT array and reduces the yield. The polymer film deposited on the TFT substrate *increases the overall resistivity and thus the charge holding time to several seconds* (e.g., more than 3.5 sec for FLC devices). This polymer film also helps to *eliminate electrical short circuits* in thin cells.

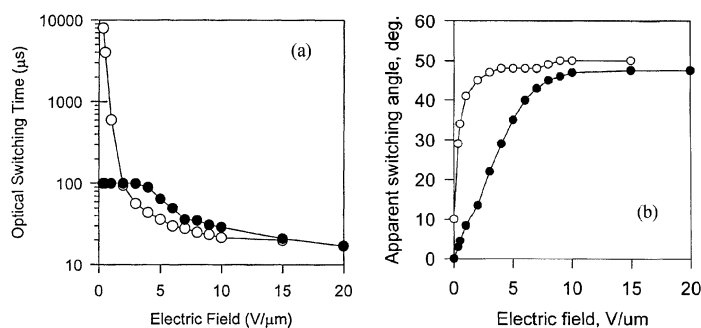
### 3.5 Modification of the electro-optical behavior

Additional major advantages of the PSCOF emerge from modification of electro-optical behavior of ferroelectric and antiferroelectric LCs. These features are discussed in detail in the following sections.

## 4. Ferroelectric LC devices

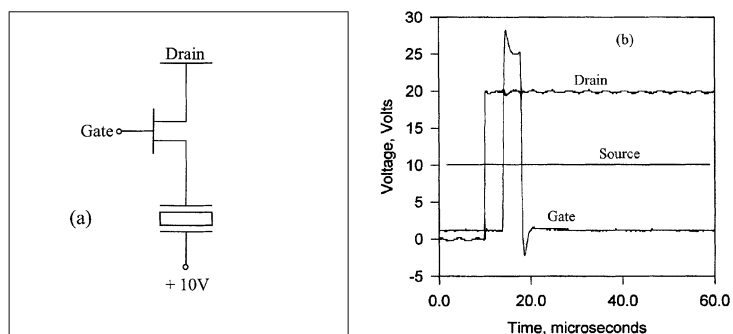
The SSFLC cells exhibit bistability [7] and electric field dependent switching times (figure 5a). In a PSCOF device containing the liquid crystal Felix-15-100 (Hoechst, Germany), switching at low fields is two orders of magnitude faster than in SSFLC. Also, the switching angle, which is the difference in molecular orientations in on and off states, is found to continuously depend on the applied field (figure 5b).

The switching angle in an FLC device determines its optical transmission between crossed-polarizers. Consequently, they *possess a continuous and natural gray scale* which is necessary in most applications. Overall light throughput in PSCOFs is much higher than ferroelectric [9, 10] PDLCs (PDFLC) because the light scattering from the small number of LC droplets embedded in the polymer film is negligible. The switching voltages are also much lower than those of the PDFLC.

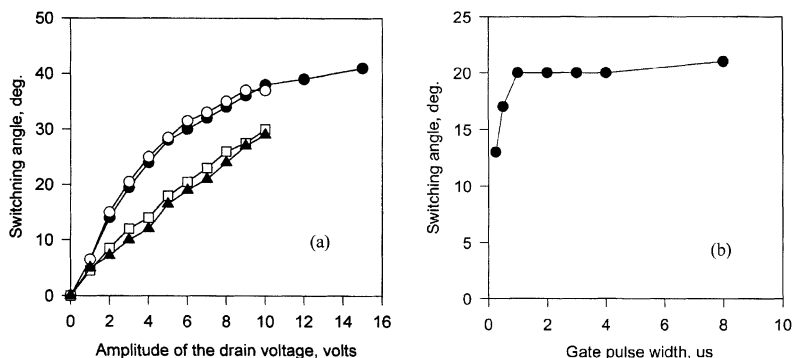


**Figure 5.** (a) Field dependence of switching time of SSFLC (open circles) and PSCOF cells (filled circles). (b) Comparison of transmission characteristics of SSFLC and PSCOF cells. The gray scale of the PSCOF device is evident.

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**Figure 6.** (a) The connections between the transistor and the LC cells are shown. (b) Source, drain and gate signals applied in the simulated active matrix mode using a MOSFET transistor.



**Figure 7.** (a) Dependence of switching angle on drain voltage, (b) Switching angle for different gate pulse widths at 6 V amplitude of drain voltage. The switching angle remains unaffected for gate pulses  $> 1 \mu\text{s}$ .

### 5. FLC-PSCOF devices in active matrix addressing mode

The suitability of FLC-PSCOF devices in active matrix (AM) addressing mode is examined in simulated AM mode using an external MOSFET transistor. The transistor was connected to the cells as shown in figure 6a. One side of the cell was kept at 10 V, while the other was connected to the source of the MOSFET. The drain voltage was square wave modulated between 0 and 20 V, thereby producing a square wave signal between  $-10$  and 10 V across the cell. The gate was opened for a short period,  $\tau$ , to effectively connect the drain to the cell, after the drain voltage changed polarity, figure 6b. The effective switching angle of the ferroelectric LC was measured for different drain voltages while reducing  $\tau$ .

Figure 7a and b show the effect of changes in the amplitude of the voltage drop across the cell and of changing gate pulse width for drain voltage at roughly half the transmission (or  $20^\circ$  switching angle). The transmission curve changes gradually as  $\tau$  is reduced, but in all cases it reaches maximum at roughly the same voltage. On the other

hand, for the fixed drain voltage of 6 V, the switching angle remains essentially unchanged down to a value of 1  $\mu$ s.

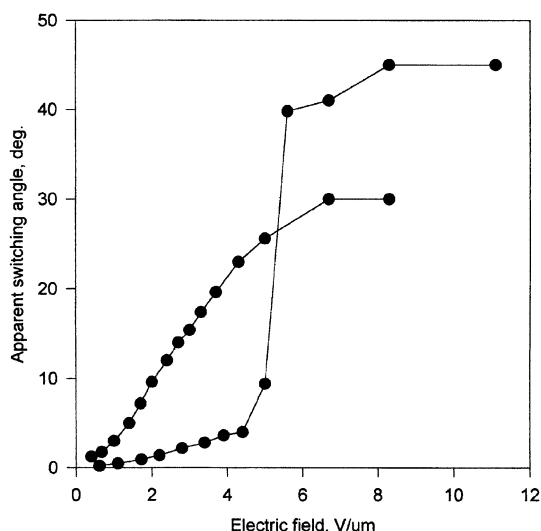
We believe that the drop for smaller  $\tau$  is due to less than ideal experimental conditions. In any case, taking the shortest usable gate pulse period to be 1  $\mu$ s, these devices are capable addressing 8000 lines at a refresh rate of 120 Hz! With further optimization of LC material and the PSCOF process it should be possible to reduce the value of shortest  $\tau$  further.

It should be pointed out that owing to higher resistivity of the internal polymer layer in cells prepared with PSCOF process, the charge retention time is increased. The cell maintains its transmission higher than 99% of the maximum for a long period of 3.5 sec. This is 10 times longer than that considered to be optimum for AMLCD devices using nematic LCs.

## 6. Antiferroelectric LC device

The electro-optical response of an AFLC–PSCOF is different from that of the pure (or surface stabilized) AFLC. In the latter, the antiferroelectric order is deformed at small field strengths. At high fields, a sharp transition from the antiferroelectric to the field induced ferroelectric state is observed [11]. This behavior is illustrated in the dependence of the apparent switching angle on the applied voltage at 75°C in the antiferroelectric phase of MHPOBC (figure 8).

After the field has been switched off, the system returns to the same antiferroelectric state. In the PSCOF structure, AFLCs exhibit threshold-less response without a transition to the field-induced ferroelectric phase. AFLC order in PSCOFs is able to withstand a much higher deformation and provide a grey scale. Furthermore, they exhibit optical



**Figure 8.** Comparison of electro-optical response of an AFLC conventional cell with PSCOF cell. In the PSCOF structure, there is no sharp transition to ferroelectric response.



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memory (bistability) as the optical transmission levels in which these devices remain after the application of positive and negative pulses are different.

The mesogenic properties of LCs do not play any role in the formation of multi-films. The phase separation can be performed in the isotropic phase, which widens the range of possible applications of the PSCOF technology to non-liquid crystalline areas. This technology should permit one to prepare sandwiches of LC between polymer films and vice-versa and self-supporting thin and flexible displays. Fabrication of multilayer structures perpendicular to the substrate, for use in switchable gratings and other diffractive optics applications, are possible with the use of masks during the phase separation.

### **Acknowledgments**

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### **References**

- [1] P Drzaic, *Liquid Crystal Dispersions* (World Scientific, 1995)
- [2] G Crawford and S Zumer (eds), *Liquid Crystals in Complex Geometries* (Taylor & Francis, 1996)
- [3] J W Doane, N A Vaz, B G Wu and S Zumer, *Appl. Phys. Lett.* **48**, 269 (1986)
- [4] L Blinov and V Chigrinov, *Electrooptical Effects in Liquid Crystals* (Springer Verlag, 1993)
- [5] V Vorflusev and S Kumar, *Science* **283**, 1903 (1999)
- [6] V Krongauz, E Schmelzer and R Yohannan, *Polymer*. **32**, 1654 (1991)
- [7] N A Clark and S T Lagerwall, *Appl. Phys. Lett.* **36**, 899 (1980)
- [8] R Buerkle, R Klette, E Luedar, R Bunz and T Kalltass, *SID'97 Digest* **28**, 109 (1997).
- [9] V Vorflusev and S Kumar, *Ferroelectrics* **213**, 117 (1998)
- [10] K Lee, S W Suh and S D Lee, *Appl. Phys. Lett.* **64**, 718 (1994)
- [11] A Fukuda, Y Takanishi, T Isozaki, K Ishikawa and H Takezoe, *J. Mater. Chem.* **4**, 997 (1994)