

## Confinement Effect on Ferroelectric Properties of Liquid Crystal -Polymer Composites

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We report the confinement effect on ferroelectric properties of a polymer-dispersed ferroelectric liquid crystal (PDFLC). Ferroelectric liquid crystal (FLC) droplets are formed in a photo-sensitive polymer matrix and they exhibit the ferroelectric switching in a restricted geometry. It is found that PDFLC exhibits essentially no hysteresis and no threshold in the electro-optic response. The relaxation associated with the collective molecular rotation is on the order of a hundred microsecond. It is suggested that the ferroelectric properties in a restricted geometry are primarily governed by the microscopic molecular environment such as the layer ordering, the phase sequence and the pitch of the smectic C\* phase. The role of anisotropic interactions at the FLC/polymer interface on the surface ordering is also discussed.

### I. INTRODUCTION

The surface effects at a liquid crystal/polymer interface in a restricted geometry are of great importance for a basic understanding of interfacial phenomena as well as for device applications of liquid crystals (LCs). One of confinement effects can be easily explored in micron-size LC droplets dispersed in a continuous polymer matrix. In such confined LCs, a configuration transition [1], broadening and rounding of phase transitions [2], a slow dynamics of phase transitions [3], and a continuous ferroelectric effect [4] have been recently established. The physical properties of these materials are altered by several parameters such as the type of polymer matrix and LC used, the dimension of LC droplets, and the nature of surface ordering. Among them, of particular importance is anisotropic interactions at the LC/polymer interface which is governed by local microscopic environment of LC droplets.

In this paper we present the ferroelectric properties of a smectic C\* (Sm C\*) LC dispersed in a polymer matrix so that the confinement effect is examined in terms of molecular chirality, the phase transition sequence, and the nature of layer ordering. Due to the finite-size effect, the first-order transition becomes weak, and the polarization reversal current is greatly suppressed and appeared in delayed time. Experimental results for temperature- and field-dependences of the spontaneous polarization in a bulk ferroelectric LC (FLC) and a polymer-dispersed FLC (PDFLC) are presented, and the essential differences between them are described in terms of the confinement effect. Moreover, a fast linear electro-optic effect is observed, which has no hysteresis and no threshold for the EO switching. In Section II, details of sample preparation and measurements of the spontaneous polarization and the electro-optic (EO) response of the PDFLC are described. Experimental results are presented and discussed in Section III. In the remaining section some conclusions are made.

### II. EXPERIMENTAL

FLC cells are made up of conductive indium-tin-oxide-coated glasses, which were treated with a surfactant, poly(1,4-butylene terephthalate) [5]. The thickness of the polymer layer was about 300 Å, and the internal surfaces of the cell were unidirectionally rubbed so as to give sites for planar, homogeneous growth of LC [6]. The cell gap was maintained by glass spacers of 5 μm thick, and the effective electrode area was 0.64 × 0.64 cm<sup>2</sup>. The FLC material was filled in the isotropic state and cooled into the mesophase. Electrical contacts were made directly to the internal surfaces of the glass so that the ferroelectric switching of the material could be studied by the application of an external electric field.

PDFLC composites are formed by a two-step process; first, a low-molecular weight FLC and a polymer precursor are initially mixed together to form a uniform solution; second, the polymer is hardened, during which process the FLC phase separates from the matrix as microdroplets. Hardening can be carried out by several methods [7-9]. We used the ultraviolet (UV)-curing technique to increase matrix molecular weight via cross-linking reactions [9,10]. The volume fraction of the FLC in the polymer matrix is about 50%. Typically, the LC concentration is in the range of 10% to 60% in volume. The complete mixture was introduced into the sample cell in the isotropic state, followed by UV curing for a few minutes. The UV light intensity used for curing the sample was about 10 mW/cm<sup>2</sup>.

The FLC material used in this study was CS2004 of Chisso, and the polymer matrix was a UV-curable optical adhesive (NOA61) of Norland, a blend of monomers, oligomers, and a photoinitiator [11]. The FLC has a ferroelectric smectic C\* (Sm C\*) phase at room temperature, and no smectic A (Sm A) phase is present. The phase sequence of this material is as follows: isotropic - cholesteric (Ch) - Sm C\* - crystalline phase.

The sample cell was mounted in a microfurnace for

measuring the spontaneous polarization with varying temperature. The study of the alignment and domain structures of FLC microdroplets in the polymer matrix has been reported previously [4,12]. Temperature fluctuations inherent to the furnace were approximately  $0.01^\circ\text{C}$ . For a direct measurement of the polarization, we used the triangular wave method which is easy for subtracting the background current [13]. The polarization current, converted into a voltage signal through an amplifier, is measured in a digitizing oscilloscope and fed into a computer for data analyses. The amplitude of an applied voltage was randomly generated by an arbitrary waveform generator so as to avoid any systematic error involved.

The EO response of the PDFLC to an external electric field was measured by monitoring the change in the transmitted light intensity through the sample cell between crossed polarizers. The transmission through the PDFLC was about 60 %, diminished by scattering. Measurements were made with a 50 Hz square wave of variable amplitude at room temperature. The sample cell was placed such that one of the crossed polarizers made an angle of  $22.5^\circ$ , which maximized the optical modulation.

In the following section, we first present experimental results for the spontaneous polarizations in both the FLC and the PDFLC, and show the EO characteristics of the PDFLC which are quite different from those of a surface-stabilized FLC (SSFLC) [14]. The main features of the experimental data are then described in terms of the confinement effect.

### III. RESULTS AND DISCUSSION

Fig. 1 shows the polarization reversal currents in a confined PDFLC and a bulk FLC at  $30.0^\circ\text{C}$ . Each polarization current consists of the capacitive, resistive, and polarization reversal parts. As shown in Fig. 1, the capacitive part of the PDFLC is much higher than that of the FLC, and its current peak is shifted because of the contribution from the polymer matrix. Moreover, the suppression of the current peak comes from the finite-size effect which will significantly alter the nature of anisotropic interactions at the FLC/polymer interface. From x-ray measurements, it was found [15] that the smectic layers in finite-size droplets are formed only near the interface since the growth of the smectic layers around the center of the droplets in the Ch phase is not energetically favorable. In this case, the smectic layers will be less ordered, and thus the electric field needed for reorienting the molecules is higher in a microdroplet than in the bulk. As the helical pitch in the Ch phase increases, the formation of more ordered smectic layers will be favored, and therefore the suppression of the current peak

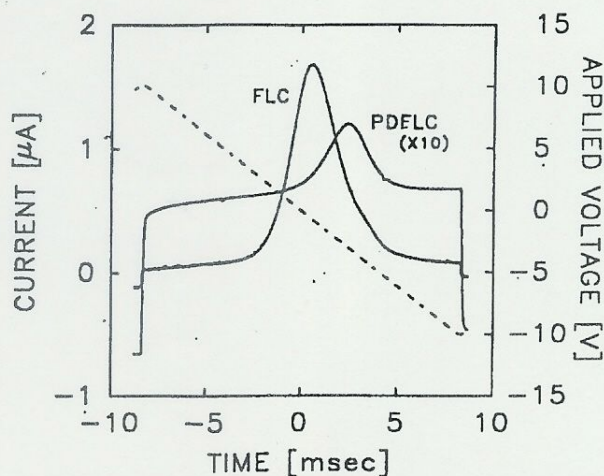


Fig. 1. Polarization reversal currents for the FLC and the PDFLC at  $30.0^\circ\text{C}$ . The dashed line represents the applied voltage of 30Hz.

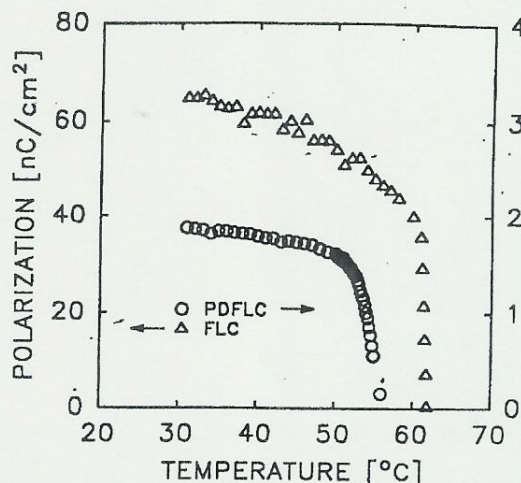


Fig. 2. Temperature-dependence of the spontaneous polarization  $P_s$  in the FLC and the PDFLC, measured with a triangular wave of 10 V at 30 Hz. The triangular and circular symbols represent the FLC and the PDFLC, respectively.

becomes less pronounced. Fig. 2 shows the temperature-dependence of the spontaneous polarization in both the FLC and the PDFLC. A triangular wave of 10 V at 30 Hz was used for measuring the polarization reversal current. From Fig. 2, it is clear that in relative to the FLC, the PDFLC exhibits a shift, broadening, and rounding of the phase transition. In the confined PDFLC, the critical temperature,  $T_c$ , for the Ch - Sm C\* phase transition was found to be  $56.0^\circ\text{C}$  which is about  $5.9^\circ\text{C}$  lower than that in the bulk FLC. Probably, the elastic strain stored in the microdroplets and possible chemical impurities caused this shift. One indication is that calorimetric measurements showed a small shift

in the nematic-isotropic transition for nCB LCs confined in membrane pores [2]. However, no shift in a direct isotropic - Sm A transition was detected. Note that in our case the Ch - Sm C\* transition is involved. Furthermore, molecular chirality as well as ferroelectricity should be taken into account for the large shift observed in our PDFLC. Physically, both the elastic distortion and the disorder of smectic layers are primarily responsible for such a large shift in the Ch - Sm A\* transition. Chemically, a subtle change in anisotropic interactions at the FLC/polymer plays a secondary role in the transition shift.

As shown in Fig. 2, the Ch - Sm C\* transition temperatures for the PDFLC and the FLC are 56.0° C and 61.9° C, respectively. A weakly first order-like behavior was observed in the PDFLC. In addition, the spontaneous polarization  $P_s$  of the PDFLC is about 30 times less than that of the FLC. This manifests itself as one of the confinement effects. A simple mean-field prediction for the second order Sm A - Sm C\* transition,  $P_s \propto (T - T_c)^{1/2}$ , can not fit the experimental data. This tells us that the transition for the PDFLC possesses still a first order-like nature although it shows a gradual change in  $P_s$ . With varying the droplet size, i. e., the elastic distortion energy stored in the droplets, a second order transition for the PDFLC could be achieved.

We now discuss the results for the field-dependence of  $P_s$ , measured with a triangular wave of 30 Hz at 45.0° C. The polarization  $P_s$  in the FLC as well as the PDFLC are shown in Fig. 3. For the FLC,  $P_s$  saturates at about 2 V/ $\mu$ m and remains constant in the high field regime, which is similar to that for a bulk FLC [16]. For the PDFLC, however,  $P_s$  increases almost linearly with the electric field except for the low field regime ( $\leq 1$  V/ $\mu$ m), and keeps increasing without a limit in the range of the field we studied. We speculate that the helix unwinding process is dominant in the low field regime while the layer ordering process within the finite-size droplets plays a critical role in  $P_s$  at relatively high fields. Note that the elastic distortion energy increases with decreasing the droplet size. Therefore, the energy cost to reorient the molecules in a smaller droplet will be higher than that in a larger one. In other words, the ferroelectric switching in less ordered smectic layers will require more energy and it will occur only at higher fields. This is also supported by the results for the temperature-dependence of  $P_s$ .

Now, we describe the EO characteristics of the PDFLC and the relaxation of the collective molecular rotation in the droplet structure. The optical transmission of the PDFLC, showing a nearly linear EO effect at relatively low fields, is plotted as a function of the field in Fig. 4. With increasing the field  $E$  above 2.5 V/ $\mu$ m, the transmission becomes saturated. This is attributed to a continuous unwinding of the helix, in which process the molecules tend to orient along the field direction, keeping the tilt angle fixed. In contrast to SSFLCs [14], the

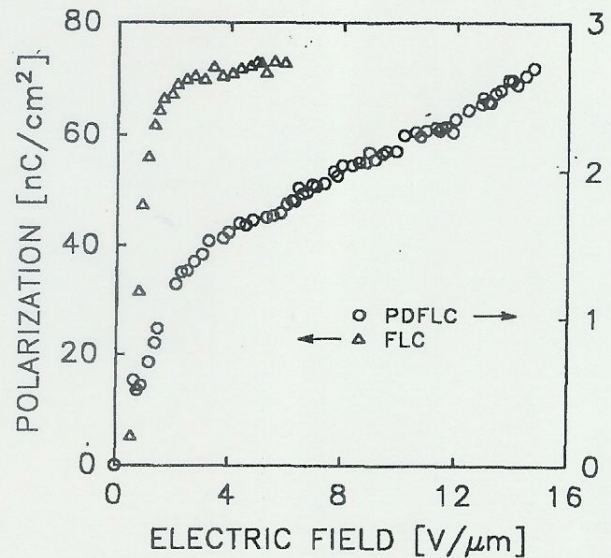


Fig. 3. Field-dependence of the spontaneous polarization  $P_s$  in the FLC and the PDFLC, measured with a triangular wave at 30 Hz. The temperature was kept at 45.0° C. The triangular and circular symbols represent the FLC and the PDFLC, respectively.

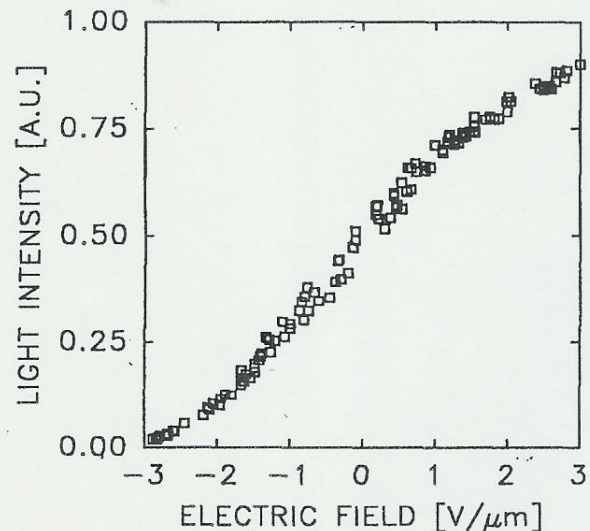


Fig. 4. The optical transmission of the PDFLC as a function of the field  $E$  at room temperature.

PDFLC has essentially no hysteresis and no threshold for the EO switching. Again, this is consistent with the results for the field-dependence of  $P_s$ .

Fig. 5 shows the EO response time as a function of the electric field  $E$ . The response time decreases with increasing the field, and it is on the order of a hundred microsecond. Generally, it is known to be inversely proportional to  $E$ , which is an intrinsic property of the ferroelectric switching. Strictly speaking, the functional form

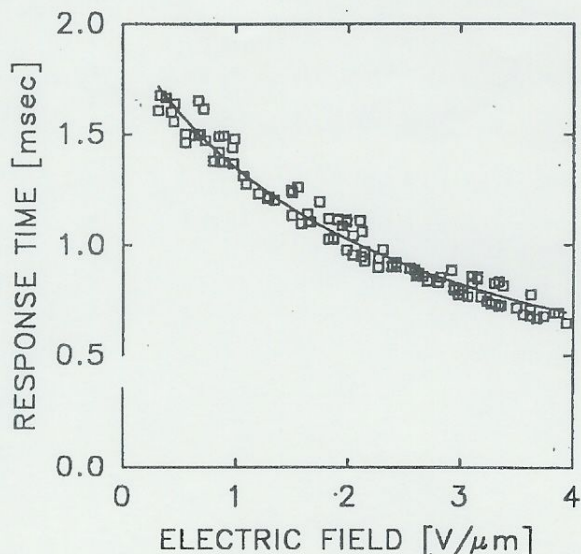


Fig. 5. The EO response time of the PDFLC as a function of the field  $E$  at room temperature.

will not be exactly  $E^{-1}$  but there is a shift due to the elastic relaxation in a restricted geometry.

#### IV. CONCLUDING REMARKS

We have presented temperature- and field-dependences of the spontaneous polarization in both a bulk FLC and a PDFLC composite. The shift, broadening, and rounding of the Ch - Sm C\* transition were described in terms of the confinement effect. The associated ferroelectric switching, resulting from the polarization reversal, strongly depends on the elastic distortion, the layer ordering, and the anisotropic interactions at the FLC/polymer interface. Moreover, the EO characteristics of the PDFLC composite exhibits essentially no hysteresis and no threshold, which is consistent with the results for the polarization. The relaxation of the collective molecular rotation is on the order of a hundred microsecond. It is suggested that the ferroelectric properties in a restricted geometry are primarily governed by the microscopic molecular environment such as the layer

ordering, the phase sequence, and the pitch of the Sm C\* phase. Further studies on the surface ordering at the polymer/FLC interface will be useful for obtaining a complete picture of the confinement effect on other physical phenomena.

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#### REFERENCES

- [1] J. H. Erdmann, S. Zumer and J. W. Doane, *Phys. Rev. Lett.* **64**, 1907 (1990).
- [2] G. S. Iannacchione and D. Finotello, *Phys. Rev. Lett.* **69**, 2094 (1992).
- [3] H.-S. Kitzerow, H. Molsen and G. Heppke, *Appl. Phys. Lett.* **60**, 3093 (1992).
- [4] K. Lee, S.-W. Suh and S.-D. Lee, *Appl. Phys. Lett.*, in press (1994).
- [5] J. S. Patel, T. M. Leslie and J. W. Goodby, *Ferroelectrics*, **59**, 137 (1984).
- [6] J. S. Patel and J. W. Goodby, *J. Appl. Phys.* **59**, 2355 (1986).
- [7] J. W. Doane, N. A. Vaz, B.-G. Wu and S. Zumer, *Appl. Phys. Lett.* **48**, 269 (1986).
- [8] J. L. West, *Mol. Cryst. Liq. Cryst.* **157**, 427 (1988).
- [9] N. A. Vaz, G. W. Smith and G. P. Montgomery, Jr., *Mol. Cryst. Liq. Cryst.* **146**, 1 (1987).
- [10] G. W. Smith, *Mol. Cryst. Liq. Cryst.* **196**, 89 (1992).
- [11] Norland Products, Inc., North Brunswick, NJ.
- [12] K. Lee, S.-W. Suh, and S.-D. Lee, *J. Korean Phys. Soc.*, in press (1994).
- [13] K. Miyasato, S. Abe, H. Takezoe, A. Fukuda and E. Kuze, *Jpn. J. Appl. Phys.* **22**, L661 (1983).
- [14] N. A. Clark and S. T. Lagerwall, *Appl. Phys. Lett.* **36**, 899 (1980).
- [15] J. T. Mang, K. Sakamoto and S. Kumer, in *Proc. of OLC* (Cocoa Beach, Florida, 1991).
- [16] J. S. Patel and J. W. Goodby, *Chem. Phys. Lett.* **137**, 91 (1987).