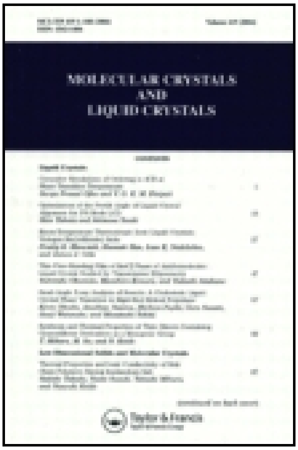

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

The effect of polymer networks on ferroelectric liquid crystals

S. N. Lee [a] & L.-C. Chien [a]
[a] Chemical Physics Interdisciplinary Program and Liquid Crystal Institute, Kent State University, Kent, OH, USA

To cite this article: S. N. Lee & L.-C. Chien (2004): The effect of polymer networks on ferroelectric liquid crystals, Molecular Crystals and Liquid Crystals, 410:1, 183-190

To link to this article: http://dx.doi.org/10.1080/15421400490436322

Mol. Cryst. Liq. Cryst., Vol. 410, pp. 183/[711]–190/[718], 2004

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490436322

THE EFFECT OF POLYMER NETWORKS ON FERROELECTRIC LIQUID CRYSTALS

S. N. Lee and L.-C. Chien[*]
Chemical Physics Interdisciplinary Program and Liquid Crystal Institute, Kent State University, Kent, OH 44242, USA

Using a relative small amount of reactive mesogenic monomer and a quasi-bookshelf texture of ferroelectric liquid crystals (FLCs) we developed submicron-scale templated polymer fibrils from the two-dimensionally ordered hosts. The polymer fibrils capture the orientation of the host with thin polymer fibrils interweaving the smectic layers that act as additional surfaces for controlling the reorientation of FLC molecules. The SEM study shows the difference in morphology of the polymer fibrils depending on the polymerization conditions and FLC hosts. There are two distinctive electro-optical properties of polymer modified FLC such as the fast switching at a lower applied field and the voltage independence of switching time achieved by polymer stabilization using a mesogenic monomer. Further, we describe how the polymer network and the type of FLC enhance the realization of V-shaped switching behavior.

Keywords: polymer network; polymer-stabilized ferroelectric liquid crystal; V-shaped switching

INTRODUCTION

The discovery of surface-stabilized ferroelectric liquid crystals (SSFLCs) [1] has attracted a great of interest of physical investigations and applications in flat panel displays (FPDs) in the last two decades. The characteristic features of SSFLCs such as fast response speed, bistability, and wide viewing angle have been regarded as the most likely candidate for the next generation of the FPDs. Despite of these advantages, defects of alignment – Rieker *et al.* [2] observed the chevron layer structure that usually results in zigzag defect in an SSFLC cell by using the X-ray diffraction method – have slowed down the FLC devices to become a major flat panel display product.

This research was supported in part by AFOSR and NSF ALCOM.

[*] Corresponding author. E-mail: lcchien@lci.kent.edu

Recently, several new ferroelectric liquid crystal displays (FLCDs) technologies were reported with the aims to improve the performance of FLCDs; for example, FLCDs exhibiting the thresholdless (V-shaped) [3,4] and half-V-shaped electro-optical switching [5]. Other approaches of fabricating FLCDs include using the side chain or main chain liquid crystalline polymers to enhance the FLC properties. Another breakthrough is by using a small concentration of polymer network to stabilize various optical states of FLCs and to realize the V-shaped or half-V-shaped switching behavior in polymer-stabilized FLCDs, depending on the conditions of forming polymer networks.

Polymer-stabilized liquid crystals (PSLCs) have rapidly developed into a unique class of electro-optical materials and led to the development of new display [6–8] and photonic [9–12] technologies. The polymer network morphology of PSLCs, unique among these applications, plays a critical role in the performance of each device. The PSLCs are typically formed via photopolymerizing of a small amount of reactive monomer and variety of optical pattern forming states of the nematic or cholesteric liquid crystal host [13]. Prior to polymerization the reactive monomer molecules follow the local director orientation of the liquid crystal. After polymerization, the resultant polymer networks not only mimic the phases and structures of the LC host, but also, under an applied external field, control the degree of reorientation of liquid crystal molecules in the vicinity of polymer network. The polymer morphology itself is of considerable interest in the study of polymerization-induced phase separation in orientationally-ordered media. Despite reports on polymer-stabilized ferroelectric liquid crystals (PSFLCs) [14–17] the specific polymer network morphology and its precise connection to the electro-optical properties of ferroelectric liquid crystal system remain open issues. It is the aim of this paper to exploit the morphology of polymer networks formed in FLCs. Specifically, we used two FLC mixtures having different phase sequences to investigate the influence of network morphology on electro-optical properties of the composites.

EXPERIMENTAL

The materials used for the preparation of PSFLCs were the FLC CS2005 (Chisso Japan) and FELIX M4851-100 (Clariant Japan) as the hosts (96.85 wt%), a reactive monomer RM257 (3 wt%, Merck), and a photo initiator Irgacure 651 (0.15 wt%, Ciba Additive). The FLC CS2005 has a cholesteric to a smectic C* phase transition and shows a tilt angle 43° at 25°C. The FLC FELIX M4851-100 has a smectic A to smectic C* transition and a tilt angle of 30° at 25°C. An example of a PSFLC sample was prepared by mixing CS2005, RM257 and IGC651 at a weight ratio percentage of

96.85: 3: 0.15. The mixtures of FLC/monomer/photo initiator were loaded into commercial electro-optical cells with 2 μm or 4 μm cell-gap between the anti-parallel rubbed polyimide alignment layers (electrode area of $1.0 \times 1.0\,\text{cm}^2$) by a capillary action. The polymer stabilization of the FLC mixtures were carried out by illuminating the sample using an UV light source of 365 nm and $0.4\,\text{mW/cm}^2$ at room temperature for 30 minutes and under the application of electric field ($5 \sim 10\,\text{V}/\mu\text{m}$, 34 Hz). Prior to polymerization the samples were heated on a hot stage to isotropic liquid and cooled to room temperature under the applied electric field. The FLC alignment and transition temperatures examined by using a polarizing optical microscopy indicated a slight decrease in transition temperatures compared to those of the FLCs because of the addition of a reactive monomer. The spontaneous polarization measurements on the pure and polymer-stabilized FLCs were carried out using a reported triangle wave method [18]. The polarization reversal current data were measured across a 30 **Ω** resistor and detected with a digital oscilloscope and transferred onto a PC for further evaluation. Before taking temperature dependence of polarization measurement, PSFLC samples were placed on a Mettler FP 5 hot stage for temperature control within 0.1 degree Celsius and the electric fields were applied using a function generator in combination with a power amplifier. Multiple measurements were taken for each temperature to reduce statistical errors. Other physical characterization including the response time, alignment, and polymer network morphology were carried out using a conventional technique. The tilt and switching angles were obtained by the optical extinction method [19].

RESULTS AND DISCUSSION

PSFLC of CS2005

Figure 1a shows the optical micrograph of a PSFLC prepared from FLC CS2005 at the absence of external field. The corresponding SEM image of the network morphology is shown in Fig. 1b. As one can see, submicron-scaled polymer fibrils are templated by the FLC host (follow the orientation of the host during the switching exhibiting thin root-shaped polymer fibrils), and located between the smectic layers. The defects in alignment contributes to the less uniform of polymer fibrils because the host FLC lacks of a smectic A phase.

The temperature dependence of spontaneous polarization of the PSFLC sample under the applied field of $5\,\text{V}/\mu\text{m}$ and 34 Hz (Fig. 2a) shows a maximum spontaneous polarization (P_S) value of $66\,\text{nC/cm}^2$ at 25°C. The measured spontaneous polarization shows a continuous increase with a decrease in temperature. Compared to the P_S value of host FLC CS2005

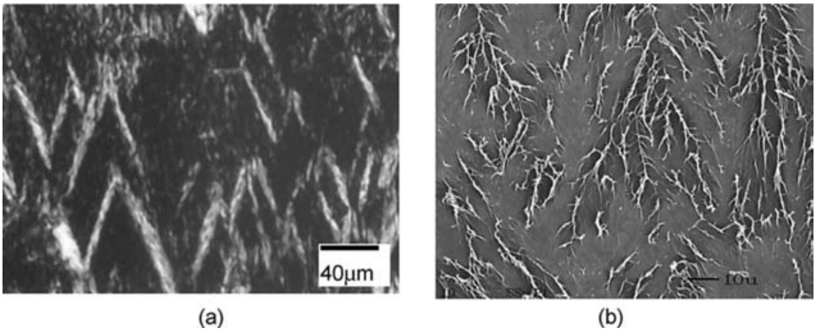

FIGURE 1 (a) The optical micrograph at the absence of external field and (b) the SEM image of polymer fibrils of a PSFLC prepared from FLC CS2005 and RM257.

(75 nC/cm^2 at 25°C), a slightly decrease in temperature dependence of spontaneous polarization of the PSFLC is observed. The decrease in P_S value is because of the formation of polymer network, which stifles the molecule tilt angle of the FLC.

Figure 2b shows the voltage dependence of spontaneous polarization of a PSFLC at various temperatures. As shown in Fig. 2b, we observed a slight decrease in Ps values of PSFLC compared with those of the pure FLC due to the smaller tilt angle as a result of the formation of polymer network in FLCs.

The measured voltage dependence of switching of the same PSFLC sample at various temperatures is illustrated in Fig. 3a. At higher temperature (55°C), the PSFLC shows faster switching times (~55 μs) than those of lower temperatures. Strikingly, the response time is fairly independent

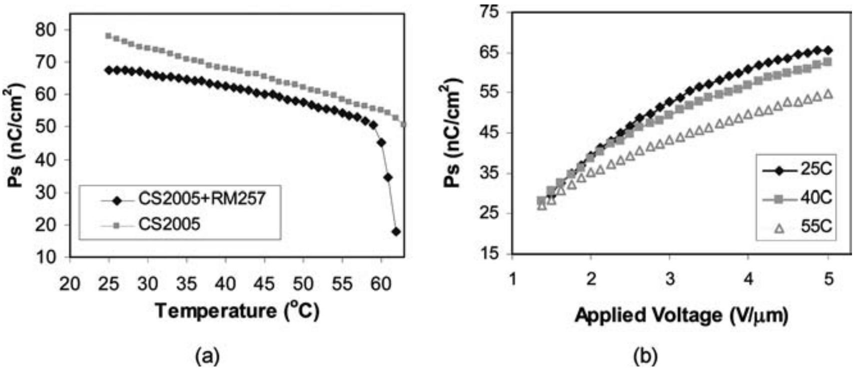

FIGURE 2 The plots of (a) the spontaneous polarization versus temperature and (b) the spontaneous polarization versus applied field at various temperatures for a PSFLC prepared from FLC CS2005 and RM257.

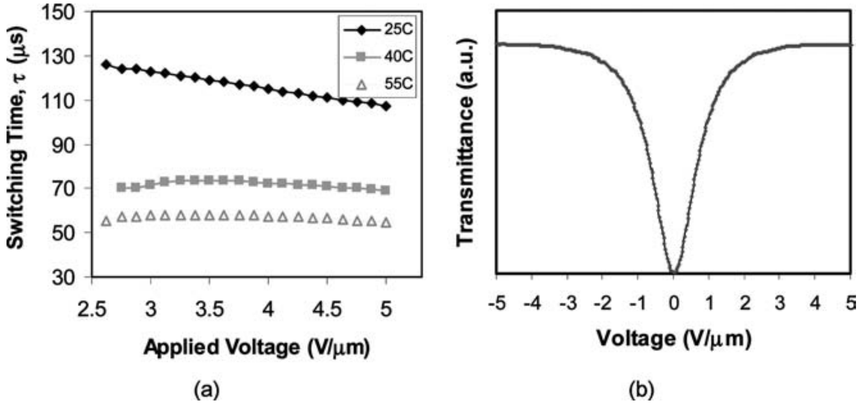

FIGURE 3 (a) The switching time versus applied voltage at various temperatures, and (b) the transmittance versus the applied voltage of a PSFLC prepared form FLC CS2005 and RM257.

on applied voltage for the PSFLC for the three measured temperatures, while the response time of a pure FLC sample depends on the applied field. Figure 3b illustrates the analog switching behavior of the PSFLC sample. As stated earlier, the occurrence of the analog (or V-shaped) switching behavior is because of the suppression of FLC symmetric rotation by the polymer network.

The temperature dependence of tilt angle of a PSFLC shows an approximately 40% decrease in tilt angle compared with pure FLC (Fig. 4a, 4 μm

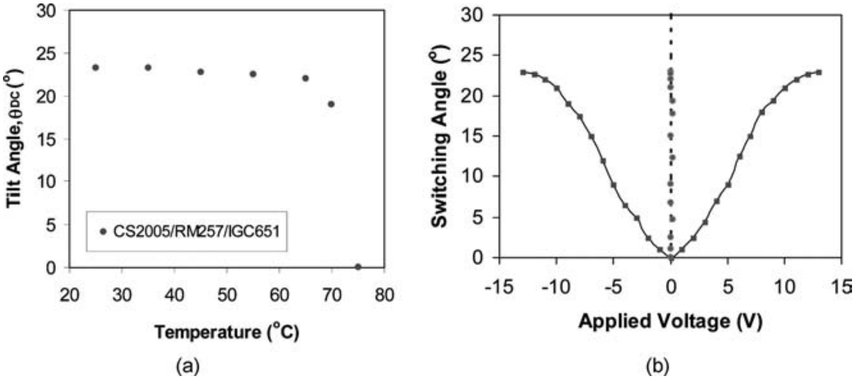

FIGURE 4 (a) Temperature dependence of the tilt angle and (b) applied voltage dependence of switching angle of a PSFLC prepared form FLC CS2005 and RM257. The open circles represent the deviation of mean values.

thickness cell). One interesting observation is that the tilt angle is fairly independent of temperature variation. Figure 4b shows the voltage dependence of the switching angle of a PSFLC with the application of a DC voltage across the cell at room temperature. Below ±10 volts of the applied voltage the measured value depends on the magnitude of the applied electric field, but above this value the switching angle saturates. The solid line through the data shows that the two optical states are symmetrically disposed about the extinction position in the smectic C phase. It is found that the mean values is slightly skewed towards one of the states, presumably due to asymmetry introduced by buffing one of the surfaces of the cell.

PSFLC of M4851-100

For the purpose of comparison, we studied the electro-optical properties of a PSFLC prepared from a FLC host with a smectic A phase. The transmittance versus applied field at 34 Hz, triangular wave of a PSFLC sample at room temperature is shown in Fig. 5. According to the measured T–V curve, the analog switching behavior is also observed for the PSFLC. On the right side, we show photomicrographs of textures switched by different applied voltages. This result serves as an evidence of optical gray scale achieved by a PSFLC device.

Figure 6 displays the optical textures and SEM images of PSFLC samples with 2-μm and 4-μm thickness cells. The applied electric fields are 5 V/μm during photopolymerization. The photomicrographs of the PSFLCs viewed between crossed polarizers at zero voltage, uniform stripped

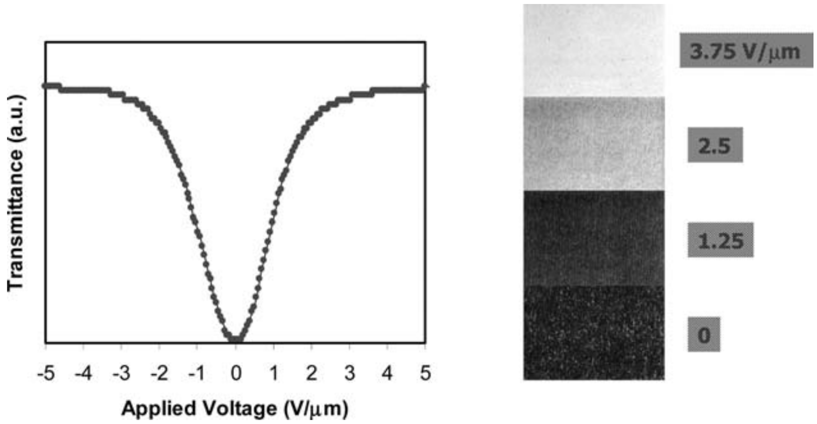

FIGURE 5 The transmittance versus applied field at 34 Hz, triangular wave of a PSFLC fabricated using M4851-100 and reactive monomer RM257 in 2-μm cell.

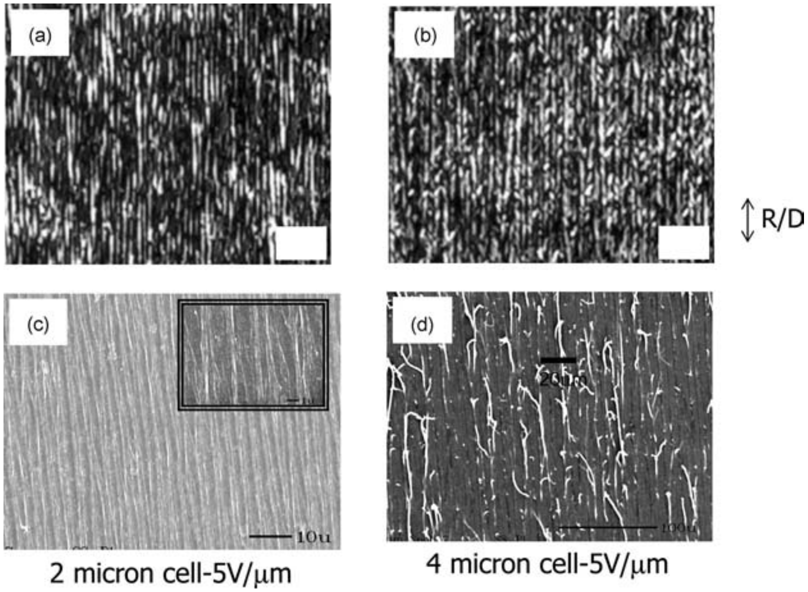

FIGURE 6 The optical textures (a,b) at the absence of external field and SEM images (c,d) of PSFLC samples (prepared from FLC M4851-100 and RM257 using 2 and 4 μm cells and under electric field 5 V/μm during photopolymerization).

textures are observed and the spacing of striped texture of the 2-μm cell (Fig. 6a) is much narrower compared with that of the 4-μm cell (Fig. 6b), indicating a better alignment.

The polymer network morphology is evaluated and the corresponding SEM pictures are shown in Fig. 6c and 6d. As one can see, the polymer fibrils aligned fairly well along the rubbing direction with a slightly variation in network orientation due to the switching during polymerization. Also, the densely-packed polymer fibrils are observed for the thinner sample cell as a result of total cell volume.

SUMMARY

We observed the formation of submicron-scale root-shaped or ordered polymer fibrils using the quasi-bookshelf optical texture of FLC as a template. For PSFLC sample of M4851-100 the polymer fibrils formed along the smectic layers act as the additional surfaces for controlling the reorientation of FLC molecules in the vicinity of polymer fibrils. The templated polymer fibrils suppress the symmetric rotation of FLC under applied field and transpire the occurrence of analog (V-shaped) switching with a better contrast between the bright and dark states corroborated by the PSFLC sample of M4851-100. A PSFLC sample of CS2005 shows unique features of fast switching at a lower applied field and voltage independence of switching. Our findings serve as a base for advancement in analog switching FLC displays.

REFERENCES

[1] Clark, N. A. & Lagerwall, S. T. (1980). *Appl. Phys. Lett.*, *36*, 899.
[2] Rieker, T. P., Clark, N. A., Parmar, G. S., Siro, E. B., & Safinya, C. R. (1987). *Phys. Rev. Lett.*, *59*, 2658.
[3] Inui, S., Iimura, N., Suzuki, T., Iwane, H., Muyachi, K., Takanishi, Y., Takezoe, H., & Fukuda, A. (1996). *J. Mater. Chem.*, *6*, 67.
[4] Yoshida, T., Tanaka, T., Ogura, J., Wakai, H., & Aoki, H. (1997). *SID Dig. Tech. Pap.*, *28*, 841.
[5] Asano, Y., Togano, T., Terada, M., Moriyama, T., Nakayama, S., & Iba, J. (1999). *Jpn. J. Apll. Phys.*, *38*, 5977.
[6] Chien, L.-C., *et al.* (1996). In: *Liquid-Crystalline Polymer Systems: Technological Advances*, ACS Symposium 632: Washington DC, Chap. 11.
[7] Yang, D. K., Chien, L.-C., Doane, J. W. (1992). *Apl. Phys. Lett.*, *60*, 3102.
[8] Yang, D. K., Chien, L.-C., & Fung, Y. K. (1996). In: *Liquid Crystals in Complex Geometries*, Crawford, G. P. & Zumer, S. (Eds.), Taylor and Francis: London, Chap. 4.
[9] Nose, T., Masuda, S., Sato, S., Li, J., L.-C. Chien, & Bos, P. J. (1997). *Opt. Lett.*, *22*, 351.
[10] Lee, S. N., Chien, L.-C., & Sprunt, S. (1998). *Appl. Phys. Lett.*, *72*, 885.
[11] Nourry, J., Sixou, P., Mitov, M., Glogarova, M., & Bubnov, A. M. (2000). *Liq. Cryst.*, *27*, 35.
[12] Lee, S. N., Sprunt, S., & Chien, L.-C. (2001). *Liq. Cryst.*, *28*, 637.
[13] Kang, S. W., Sprunt, S., & Chien, L.-C. (2001). *Adv. Mater.*, *13*, 1179.
[14] Hikmet, R. A. M., Boots, H. M. J., & Michielsen, M. (1995). *Liq. Cryst.*, *19*, 65.
[15] Li, J., Wang, A., Cai, Y., & Huang, X. (1998). *Ferroelectrics*, *213*, 91.
[16] Furue, H., Limura, Y., Hasebe, H., Takatsu, H., & Kobayashi, S. (1999). *Mol. Crst. Liq. Crst.*, *331*, 399.
[17] Dierking, I., Osipov, M. A., & Lagerwell, S. T. (2000). *Eur. Phys. J. E*, *2*, 303.
[18] Miyasato, K., Abe, S., Takezoe, H., Fukuda, A., & Kuze, E. (1983). *Jpn. J. Appl. Phys.*, *22*, L661.
[19] Patel, J. S. & Goodby, J. W. (1987). *Mol. Cryst. Liq. Cryst.*, *144*, 117.