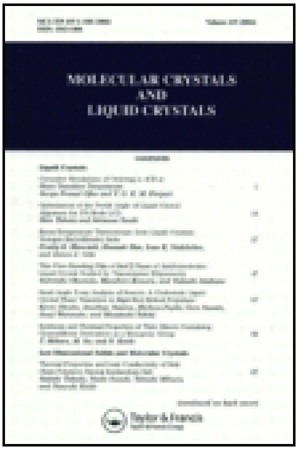

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

The Effect of Weak Polymer Stabilization on the Switching Properties of Cholesteric Liquid Crystals

L. V. Natarajan [a], E. R. Beckel [a], V. P. Tondiglia [a], R. L. Sutherland [a], T. J. White [a], J. Voss [a] & T. J. Bunning [a]

[a] Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson Air Force Base, OH, USA

Version of record first published: 01 Jun 2009

To cite this article: L. V. Natarajan, E. R. Beckel, V. P. Tondiglia, R. L. Sutherland, T. J. White, J. Voss & T. J. Bunning (2009): The Effect of Weak Polymer Stabilization on the Switching Properties of Cholesteric Liquid Crystals, Molecular Crystals and Liquid Crystals, 502:1, 143-153

To link to this article: http://dx.doi.org/10.1080/15421400902816363

Mol. Cryst. Liq. Cryst., Vol. 502, pp. 143–153, 2009
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400902816363

The Effect of Weak Polymer Stabilization on the Switching Properties of Cholesteric Liquid Crystals

L. V. Natarajan, E. R. Beckel, V. P. Tondiglia,
R. L. Sutherland, T. J. White, J. Voss,
, and T. J. Bunning
Materials and Manufacturing Directorate, Air Force Research
Laboratory, Wright-Patterson Air Force Base, OH, USA

We examine the differences in electro-optical behavior of weakly polymer stabilized cholesteric liquid crystals (PSCLC) when formed using either a flood lit UV lamp, a flood lit UV laser, or a holographically patterned UV laser. Both samples formed with the UV laser exhibit symmetry in their dynamic electro-optical properties relative to the front and rear surface of the polymerized cell. These cells exhibit a reversible ~100 nm blue shift tuning of the notch upon application of a field when the reflectivity is measured from either side. The UV lamp sample exhibits large differences in behavior when examined from the front or back relative to the direction of the polymerizing source. The front surface exhibits tuning of the notch while measurements from the back surface yield only the typical binary switching behavior of a CLC. The overall switching fields in flood lit UV laser and UV laser holographically patterned samples are also considerably lower. These differences are explained due to the presence of a strong polymer gradient across the cell gap in the UV lamp flood lit samples which is not present for the UV laser stabilized samples. We also present novel electro-optical results when these laser cured cells are examined in transmittance mode. Strong anchoring at the two surfaces causes a strong anisotropic local LC structure across the cell gap when a field is applied. The two local environments next to each surface act to strongly pin the CLC structure whereas within the bulk, ample reorientation of the LC molecules occurs. When probed in transmission, unusual fringe patterns which change with the strength of the applied field are observed.

Keywords: cholesteric liquid crystal; electro-optical; holographic gratings; polymer stabilization

The authors are grateful to Prof. L. C. Chien of Liquid Crystal Institute, Kent State University, Ohio, USA for helpful suggestions. We gratefully acknowledge the support from AFRL/RX at the Wright-Patterson Air Force Base, Ohio.

Address correspondence to L. V. Natarajan, Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson Air Force Base, OH 45433, USA. E-mail: natarajanl@saic.com

INTRODUCTION

Cholesteric liquid crystals (CLCs) have applications in electro-optic devices, light shutters, light switches and display applications. CLCs selectively reflect light due to the presence of a macroscopic helical structure, where the wavelength of the reflected light is on the order of the helical pitch of the LC. When an AC field is applied to a planar aligned CLC cell at low voltages, the macroscopic helix is broken into domains of smaller helices that are oriented in random directions. This state, called the focal conic condition, causes the cell to be highly scattering. At much higher field strengths, the LC molecules in the focal conic regions are realigned to a homeotropic alignment which leads to high transmittance of the cell. When the field is removed, the return to the planar state is inhibited due to the long lifetime of the highly scattering focal conic state [1–3]. It has been demonstrated that addition of a small amount of polymer network generates an elastic memory for the rapid reorientation back to the planar aligned state [3]. Despite this polymer stabilization, large applied voltages are still required to reach the maximum transmission of the homeotropically aligned clear state.

In a previous paper, we reported the advantages of holographically patterning the polymer network (4). By increasing the LC domain size in a single dimension (z) by confining the periodic polymeric and crosslink-rich layers on a spatial length scale commensurate with the patterning, the field necessary to reach the clear state was decreased by 30% and the overall transmission for the homeotropic state significantly increased to >90% [4]. These samples initially had approximately 10 wt% reactive monomer which was initiated preferentially in the high intensity regions of the interference pattern. Compared to flood lit systems of comparable concentrations, the results from these strongly stabilized samples indicate segregation of the final polymeric network in the x-y plane relative to the z (parallel to grating vector) dimension.

It was also shown recently by others that reflection notch tuning instead of the typical switching behavior [5,6] could be observed in weakly stabilized conditions upon polymerization with a UV lamp. These were obtained by reducing the LC monomer content to 5% and reducing the ratio of LC diacrylate to the photoinitiator concentration to 100:1. These samples showed unique anisotropic reflection from one side of the cell. Tuning of the notch wavelength was observed when probing the reflectivity from the side of sample closest to the polymerizing light source. Probing the reflectivity from the reverse side of the cell resulted in the usual switching behavior. These results indicate a strong anisotropy in the polymer structure throughout the cell. At the front surface, a polymer network structure competes with the typical reorientation of the LC molecules under the influence of a field and causes a distortion of the helix structure (and thus tuning of the notch). Results from the back side reflectivity measurements indicate that much less polymer network is present. This behavior is observed partially because of the weak stabilization conditions used (little reactive monomer and weak initiation rate).

In the work reported here, we present results from a similar material system and stabilization conditions except that curing was accomplished either using a flood lit or holographically patterned UV laser source. Reversible tuning $>100\,\text{nm}$ is observed upon reflectivity measurements from either side for either system albeit at much lower switching voltages. This difference is discussed in the context of the overlap with the photoinitator dye absorption spectra. We also present some atypical electro-optical behavior related to anisotropy in the cell induced by strong anchoring conditions when examined using transmitted light.

EXPERIMENTAL

The CLC was a mixture of nematic LC E44 and chiral dopant CB15 (EMD Chemicals). The monomer for polymer stabilization was the liquid crystalline diacrylate RM257. Photocuring was initiated with the UV sensitive photoinitiator Irgacure 651 (Ciba Speciality Chemicals). The prepolymer syrup for polymer stabilization consisted of E44 (62.2%), CB15 (32.75%), LC diacrylate RM257 (5%) and photoinitiator Ir651 (0.05%) [5]. An ITO cell (5 or 10 micron) whose inner sides were coated with polyimide for planar alignment was filled with the prepolymer syrup by capillary action at elevated temperature. Reflection gratings were written on the cells using a single prism geometry in combination with 364 nm UV laser line from an Argon ion laser [4]. The incoming laser beam enters the sample and is totally internally reflected from the rear glass substrate. The reflected beam interferes with the incident beam forming an interference pattern within the sample. This interference pattern results in a sinusoidal distribution of light intensity within the exposed cell leading to the formation of a patterned polymer structure [4]. A very low power of $4.5\,\text{mW/cm}^2$ was incident on the cell for 30 seconds. For comparison, curing was also done with a UV lamp at 365 nm with a low power of $0.4\,\text{mW/cm}^2$ for 30 minutes. Characterization of the reflection notch was made using an Ocean Optics spectrometer. The electro-optical response was investigated by applying a square wave AC voltage with a frequency of 1 kHz between ITO plates. The reflected spectra measurements were carried out at normal incidence using white light illumination.

RESULTS AND DISCUSSION

Recently, we demonstrated that holographic patterning during the curing of a 'strongly' polymer stabilized CLC resulted in enhanced electro-optical properties [4]. At optimum conditions, holographic patterning of the stabilization allowed for a ~20% increase in the clear state transmission of the device and a reduction in the switching field (30%) compared to a floodlit irradiated PSCLC. Although switching times were increased nearly threefold with holographic patterning, relaxation times were faster (<20 msec). The experimental conditions including high laser power on the cell (60 mW/cm^2) for long exposure time (60 secs) led to the formation of a high number of crosslinks within the polymer network with a spatial anisotropy on a length scale commensurate with the interference pattern. This resulted in larger LC domains in the z-direction leading to lower polymer/LC surface–to-volume ratio of the directionally patterned sample. The lower onset of switching field applied parallel to the z-direction supported this conclusion.

A very different electro-optical behavior was observed by others [5] when the ratio of LC diacrylate to the photoinitiator concentration was reduced to 100:1 as was the total amount of LC acrylate. This 'weakly' stabilized condition has a much lower overall density of polymer network in the sample after UV lamp curing. When the reflectivity of the side closest to the lamp was examined, tuning (or shifting) of the cholesteric notch was observed [5,6] instead of the usual switching. This blue shifting of the notch was attributed to the strong interaction of the LC molecules with a much different polymer network at the front side relative to the back side. Interestingly, probing of the reflectivity from the back side of the cell showed the usual switching behavior of a notch. It was speculated that because of the small amount of monomer present and the low rate of polymerization, an inhomogeneous distribution of polymer network is formed across the cell thickness due to monomer diffusion and absorptive effects. The results suggest that very little polymer is formed at the back side of the cell and as such, this relatively unaffected region exhibits the usual behavior readily forming a focal conic structure.

We have extended this study to observe the effects of holographic patterning in a similarly, weakly polymer stabilized CLC system. Interestingly, we observed results different from the UV lamp flood lit exposure study when using an UV laser source in either a flood lit or holographically patterned geometry. Holographic patterning with a very low UV laser power (4.3 mW/cm^2 for 30 secs) results in the tuning (and broadening) of the reflection notch when the cell is examined from either side. The tuning range was ~100 nm and the reflection intensity decreased with tuning as shown in Figure 2. The electric fields required to observe tuning in the patterned samples were much less than compared to those of the UV lamp flood lit sample. Comparison of Figures 1 and 2 shows a notch shift of ~80 nm achieved by applying 20 V for the patterned cell whereas 80 V was needed for a similar magnitude notch shift for the flood lit sample. Comparison to a laser flood lit sample (4.3 mW/cm^2 for 30 secs) yields a similar range of wavelength blue shifts (Fig. 3) at an intermediate voltage (40 V) again from both sides.

The large differences in UV versus laser flood lit results lead to an examination of spectral signature of the light sources relative to the dye absorption spectrum. Figure 4 shows the absorption spectrum of the initiator dye in the 5 micron cholesteric cell before curing. The distribution of light from the UV laser is much narrower while the area under the curve is much larger for the UV lamp (Fig. 4). Stronger absorption results in more initiating free radicals, more crosslinks and a larger polymer network as a function of the local intensity. Relative to the UV lamp, one might expect a longer penetration depth into the cell for the laser thereby minimizing the initial inhomogeneity in

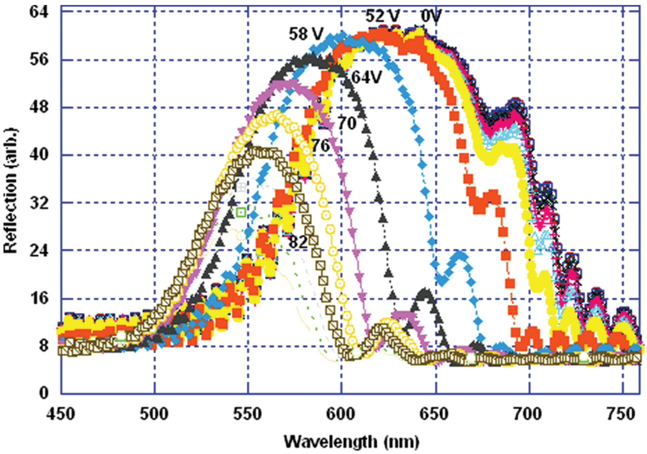

FIGURE 1 Reflection spectra from the front side of the UV lamp cured PSCLC cell as a function of applied voltage.

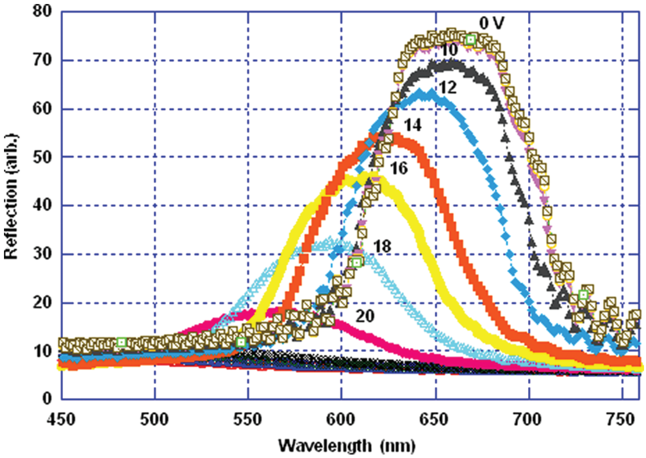

FIGURE 2 Reflection spectra of UV laser patterned PSCLC cell as a function of applied voltage.

the polymerizing species. In the extreme where there is no absorption gradient through the cell, a uniform weak polymer network would be formed evenly throughout the cell. Thus, measuring the reflectivity from the front and back surface would be identical for the UV laser

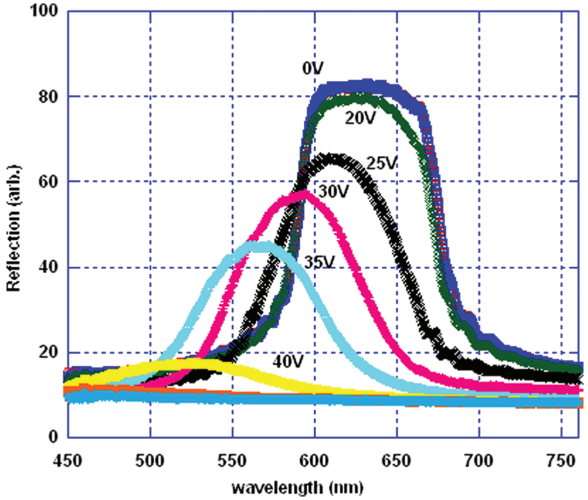

FIGURE 3 Reflection spectra of UV laser flood lit cured PSCLC cell as a function of applied voltage.

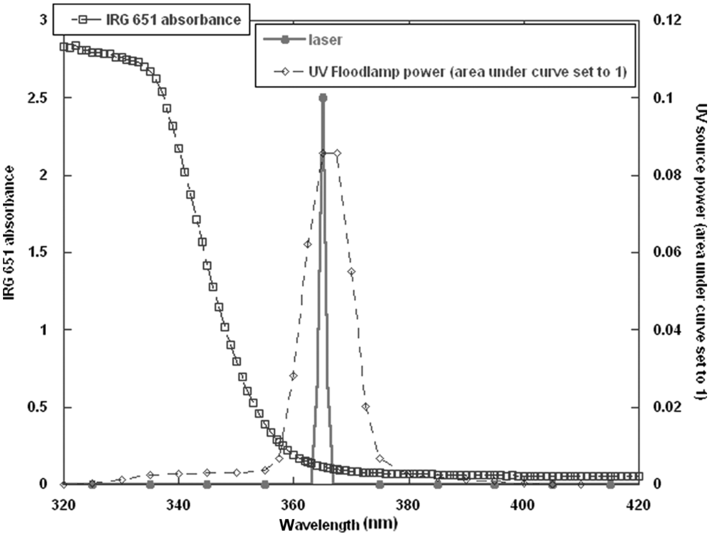

FIGURE 4 Comparison of the spectra of Ir 651 absorbance, the UV lamp output and the UV laser line.

flood lit sample. The differential reflectivity from the front and rear side of the cell for the UV flood lit lamp is a consequence of inhomogeneous distribution of the polymer network through the thickness of the cell.

For the laser patterned cell, one would expect symmetry at the front and back surfaces due to the nature of the writing geometry. The two UV laser beams overlapping in the cell to write the pattern are nearly identical in intensity and hence no local difference in polymer structure for the same distance into the cell would be expected relative to the front or back surface. The tuning and the blue shift of the notch with notch broadening and a decrease of reflection intensity is due to a tilting of the helix induced by competition between the network elastic forces and the electric field [7,8]. The lower switching voltage in the case of patterned cell may be attributed to the spatially segregated polymer regions which result in larger LC cell dimensions in the z-direction. It is worth mentioning that when the writing power was increased to $>5\,\mathrm{mW/cm^2}$, tuning of the notch was no longer observed as the normal switching response of the CLC was seen. Thus there is a fine balance between the local polymer network structure and the electro-optical response of the CLC.

A second atypical, unrelated observation of the system was observed when examining the optical response in transmission mode of either the UV flood lit or holographically patterned cells. Tuning of the notch was not seen in this measurement geometry at all as instead a scattering texture attributed to the formation of focal conic structure was evident. Upon application of a field >30 V, the cholesteric notch texture disappears and the formation of fringes was seen in the optical spectra as shown in Figure 5. With increasing voltage, these fringes grow in amplitude and at >100 V, tuning of the fringes to the blue region of the spectrum was observed as shown in Figure 6. A further increase in voltage >170 V resulted in the disappearance of the fringes as shown in Figure 7. A final transition to a very high transmission (>90%) homeotropic state was seen at voltages >190. Turning the electric field off restores the original notch. The formation and tuning of these 'fringes' are attributed to phase retardation and modulation phenomenon. This behavior was not observed for the UV lamp cured samples.

We hypothesize this behavior is due to surface anchoring effects at the two substrates of the cell. As a result, the unwinding of the helix leading to a homeotropic state is not uniform throughout the cell. Because of strong surface forces at the glass substrates there are relatively thin regions of the sample that remain in a cholesteric phase even at some applied field. With an applied field, the pitch of these thin cholesteric phases may be distorted resulting in a spectrally broader reflection. At the center of the cell, a focal conic texture is

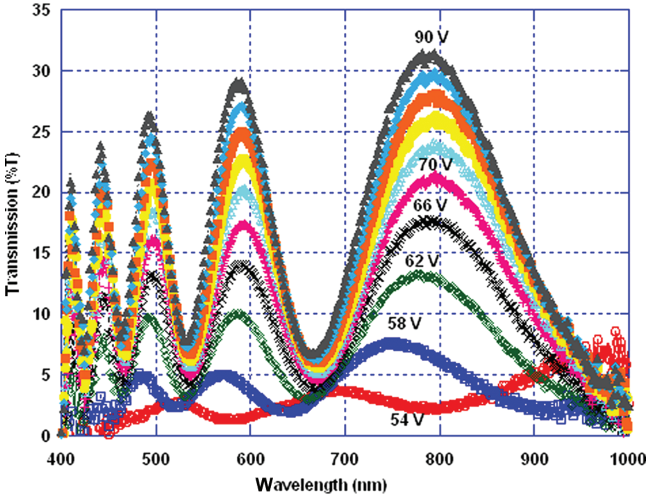

FIGURE 5 Fringe formation observed in the transmission mode. The PSCLC cell patterned with UV laser line. Applied voltage 54–90 V.

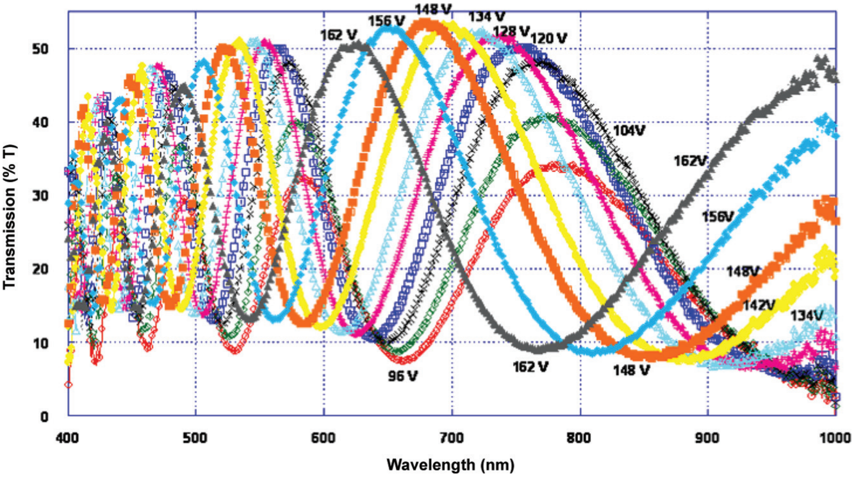

FIGURE 6 Tuning of the fringes observed in the transmission mode. The PSCLC cell patterned with UV laser line. Applied voltage 96–190 V.

formed and with an increase of voltage, the focal conic state becomes progressively aligned into a homogeneous nematic state resulting in the increase of overall transmission (Fig. 8). The thin cholesteric

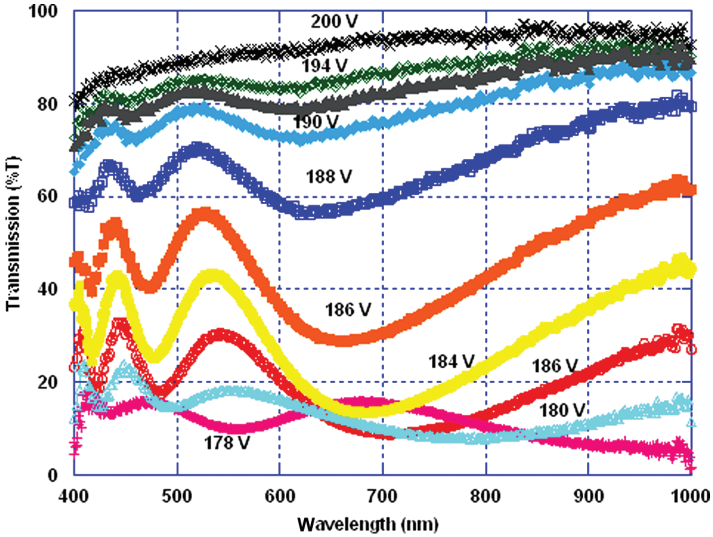

FIGURE 7 Disappearance of fringes at higher voltage in the patterned PSCLC cell. Applied voltage 170–200 V.

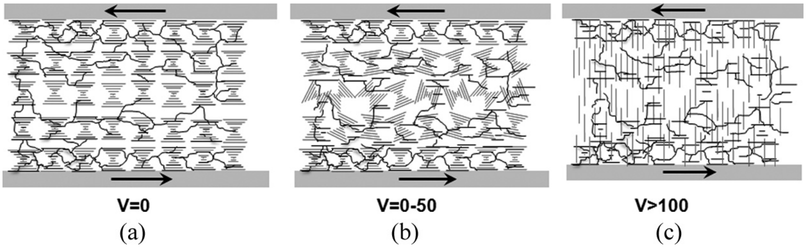

FIGURE 8 Schematic representation of switching observed in the transmission mode. (a) No field applied. Planar alignment. (b) Low field <50 V. Formation of focal conic state in the center. The alignment is not perturbed at the two surfaces. (c) Higher field >100 V. Complete switching to a homeotropic state.

region near the window partially polarizes incident light producing elliptical polarization on transmission. As elliptically polarized light traverses the nematic region, the birefringence of the medium induces a phase retardation and rotation of the polarization ellipse. The thin cholesteric layer at the other window acts like an analyzer attenuating part of the polarized light producing an amplitude modulation. The LC molecules at the center orient with increasing voltage changing the net birefringence and phase retardation resulting in a tuning of the modulation fringes. At much higher voltage, the nematic region becomes homeotropic causing the fringes to disappear. The thin CLC regions also disappear completely as shown in Figure 8.

CONCLUSIONS

We have demonstrated that by UV laser holographic patterning or laser flood lit curing, a weakly polymer stabilized cholesteric LC is formed. The electro-optical properties of these cells significantly differ from similar UV lamp cured samples. Tuning was observed from both laser cured samples from either side of the cell whereas the lamp sample showed huge differences in electrooptical behavior depending on the measurement geometry. The electric field required to observe the tuning was very low and interesting phase retardation effects were seen. The strong surface effects contributing to the stabilized cholesteric structure explain the reflectivity observed from both surfaces. The differential reflectivity from the front and rear side of the cell for the UV lamp flood lit is a consequence of inhomogeneous distribution of the polymer network through the thickness of the cell. The strong polymer net work anchoring on the front side suppresses the formation of focal conic/finger print textures.

REFERENCES

[1] Blinov, L. M. & Chigrinov, V. G. (1993). *Electro-optic Effects in Liquid Crystal Materials*, Springer:New York 310–330.

[2] Kitzerow, H. & Bahr, C. (2001). *Chirality in Liquid Crystals*, Springer: New York, 375–432.

[3] De Gennes, P. G. & Prost, J. (1993). *The Physics of Liquid Crystals*, Oxford Science Publishers: Oxford, 263–329.

[4] Beckel, E. R., Natarajan, L. V., Tondiglia, V. P., Sutherland, R. L., & Bunning, T. J. (2007). *Liq. Cryst.*, *34*, 1151–1158.

[5] Lu, S. & Chien, L. C. (2007). *Appl. Phys. Letts.*, *91*, 131119.

[6] Lu, S., Golvin, A., & Chien, L. C. (2007). *SPIE Proceedings*, *6487*, 64870.

[7] Hikmet, R. A. M. & Kemperman, H. (1998). *Nature*, *392*, 476.

[8] Hikmet, R. A. M. & Kemperman, H. (1999). *Liq. Cryst.*, *26*, 1645.