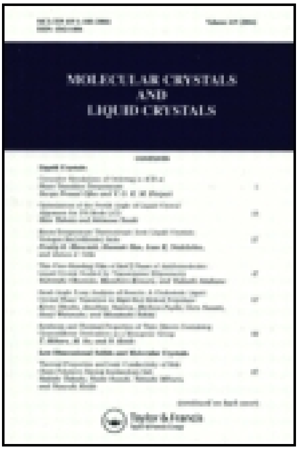

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Improving the Voltage Response of Holographically-Formed Polymer Dispersed Liquid Crystals (H-PDLCs)

Chris C. Bowley [a], Pavel Kossyrev [a], Sorasak Danworaphong [a], Jenny Colegrove [b c], Jack Kelly [b], Tom Fiske [c], Haiji Yuan [c e] & Gregory P. Crawford [d]

[a] Department of Physics

[b] Liquid Crystal Institute, Kent State University, Kent, Ohio, 44240

[c] dpiX LLC, Palo Alto, California, 94304

[d] Division of Engineering, Brown University, Providence, Rhode, Island, 02912

[e] Philips Flat Display Systems, San Jose, California, 95134

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[a]Department of Physics, [b]Liquid Crystal Institute, Kent State University, Kent, Ohio 44240, [c]dpiX LLC, Palo Alto, California 94304 and [d]Division of Engineering, Brown University, Providence, Rhode Island 02912

We report a significant improvement in the switching voltage of holographic PDLCs. This is achieved by doping the prepolymer with small amounts of organic surfactants. The effect of these dopants on other important H-PDLC performance parameters is also investigated. Possible explanations for the reduction in switching voltage are discussed in relation to simple phenomenological switching models.

Keywords: holographic polymer dispersed liquid crystal; switching voltage

INTRODUCTION

Switchable gratings formed by the holographic exposure of a liquid crystal and photopolymer mixture are an exciting new composite material with many potential device applications. The first switchable polymer dispersed liquid crystal (PDLC) gratings were formed using shadow-mask techniques and holographic techniques in the UV [1]. Holographic formation of PDLC

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* Current Address: Philips Flat Display Systems, San Jose, California 95134.

transmission gratings using visible wavelengths was reported in 1993 [2]. Switchable reflection gratings made using similar techniques were reported shortly thereafter [3]. These holographic PDLCs (H-PDLCs) are a slightly evolved form of the PDLC materials so intensely studied in the 1980's [4]. Conventionally, a PDLC is formed by the blanket exposure of a homogeneous prepolymer and low molecular weight liquid crystal (LC) mixture to radiation to which the prepolymer has been sensitized. This initiates a free radical polymerization reaction in the prepolymer mixture. As the molecular weight of the polymer increases, the single phase system is driven into a state where two phases are more energetically favorable. At this stage phase separation occurs and the low molecular weight LC forms discrete nematic droplets, randomly dispersed in a rigid polymer binder. In PDLCs the size of the droplets is strongly governed by the initial concentration of LC and monomer, among other things, and are typically on the order of 0.5-2.5μm in size [5]. The nematic LC self assembles into well defined director configurations, depending on the

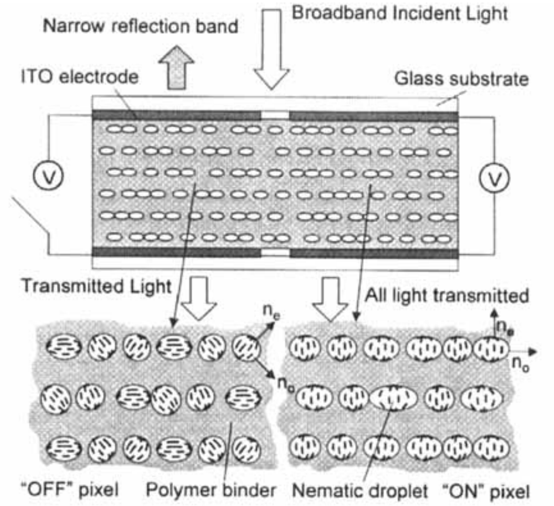


FIGURE 1. Schematic diagram showing H-PDLC operation. There is no field applied to the pixel on the left, which Bragg reflects a narrow wavelength band of light. Sufficient field is applied to the pixel on the right, leading to an index-matched condition. No Bragg reflection occurs.

droplet shape and preferred anchoring of the LC molecules to the polymer wall [6]. For acrylate-based systems, where homogeneous anchoring is preferred, a bipolar configuration commonly forms. The PDLC forms such that the symmetry axes of the bipolar droplets are randomly oriented through the film. On average, there exists a refractive index mismatch between the nematic droplets and the polymer binder. The droplets are on the order of the wavelength of visible light and the films strongly scatter incident light, assuming a white, opaque appearance. Application of an external electric field aligns the bipolar axes along the direction of the field (when the LC has $\Delta\varepsilon > 0$). Typically, materials are selected such that the ordinary index of the LC, n_o, is approximately equal to the polymer index. In this case, the aligned bipolar directors result in index-matching the droplets to the polymer for light incident along the optic axis, and the material becomes transparent. Thus PDLCs behave as switchable light scatterers, and have found many applications such as in direct-view displays [7], projection displays [8] and privacy windows [9].

Holographic polymer dispersed liquid crystal (H-PDLC) materials operate on the same premise as PDLCs, but have two distinct morphological differences. The average droplet size in H-PDLCs is significantly smaller ~20-200nm and the droplets are confined to distinct periodic planes, interspersed with continuous polymer-rich planes . The random alignment of the nematic director configurations between droplets again results in an index of refraction mismatch between the droplets and the binder. At optical wavelengths this manifests itself as a periodic modulation in the refractive index, and the material behaves as a phase grating, coherently scattering light. Application of an external field of sufficient intensity reorients the LC in the droplets, and index matching erases the grating. In this "on-state" the material is transparent to all visible wavelengths. Reflection and transmission Bragg gratings, and Raman-Nath type gratings have been formed in these materials [10]. Fig. 1 shows the operation of a Bragg reflection grating.

Holographic PDLC gratings are formed by the exposure of a homogeneous liquid crystal and monomer mixture to an interferogram formed by two coherent laser beams. A suitable photoinitiator is included in the prepolymer mixture to sensitize the monomer to the wavelength of laser radiation being used. Free radical polymerization is initiated in the bright fringes of the interference pattern, creating a monomer concentration gradient between the light and dark fringes. Monomers diffuse into the bright fringes displacing the inert liquid crystal materials into the dark fringes. Usually a monomer with a high functionality is used, resulting in the formation of a rigid, highly cross-linked polymer network. The high concentrations of liquid crystal in the dark fringes result in discrete droplets phase separating out of the polymer matrix in these regions.

Holographic PDLCs show great promise for a number of potential device applications which include full-color direct-view reflective plat panel displays [11], switchable color filters for remote sensing and other applications, fiber-optic switches [12], and switchable lenses [13]. Recently, new material sets have yielded films with extremely high efficiency [14], but the suitability of these materials for many applications is hindered by their voltage response. For example, the drivers for active-matrix liquid crystal displays (AM-LCDs) operate between ±7V. Currently, high-efficiency reflective H-PDLCs require >15V/μm to achieve 10:1 contrast, which requires a voltage of 60V for a 4μm thick film. Improvements in the switching voltage of such films have been achieved by doping the prepolymer with small amounts of surfactant [15] or dye [16]. In this paper we discuss the parameters affecting the voltage response of H-PDLCs and describe the effects of several such dopants on the electro-optic properties of these films.

VOLTAGE RESPONSE OF H-PDLCS

There are several parameters that influence the switching voltage of H-PDLC films. These include the droplet size and shape, the anchoring strength and alignment, the intrinsic dielectric anisotropy of the liquid crystal, and the droplet order parameter. There are also other performance issues that should be considered when trying to address the voltage response of these materials, including the dielectric integrity of the film, the degree of index-matching achievable in the "on-state", and the spectral wavelength shift of the Bragg peak.

H-PDLCs are field response materials and as such the voltage required to switch a film scales with the film thickness. For this reason it is more appropriate to consider the electric field strength (applied voltage divided by film thickness) when comparing materials, as film thickness' may vary.

The reorientation field required to switch an H-PDLC is determined by the balance of elastic forces, resisting the reorientation, and electric forces, promoting it. This can be expressed analytically using Frank elastic theory, which expresses the free energy density of a nematic liquid crystal as

$$f=\frac{1}{2}[K_1(\nabla\cdot\hat{n})^2+K_2(\hat{n}\cdot(\nabla\times\hat{n}))^2+K_3(\hat{n}\times\nabla\times\hat{n})^2-\varepsilon_0\Delta\varepsilon(\hat{n}\cdot\bar{E})^2] \quad (1)$$

where K_1, K_2, and K_3 are the bend, twist and splay elastic constants, respectively, the nematic director, $\hat{n}$, and $\overline{E}$ the electric field. For simplicity we have ignored the surface elastic terms in Eq. 1. The low molecular weight nematic liquid crystal possess a dielectric anisotropy ($\Delta\varepsilon$), which means that the molecules will have a preferred orientation in an applied electric field. The effective dielectric anisotropy of the nematic droplet is determined as the product of the nematic order parameter and the intrinsic dielectric anisotropy of the material in the liquid crystalline state. It is immediately apparent that the director configuration and degree of ordering in the droplet will have important implications on the switching voltage.

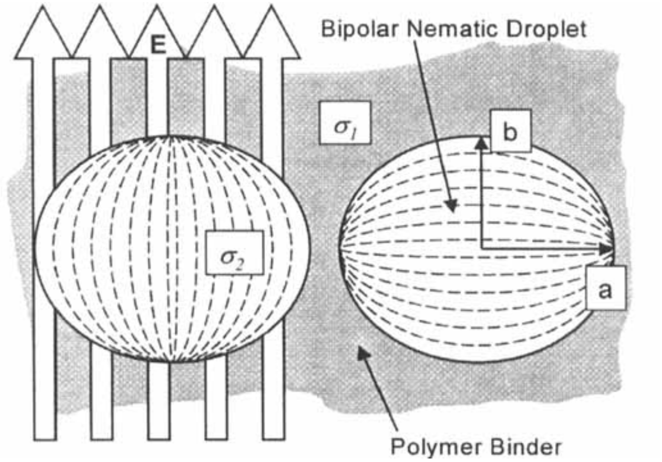
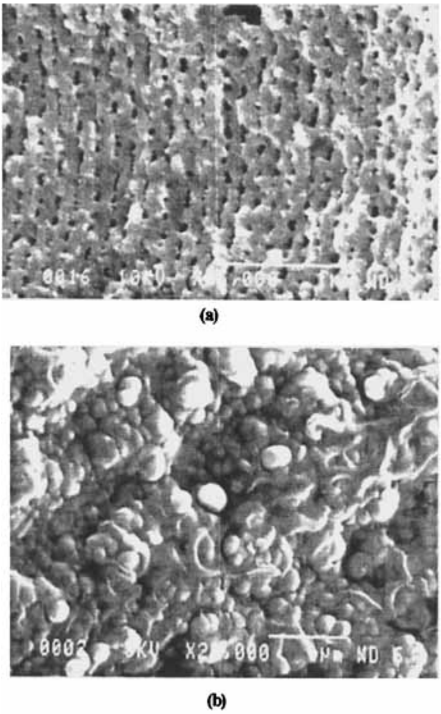


FIGURE 2. Schematic showing bipolar ellipsoidal droplet reorientation in applied electric field. The semi-major, a, and semi-minor,b, axes are shown. The polymer has conductivity σ_1 and the liquid crystal σ_2.

Wu and coworkers have investigated the effect of droplet size and shape on the voltage response of PDLC light shutters and compared experimental results to the theoretical droplet model for bipolar director configurations [14]. This model was developed to describe the micron-sized droplets in PDLCs, but can be readily applied to the smaller droplets in H-PDLCs and proves to be a good starting point from which to analyze H-PDLC voltage response. This model treats droplets that are slightly ellipsoidal in shape. This elongation is pronounced in H-PDLCs, the droplets being extended in the direction of the Bragg planes. Fig. 3(a) shows a scanning electron microscope (SEM) micrograph of a typical acrylate-based H-PDLC. This clearly shows the elongation of the droplets in the plane.


(a)

(b)

FIGURE 3. SEM micrographs showing H-PDLC polymer morphology prepared with (a) no surfactant, and (b) 8 wt.% sorbitan monooleate.

For bipolar configurations, the free energy is minimized when the bipolar axis is oriented in the direction of the long axis of the droplet, where both splay and bend deformations are minimized. The effect of the electric field is to reorient the bipolar axis. In this model there is a critical voltage for a film of thickness d_0 given by

$$V_c = \frac{d_0}{3a}\left(\frac{\sigma_2}{\sigma_1}+2\right)\left(\frac{K(l^2-1)}{\Delta\varepsilon}\right)^{\frac{1}{2}} \tag{2}$$

where a and b are the lengths of the semi-major and semi-minor axes, respectively, $l \equiv a/b$ is the aspect ratio of the droplet. The conductivity's of the polymer and liquid crystal are denoted σ_1 and σ_2 respectively. Dividing this equation by d_0 yields an expression for the critical field. It is important to review the assumptions of this model: (i) the model assumes the one constant approximation; (ii) surface anchoring terms are ignored; and, (iii) the surface elastic constants are ignored. Despite these assumptions the model is adequate for understanding the underlying physics involved in droplet field response of H-PDLCs.

Several important dependencies are evident in this expression. There exists an inverse relationship between the critical field and the droplet size. We immediately expect a dramatic increase in the critical voltage between micron-sized PDLC droplets and the 10-200nm sized droplets in H-PDLCs. Also the critical voltage has a dependence on the aspect ratio of the droplet, l, hence for highly elongated droplets we expect increased critical voltages. The effect of these parameters on the critical field is shown in Fig. 4.

This model also indicates that the critical voltage can be improved selecting a liquid crystal with a high dielectric anisotropy ($\Delta\varepsilon$), or by increasing the conductivity of the polymer binder (σ_1). Of course this model is limited to describing the reorientation of a bipolar droplet, and for highly elongated droplets deviations from a bipolar configuration are expected to yield a lower free energy than the enormous bend deformation required in a field aligned bipolar droplet. Hence discrepancies between the true voltage response of an H-PDLC and this model are to be expected.

Several approaches have been adopted to improve the voltage response of these materials. First, a liquid crystal material with a high dielectric anisotropy is chosen ($10 < \Delta\varepsilon < 30$). The dielectric anisotropy can be further increased by the addition of various dichroic dyes. Another approach is to modify the interaction between the liquid crystal and the polymer binder by the introduction of a surface-active agent (surfactant). Crawford et. al. investigated the effect of an aliphatic acid on the anchoring energy of a nematic liquid crystal confined to a cylindrical cavity [15], and found that under certain circumstances the anchoring energy could be reduced to extremely small values, immeasurable by their magnetic resonance technique. In small H-PDLC cavities, where surface-to-volume ratios are extremely large, this appears to be the most promising approach to reducing the switching voltage.

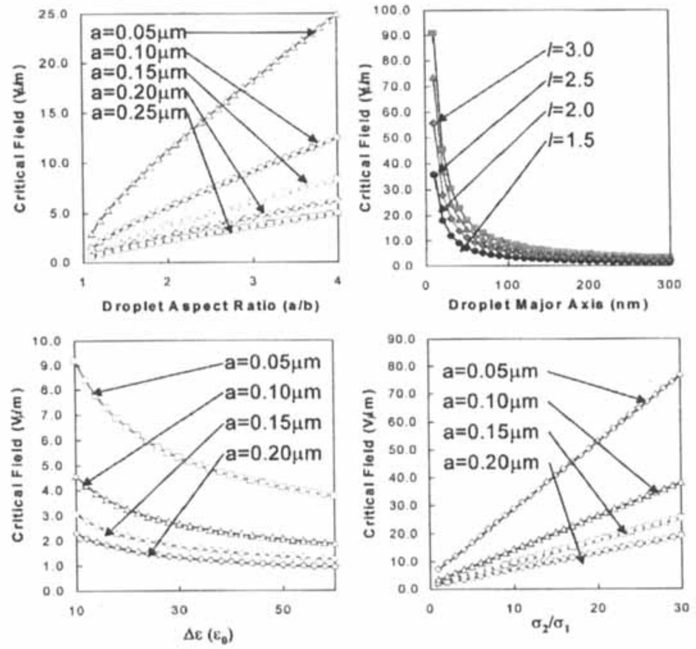


FIGURE 4. Predictions of PDLC droplet model in the H-PDLC regime.

Because the surfactant is present in the prepolymer material it is expected to effect such things as the cure dynamics and morphological properties of the polymer, as well as the anchoring of the LC to the polymer. For this reason it can dramatically affect the optical properties of the H-PDLC in addition to the voltage response.

Typically, a surfactant will also introduce charge carriers into the H-PDLC. This can reduce the critical voltage of the material by increasing the conductivity of the polymer binder, but is considered an undesirable effect as it degrades the dielectric properties of the film and results in a depolarization field due to accumulation of extra charges. This is an important consideration for display applications where the viability of the material for active matrix display purposes depends on the voltage holding ratio (*VHR*) [16]. This parameter is defined as the ratio of the RMS voltage for a frame period, divided by the initial value on the electrode, and is given by

$$VHR = \left\{ \frac{\tau}{2T} \left[1 - e^{-\frac{2T}{\tau}} \right] \right\}^{\frac{1}{2}} \tag{3}$$

where T is the frame period and τ is the RC time constant of the pixel. Increased conductivity in the film will decrease the RC time constant of the pixel and hence reduce the *VHR*.

EXPERIMENTAL DETAILS

Holographic PDLC films were prepared with prepolymer materials consisting of a blended multi-functional urethane acrylate monomer [11], and the nematic liquid crystal BL038 ($\Delta\varepsilon = +16.4\varepsilon_0$), obtained from EM Industries. The monomer was sensitized to the 514.5nm Ar+ laser radiation by the addition of a small amount of Rose Bengal and n-Phenylglycine, both from Sigma-Aldrich. Once homogenized, small amounts of the prepolymer were mixed with different amounts of various commercially available surfactants. These included S270 and S271 from Chemical Services, and non-ionic Tergitol surfactants from Union-Carbide.

Single pixel sample cells were prepared using ITO-coated 1"×1" glass substrates. Cells were drop-filled and vacuum pressed to ensure uniform filling. Fiber spacers (4μm or 5μm) were used to control the cell gap. The filled cells were typically exposed to the interference pattern for 30 seconds.

H-PDLC reflectance was measured using a Photoresearch Spectrascan 705 spectraradiometer. To measure the voltage response a 1kHz square wave was applied across the ITO electrodes. This was generated by a Hewlett-Packard 33120A function generator and amplified using a Trek 50/750 high voltage amplifier. The applied voltage was monitored using a Hewlett Packard 34401A multimeter. The voltage holding ratio of each sample was measured using an Elsicon VHR-100. Film thickness was verified using a Dektak II profilometer.

The polymer morphology of the H-PDLC films was studied using low voltage scanning electron microscopy (SEM). Films were freeze fractured in liquid nitrogen and an LC extraction performed using reagent alcohol. They were then mounted edge-on atop aluminum stubs and sputtered with AuPd to avoid charging.

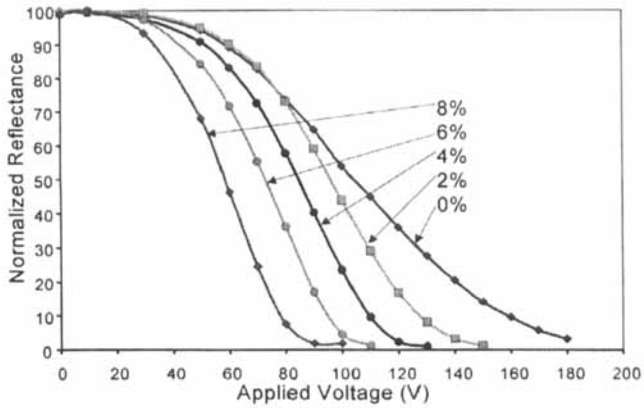
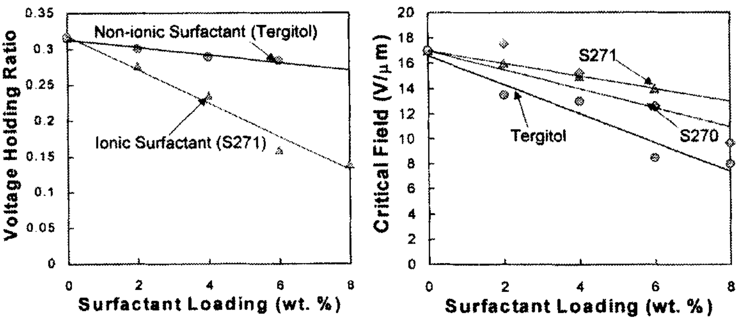


FIGURE 5. Effect of surfactant on H-PDLC voltage response. Switching curves are shown for four different surfactant loadings and compared to a film with no surfactant. At 8 wt.% surfactant the switching voltage is reduced by more than 50%, with high contrast still achievable.

RESULTS AND DISCUSSION

The effect of doping an H-PDLC with a small amount of surfactant on the drive voltage is shown in Fig. 5. This plot shows the switching curves for four different surfactant loadings (S270) compared to an undoped film. H-PDLC switching shifts to lower voltages as the surfactant loading is increased. The reflection efficiency of these materials is unaffected by surfactant loadings ≤ 8 wt.%. At higher loadings the efficiency is reduced with no further improvement in the voltage response.

Surfactant doping has a significant effect on polymer morphology. Fig 3(a) shows polymer morphology in a film with no surfactant. Discrete voids aligned in planes are clearly evident. Fig 3(b) shows the same material with 8 wt.% sorbitan monooleate. No distinct voids are visible and the film displays more of a polymer-ball than droplet morphology. Note that there was minimal tradeoff in the reflection efficiency of these samples.



(a) (b)

FIGURE 6. Effect of surfactant doping on Voltage Holding Ratio (a) and critical field (b).

Surfactants such as sorbitan monooleate (S270, S271) enhance H-PDLC performance by reducing their switching voltage, however these surfactants are ionic in nature, an undesirable quality for many potential H-PDLC applications as they reduce the voltage holding ratio of the film, making active matrix addressing impossible. The *VHR* values of undoped H-PDLCs are extremely low when compared to similar PDLC samples prepared with EM Industries TL205 and PN393. These materials have been optimized for active matrix display applications and exhibited a *VHR* of 0.93. We speculate that this is due to the large number of residual charge carriers introduced by the photoinitiator and coinitiator. The free radical polymerization reaction requires charge carrying radicals to occur. These charge carriers remain in the system after curing and contribute to a depolarization field. The effect of these surfactants on the *VHR* is shown in Fig. 6(a). Undoped H-PDLCs have a voltage holding ratio of ~0.32. This falls linearly to <0.15 at an 8 wt.% loading of S271.

In an effort to overcome this problem we have investigated the effect numerous non-ionic surfactants. Fig. 6(a) also shows the *VHR* of a non-ionic Tergitol surfactant. The *VHR* is marginally reduced from the undoped value, but is significantly improved over the ionic surfactant values.

The effect of the ionic and non-ionic surfactants on the critical field is shown in Fig. 6(b). The Tergitol-doped samples switch at consistently lower critical field compared to the samples with similar loadings of ionic surfactants. This suggests that the improvement in switching voltage is not due to increased conductivity (σ_l) of the polymer binder, but rather due to morphological changes or modified surface anchoring or both.

CONCLUSIONS

We have demonstrated improved switching voltages in H-PDLC reflection gratings by doping the prepolymer materials with small amounts of surfactant. The decreased reorientation voltage comes at no expense to the reflection efficiency of the grating, however, these surfactants do adversely affect the voltage holding ratio of the material. This is due to the increase in charge carrying ions in the matrix, which manifest a depolarization field on application of an AC voltage. Use of a non-ionic surfactant minimizes this effect. Polymer morphology is dramatically affected by the introduction of surfactant, as revealed by SEM studies. This, along with a change in the liquid crystal-polymer anchoring is the most likely mechanism for the improved voltage response, although this has not been verified.

Acknowledgements

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References

[1] J. D. Margerum, A. M. Lackner, E. Ramos, G. W. Smith, N. Vaz, and C. R. Allison, United States Patent 5,096,282 (1992).

[2] R. L. Sutherland, L. V. Natarajan, V. P. Tondiglia and T. J. Bunning, *Chem. Mater.*, **5** pp. 1533–1538 (1993).

[3] K. Tanaka, K. Kato, S. Tsuru and S. Sakai, *SID Digest of Technical Papers,* **XXIV** p.109 (1993).

[4] P. S. Drzaic, *Liquid Crystal Dispersions,* World Scientific, Singapore (1995).

[5] J. Kelly, W. Wu and P. Palffy-Muhoray, *Mol. Cryst. Liq. Cryst.*, **223,** pp. 251–261 (1992).

[6] S. Zumer, *Phys. Rev. A,* **37**(10) pp. 4006–4015 (1988).

[7] J. H. Erdmann, A. M. Lackner, E. Sherman and J. D. Margerum, *SID Digest of Technical Papers,* **XXIV** pp. 57–61 (1993).

[8] M. Kunigita et.al., *SID Digest of Technical Papers,* **XXI** pp.227–230 (1990).

[9] P. S. Drzaic, A. M. Gonzales and P. van Konynenburg, *Proc. SPIE,* **2175**, pp.148–157 (1994).

[10] M. E. De Rosa, V. P. Tondiglia, and L. V. Natarajan, *J. Appl. Pol. Sci.*, **68,** p.523 (1998).

[11] G. P. Crawford, T. G. Fiske and L. D. Silverstein, *SID Digest of Technical Papers,* **XXVII,** pp.99–102 (1996).

[12] L. Domash, J. Schwartz, A. Nelson and P. Levin, *Proc. SPIE,* **1662** (1992).

[13] L. H. Domash, Y.-M. Chen, B. Gomatam, C. Gozewski, R. L. Sutherland, L. V. Natarajan, V. P. Tondiglia, and T. J. Bunning, *Proc. SPIE,* **2689** (1996).

[14] C. C. Bowley, A. K. Fontecchio, H. Yuan and G. P. Crawford, *SID Digest of Technical Papers,* **XXX,** pp.958–961 (1999).

[15] H. Yuan, J. Colegrove, G. Hu, T. Fiske, A. Lewis, J. Gunther, L. Silverstein, C. Bowley, G .Crawford, L. Chien, and J. Kelly, *Proc. SPIE,* **3690** (1999).

[16] J. Colegrove, H. Yuan, S.-T. Wu, J. R. Kelly, C. Bowley, and G. P. Crawford, to be presented at *International Display Workshop '99.*

[17] B.-G. Wu, J. H. Erdmann, and J. W. Doane, *Liq. Cryst.*, **5** (5) pp.1453–1465 (1989).
[18] G. P. Crawford, R. Ondris-Crawford, S. Zumer, and J. W. Doane, *Phys. Rev. Lett.*, **70** (12) pp.1838–1841 (1993).
[19] S. Kobayashi, H. Hori and Y. Tanaka, in *Handbook of Liquid Crystal Research*, Eds. P. J. Collings and J. S. Patel, Oxford University Press, New York, p.431 (1997).