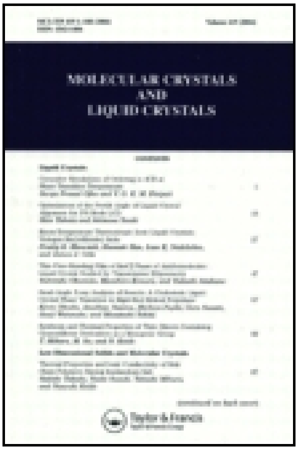

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Reflection Holograms Formed Using Polymer-Dispersed Liquid Crystals

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Version of record first published: 24 Sep 2006

To cite this article: Timothy J. Bunning, Lalgudi V. Natarajan, Vincent P. Tondiglia & Richard L. Sutherland (1998): Reflection Holograms Formed Using Polymer-Dispersed Liquid Crystals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 320:1, 127-138

To link to this article: http://dx.doi.org/10.1080/10587259808024389

Mol. Cryst. Liq. Cryst., Vol. 320, pp. 127–138
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Reflection Holograms Formed using Polymer-Dispersed Liquid Crystals

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The electrical switching characteristics of reflection gratings formed using polymer-dispersed liquid crystals are explored. First, an explanation for the lack of switching in previously formed gratings formed using E7 as the liquid crystal is proposed based on experiments on slightly slanted gratings. These confirm that the LC director orientation within the anisotropically-shaped LC domains is parallel to the grating vector(and applied electric field direction). Slight modification of the syrup leads to transmission gratings with different polarization dependencies and reflection gratings (non-slanted) that switch completely with a modest electric field. These differences are attributed to a 90° rotation in the preferred LC director orientation within the LC domains. This change in orientation results in strong coupling of the electric field with the LC dipoles in a reflection geometry thereby leading to easier switching. The microstructure of these grating structures are explored using low-voltage scanning electron microscopy and bright-field transmission electron microscopy.

Keywords: Bragg gratings; switching; morphology; polymer-dispersed liquid crystals; photopolymerization

INTRODUCTION

The use of liquid crystals (LC) dispersed in polymer matrices has received a lot of attention due to potential applications[1,2]. A number of methods to form these structures exist including light-induced polymerization. The ease of controlling the light intensity (uniform over the entire sample) and the materials formulation in the prepolymer syrup leads to considerable control over the resulting morphology. Control of this morphology including droplet size, shape and density is important because these parameters govern the electro-optical performance of PDLC films. Other considerations in the electro-optical performance are the anchoring strength between the liquid crystal and the polymer matrix and the LC director configuration within each droplet.

These parameters are also very important in dictating the performance of holographic elements formed using polymer-dispersed liquid crystals. By spatially polymerizing a starting syrup, the location of the phase-separated LC domains can be controlled thereby forming complex spatial patterns of LC domains. Our group has been successful in forming Bragg ($\Lambda<1.5$ μm) gratings both in transmission and reflection geometries using the principles of light-induced polymerization-induced phase separation of LCs[3-5]. We have demonstrated good performance in transmission-based gratings and have shown the promise of the technique for optical data storage[6]. Most other work to date on volume grating formation using PDLC's has been directed at forming Raman-Nath gratings where the spacing between planes is much larger[7,8,9]. These latter studies are of interest because there exists a delicate balance between the diffusion, polymerization, and phase separation rates. The Bragg spacing has been shown theoretically to be a major factor in understanding the formation process of these variables[10]. Studies at larger Bragg spacings generate data for systems with longer diffusion times.

Studies at very small Bragg spacings is also of interest for reflection-based systems. For reflection to occur in the visible (400-650 nm), this necessitates very small Bragg spacings on the order of Λ=130-220nm assuming an average refractive index of 1.5 ($\Lambda=\lambda/2n$). Formation of high performance static reflection systems have been achieved, most notably with the DuPont photopolymers[11-12]. High reflection efficiencies (OD's>4) can be obtained in relatively thin films (<20 microns) by inducing a fixed modulation in the refractive index by spatially controlling the crosslink density. Electro-optically switching similar structures is promising from a display perspective and so several groups have explored this geometry using spatially patterned PDLC-based structures[13-16]. In an earlier article by our group, we demonstrated the ability of forming uniform Bragg gratings with the proper spacing using the same material system[17] used to generate transmission gratings (larger Bragg spacings). However, these structures were not electrically switchable. In the work reported here, we explore reasons why switching did not occur in these films and attempts to overcome this obstacle. Specifically, we report on the morphology and switching characteristics of slanted gratings formed using our original material and of transmission and reflection gratings formed using a modified material system.

EXPERIMENTAL PROCEDURES

The material recipe for writing slanted gratings is the same recipe that has been used in the past[18]. Generically, the syrup consists of a monomer, LC, photoinitiator, and co-initiator which is sandwiched between ITO-coated glass substrates. The slanted reflection gratings were recorded using an argon-ion laser at 514 nm and 5 mW/cm^2. The LC used for these samples was E7 (Merck) and the concentration was 34% . A fluorine-containing LC(TL205) was substituted for E7 at a similar concentration to examine both transmission and reflection gratings. Standard holographic procedures were used similar to methods used previously [17,18]. Electro-optical switching was measured by applying an electric field across the ITO cells using square wave voltages at 1 kHz at variable voltages. The reading beam for the transmission gratings was from a He-Ne laser at 623.8nm and orthogonal polarizations were investigated. The spectra of the reflection gratings were measured in a λ9 Perkin-Elmer spectrophotometer. The morphology of the samples were investigated using low-voltage scanning electron microscopy (LVSEM) conducted on a Hitachi S-900 and on a JEOL 100CX transmission electron microscope (TEM) operating in a bright-field (BF) mode. Samples for the SEM were fractured in liquid nitrogen, soaked in methanol to remove the LC, and then lightly dusted with 3 nm of tungsten. The samples for the TEM were embedded on edge in an epoxy monomer, allowed to cure and sectioned (80-100 nm) by ultramicrotomy.

RESULTS AND DISCUSSION

Attempts to switch the original reflection gratings reported on previously[17] were unsuccessful. The average size of the LC domains in these samples was very small, on the order of 50 nm. Very little coalescence of the individual domains occurred and very little distribution in their sizes was observed. The lack of switching was speculated to be due to one of two things. First, the very small size of the LC domains might cause pinning of the director within the domain due to the large surface area/volume ratio as compared to conventional, large PDLC domains. A second possibility would be that the average director field within the domains points parallel to the grating vector. In this situation, application of an electric field would have no effect as the director is already pointing along this direction. This is shown schematically in the left hand image in Figure 1. Both the grating vector (K) orientation and the average LC director (n) point along the direction of the electric field (E) when applied.

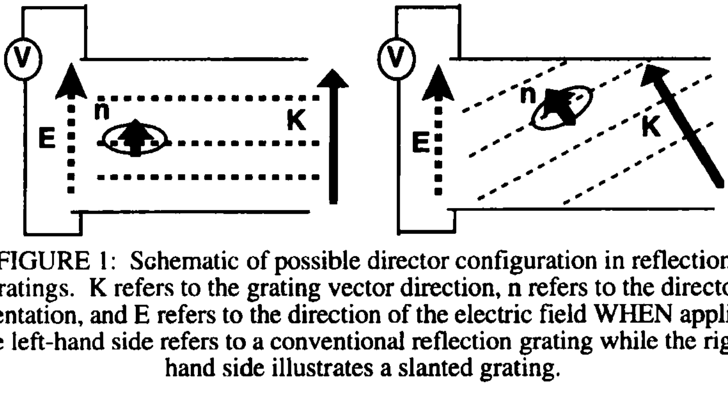

FIGURE 1: Schematic of possible director configuration in reflection gratings. K refers to the grating vector direction, n refers to the director orientation, and E refers to the direction of the electric field WHEN applied. The left-hand side refers to a conventional reflection grating while the right-hand side illustrates a slanted grating.

Since we had observed switching in transmission gratings with similar size LC domains[3-5], we decided to explore the latter possibility as the reason for a lack of switching. Specifically, using the same materials and conditions employed previously[17], a slightly slanted grating was fabricated where the grating vector was rotated less than 10° off perpendicular to the surface. As the right hand side of Figure 1 illustrates, both the K and n orientations are at an angle to the direction of the applied field (E). In this geometry, turning on the electric field should reorient the average director, n, along E causing a modulation of the reflection intensity due to the corresponding change in the refractive index profile.

Figure 2 shows LVSEM micrographs of the slanted gratings. The second image clearly illustrates a slant angle of approximately 6° present in the film. The periodicity of the grating corresponds to roughly 220 nm which is expected from the measured 650 nm reflection notch. Sizes of the LC domains range from 25-85 nm and their location is very well confined to channels approximately 85-100 nm in width. These channels are separated by dense polymer with few voids. Coalescence of domains is evident within these layers although these domains are anisotropic in shape. As shown, the average long axis director of the LC domains is perpendicular to the grating vector, opposite that previously observed with the transmission gratings[6]. This indicates that the polymerization and phase separation process has a strong effect on the shaping of the domains and that slight changes in the Bragg spacing can lead to large differences in these domain anisotropies.

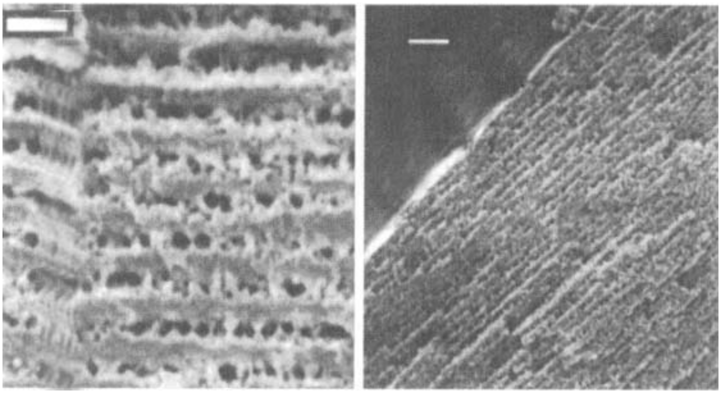

FIGURE 2: LVSEM micrographs of a slanted reflection grating. The tilt angle corresponds to approximately 6°. The scale bar on the left image corresponds to 300 nm while the scale bar on the right corresponds to 1 μm.

To confirm this switch in domain anisotropy at this Bragg spacing, BF TEM images were obtained on ultramicrotomed samples. On the upper right-hand side of Figure 3 is the surface of the film which is in contact with the epoxy binder. The dark areas are the polymer-rich regions formed by the polymerization of the syrup while the lighter areas are the remnants of LC domains which are filled with polymerized epoxy. Unlike previous samples[17], this process did not distort the dimensions as the measured spacings correspond well to those observed in the LVSEM. This image gives a good cross-sectional view of the domain shapes and sizes. It is clearly evident that the average long axis of the lighter areas are perpendicular to the grating vector as shown by the arrows on the micrograph.

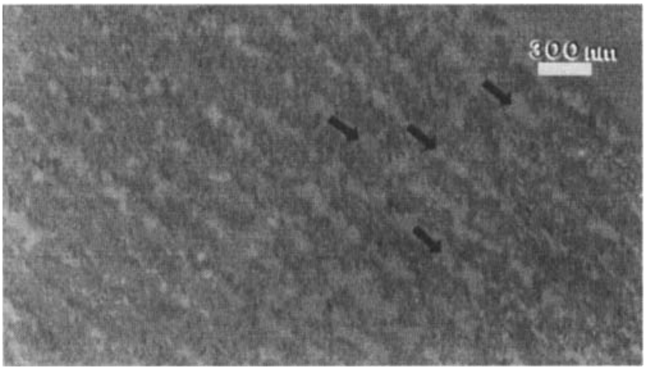

FIGURE 3: BF TEM micrograph confirming slight slant in the grating vector relative to the surface normal. Also readily apparent is the average shape anisotropy of the LC domains corresponding to a direction perpendicular to the grating vector. The scale bar corresponds to nm.

The switching characteristics of this film were examined and, unlike the previous grating (non-slanted) samples[17], this sample showed evidence of switchability as indicated by Figure 4. The film with no field applied exhibits a clear notch and about 70% baseline transmittance. Upon application of an electric field at 2kHz, several things begin to happen. First, the depth of the notch decreases indicating a decrease in the amplitude of the refractive index profile across the film. Second, the notch slightly blue shifts and third, the background baseline transmittance increases. As Figure 4 indicates, a larger voltage has a stronger effect on these observations although switching is not complete even at the higher voltage. We attribute the switchability of these films to the presence of the slight tilt angle in the sample as discussed earlier in regard to Figure 1. These results indicate that control of the director orientation is a key parameter in obtaining useful switchable holographic PDLC films.

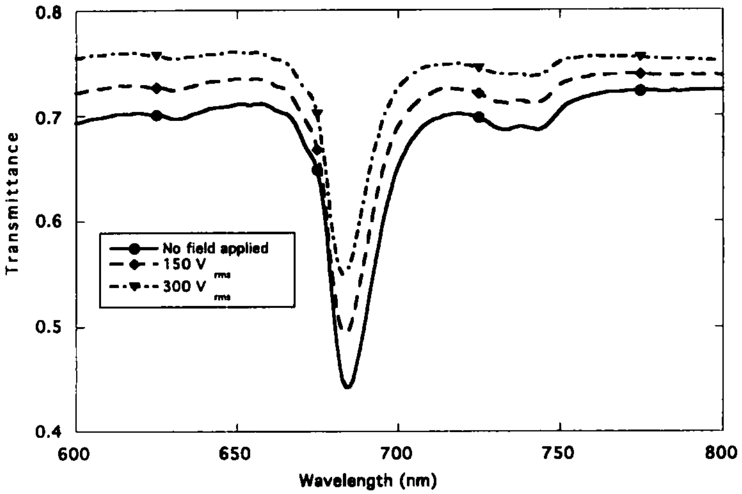

FIGURE 4: Switching characteristics of the slanted reflection grating.

In order to obtain better performance of both transmission and reflection grating samples, we have modified the material syrup by replacing E7 with TL205, a fluorine-containing LC. The use of fluorine-containing substances has been shown to lower switching voltages[19] and enhance phase separation of the LC[20] from the matrix in conventional PDLCs. To explore the effect of this new material formulation, we first made transmission gratings using this new syrup at a Bragg spacing of 0.8 micron. The morphology of these films is shown below in Figure 5. The LC-rich lamellae are composed of a more continuous LC phase rather than individual LC domains shown previously using E7 syrups at similar d-spacing[21]. This morphology is similar to that observed previously[5] using E7 at high concentrations at smaller Bragg spacings. The largest of the LC domains is approximately 350nm in diameter and the average LC-rich lamellae width is also of this size.

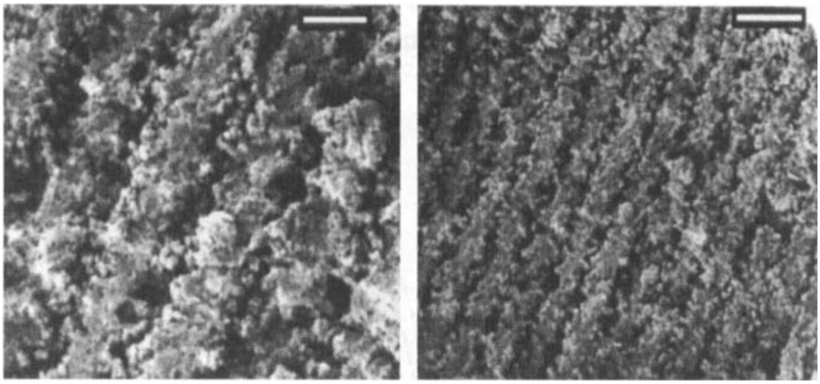

FIGURE 5: LVSEM micrographs of 0.8 mm transmission grating formed using a fluorinated-based LC syrup. The scale bar on the left corresponds to 600 nm while that on the right corresponds to 1.5 μm.

To explore the effect of the new LC on the switching behavior, the diffraction efficiency was measured as a function of applied voltage as shown in Figure 6a. The polarization dependence of the diffraction efficiency and the lack of switching was very surprising. For this sample, s-polarization was much stronger than p-polarization. This is fundamentally different than the behavior observed in transmission gratings formed using E7[22] as shown in Figure 6b. When using E7 as the LC, p-polarization diffraction efficiency is much stronger and upon reaching a critical switching field, a sharp drop in this efficiency is observed. The slight increase in diffraction efficiency at low switching fields is due to over modulation. The corresponding s-polarization diffraction efficiency is very weak and only changes slightly in intensity with switching field as shown(Figure 6b). For the TL205 sample (Figure 6a), no switching was observed in either polarization across this range of switching fields. The polarization dependence of the diffraction efficiency has been investigated previously[22] for E7 transmission gratings and attributed to the LC director orientation within the LC domains. Specifically, when the LC director orientation is along the grating vector, p-polarized radiation is able to couple much more efficiently than s-polarization radiation, and upon application of an orthogonal electric field, this director orientation is modulated. This interpretation also supports the lack of switching we observed in the previous reflection grating sample[17]. Using these arguments, the data in Figure 6a indicates that the LC director orientation is perpendicular to the grating vector in this transmission sample. Thus, s-polarization radiation is coupled much more effectively and because the director orientation is already along the electric-field direction, no modulation in diffraction efficiency is observed upon increasing the voltage.

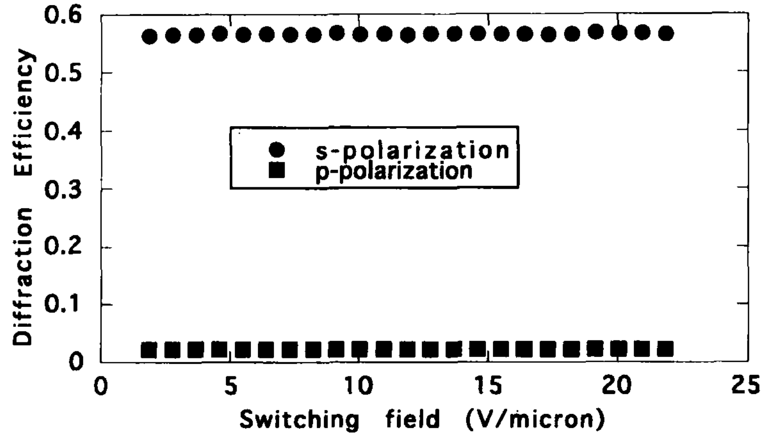

FIGURE 6a: Switching characteristics for transmission grating written with fluorinated LC.

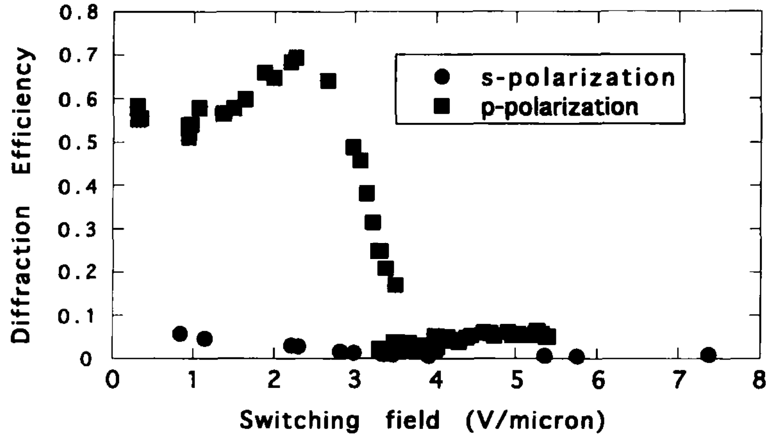

FIGURE 6b: Typical switching characteristics for a transmission grating written with E7.

This behavior in a transmission grating sample implies that the director orientation for a reflection sample would be ideal for switching (perpendicular to the grating vector) if the same anchoring direction is present relative to the grating vector. To test this hypothesis, a non-slanted reflection grating was prepared using the new recipe and the morphology is shown in Figure 7. A periodicity of 180 nm is measured which corresponds well to the notch at 540 nm indicated in Figure 8. Domain sizes range from 40-100 nm and considerable anisotropy in the average domain shapes is again observed similar to the morphology of the slanted grating shown in Figure 2.

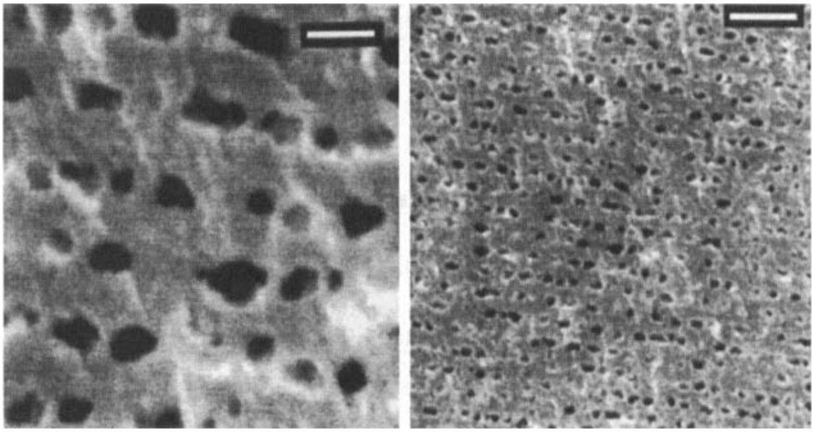

FIGURE 7: LVSEM micrographs of reflection grating formed a fluorinated-based LC syrup. The scale bar on the left corresponds to 150 nm while that on the right corresponds to 600 nm.

Finally, the switching characteristics of this reflection grating are shown in Figure 8. Before application of the electric field, one sees a very well defined notch near 540 nm. The bandwidth of the notch is very narrow (10-15 nm). Application of the electric-field causes the sample to completely lose its color as the notch disappears. The voltage used to switch this sample was $200V_{rms}$ and corresponds to a switching field near 10 V/micron. The notch essentially completely disappears although a slight blue-shifted notch remains at 525-530 nm.

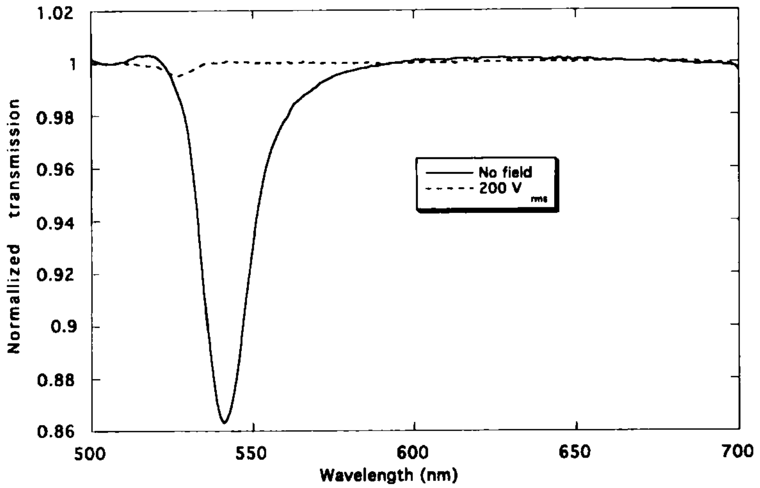

FIGURE 8: Reflection characteristics of sample written with fluorinated LC

Thus, changing our material syrup by replacing E7 with TL205 leads to several interesting observations. Most importantly, a change in the surface anchoring direction was observed using TL205 as compared to E7 as indicated by differences in reading beam polarization dependencies. This difference explains the lack of switching behavior in previous reflection gratings formed using E7. The average LC director orientation was confirmed for this formulation using a slanted reflection geometry. The switch in director orientation makes the use of TL205 in transmission gratings futile under our existing writing conditions. These transmission gratings show no evidence of switching at comparable switching fields and a flip in the dominance of the reading beam polarization dependencies. However, the cause for these observations, a flip of the LC director orientation from parallel to perpendicular to the grating vector is advantageous in a reflection grating geometry. This was confirmed by showing strong switching in reflection gratings formed using TL205 as the LC even though the LC domain sizes were very small(<100nm).

Acknowledgments

The authors acknowledge funding through US Air Force contract F33615-95-C-5423 and P.F. Lloyd for providing the BFTEM micrograph shown in Figure 3.

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