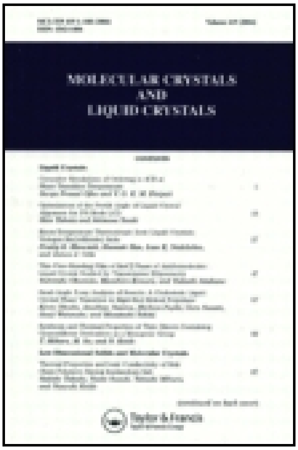

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Morphological Studies of Holographically formed Polymer Dispersed Ferroelectric Liquid Crystals

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Morphological Studies of Holographically formed Polymer Dispersed Ferroelectric Liquid Crystals

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In this contribution we describe a method to control and tailor the polarization sensitivity in holographically formed polymer dispersed liquid crystals (H-PDLCs) using a ferroelectric liquid crystal mixture with a UV curable diacrylate monomer. By controlling the FLC to monomer weight ratio we can radically manipulate the polarization sensitivity in these diffraction gratings. We show the polarization is related to the polymer morphology and hence the final alignment of the ferroelectric liquid crystal. We investigate the distinct morphologies (droplet and channel-like) into which the ferroelectric liquid crystal rich regions can be formed by imaging both the macroscopic and microscopic cross sections using optical polarizing microscopy, scanning electron microscopy (SEM) and atomic force microscopy (AFM).

Keywords: ferroelectric liquid crystals; holographic gratings; polymer dispersed liquid crystal

INTRODUCTION: NEMATIC BASED H-PDLCs

Holographically formed polymer dispersed liquid crystals (H-PDLCs) are created through a photo-induced counter-diffusion process that is initiated by interfering two or more coherent laser beams [1,2]. By exposing the prepolymer and liquid crystal mixture to an amplitude interference pattern, the intensity modulation creates a polymerization of the monomer in the high intensity regions and forces the liquid

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crystal out to the lower intensity regions to produce stratified dispersions of alternating polymer rich and liquid crystal rich planes as shown in Figure 1. The spacing (or pitch Λ) of these alternating planes is determined by Bragg's Law:

$$\Lambda = \frac{\lambda_w}{2\langle n\rangle \sin\theta}$$

where λ_w is the wavelength of the interfering laser beams (so called writing wavelength), $\langle n\rangle$ is the average index of refraction for the mixture, and θ is the half angle of the exposed beams inside the sample as shown in Figure 1. In a transmission mode H-PDLC the interfering beams illuminate the film from the same side of the sample to create a stratified grating of alternating liquid crystal and polymer planes orthogonal to the glass substrates (grating vector in the plane of the substrates). When substrates are used having a transparent conducing electrode layer of indium tin oxide (ITO) on the inner surfaces of the glass, an electric field can be applied across this film to change the electro-optic properties of the H-PDLC. Typically materials are chosen such that the refractive index of the polymer (n_p), is mismatched with one of the indices of refraction for the liquid crystal (extraordinary index, n_e) and matched for the other refractive index (ordinary index, n_o). When an incident laser light source passes through the H-PDLC, the periodic variations in refractive index from the liquid crystal (some average of n_e and n_o), and polymer (n_p), planes create a visible diffraction grating. Upon application of an electric field to this same film, the liquid crystal molecules align parallel to the electric field direction if they possess a positive dielectric anisotropy ($\Delta\varepsilon > 0$). In this case, $n_p \sim n_o$, allowing incident light to propagate directly through an optically homogeneous sample, without experiencing an index modulation.

Because these films can be switched from a diffracting state to a transparent state by an electric field, there are a plethora of applications for these active gratings that include including reflective displays [3], photonic crystals [4,5], lasing media [6–8] and telecommunication switches [9]. These composite films, typically based on nematic liquid crystal materials, often exhibit polarization sensitive electro-optical results caused by a preferential alignment of the liquid crystal inside the polymer matrix [10]. This polarization sensitive characteristic of transmission H-PDLC gratings makes them less than ideal for certain applications that operate on non-polarized light, and potentially attractive for other applications where polarization selectivity is desired. Extensive research has been done on the nematic based H-PDLC. There has been significant work on new material formulations and fabrication processes by a number of groups [11–14]. Recent publications show a new process to create H-PDLC materials, known as polymer liquid crystal polymer slides (POLYCRYPS), in which the phase separation between the liquid crystal and polymer is more complete as compared to droplet based H-PDLCs [15–17]. In this contribution we focus on creating H-PDLCs using a fluorinated ferroelectric liquid crystal (FLC) and diacrylate monomer. We present a method to control the polarization dependence by controlling the FLC alignment, for potential device applications.

INTRODUCTION: FERROELECTRIC LIQUID CRYSTALS (FLC)

Ferroelectric liquid crystals have been demonstrated as excellent candidates for fast electro-optic switching applications such as displays [18] and optical switches [19], but have seen only limited device commercialization. This is partly due to the lack of achieving suitable alignment layers that are both stabile and robust for homogeneous alignment of the FLC, as well as the annoying defect structures that often appear [20]. Over the past decade researchers have shown different techniques to aid in the alignment of ferroelectric liquid crystals by combining ferroelectric liquid crystals and polymer dispersions with shearing forces [21] or magnetic field manipulations [22]. This contribution focuses on a holographic exposure that can create different alignment states of ferroelectric liquid crystals by changing the weight ratio of liquid crystal and monomer thereby manipulating the morphology of the encapsulating polymer.

EXPERIMENTAL

Holographically formed polymer dispersed ferroelectric liquid crystals were made from a mixture of a fluorinated ferroelectric liquid crystal (*3M Company*) and a UV curable diacrylate monomer (PN393, *EM Industries*). The chemical structure for the ferroelectric liquid crystal mixture consisted of two components 7O]1222[6-] and 81222[7F8-] combined in a 1:2 weight ratio as shown in Figure 2. The 3M fluorinated ferroelectric liquid crystal was used because it was soluble in the diacrylate monomer at room temperature and possessed a wide operating SmC* phase from room temperature to 64.8°C. The spontaneous polarization (P_s) was measured at $25.8\,\mathrm{nC/cm^2}$, with a tilt angle of 23.7°, and a helical pitch of $\sim 2\,\mu\mathrm{m}$. A drop of the prepolymer and ferroelectric liquid crystal mixture

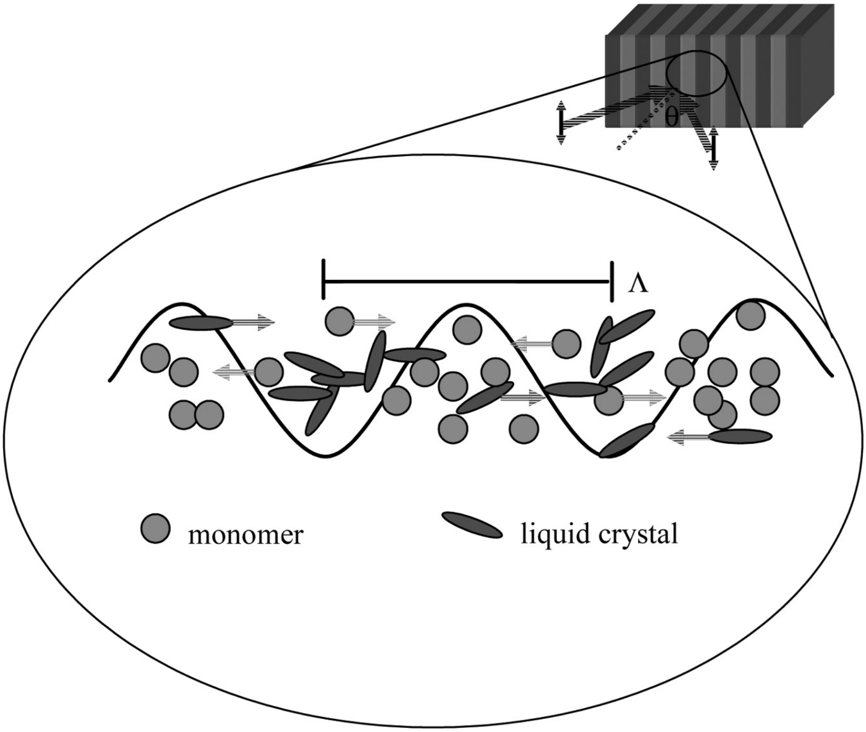
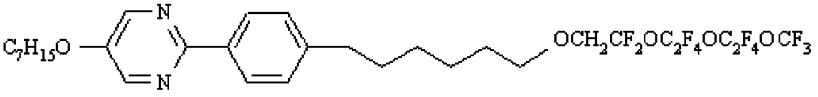


FIGURE 1 A schematic illustration showing the two beam transmission holographic setup that leads to a photo induced phase separation of liquid crystal and monomer. (See COLOR PLATE XLI)

Component: 7O]1222[6-]



Component: 81222[7F8-]

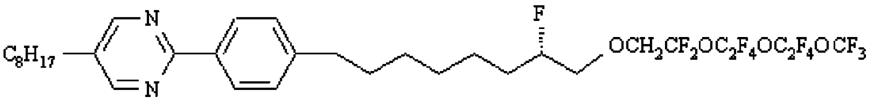


FIGURE 2 Chemical structures of the two components that make up the 3M fluorinated liquid crystal mixture. The mixture consisted of a 1:2 weight ratio of 7O]1222[6-] and 81222[7F8-]. (See COLOR PLATE XLII)

was sandwiched between two glass substrates having anti-reflection coatings on the outer surfaces and both a conducting electrode layer of ITO and refractive index matching layer on the inner surfaces. The cell gap of the H-PDFLC film was maintained by glass fiber spacers. The prepolymer and ferroelectric liquid crystal mixture was exposed to an interference pattern created from an Ar^+ laser (*Coherent Inc*), operating at $\lambda = 351\,\text{nm}$. The holographic setup used a half angle between the two beams (3°) to yield a grating pitch of ~2 μm. The beam powers were maintained at 25 mW in each beam with a beam diameter of 1 cm.

Samples were first characterized using an optical polarizing microscope (*Olympus Inc.*) to investigate the macroscopic properties of the grating structures. From this we were able to qualitatively determine whether the H-PDFLC gratings were polarization dependent or independent by rotating the grating between crossed polarizers. The microscope studies were followed up with morphological studies of the polymer using scanning electron microscope (SEM) and atomic force microscope (AFM). Samples were prepared for SEM analysis by freeze fracturing the grating to remove the top substrate, and rinsing the FLC away with a solvent to image only the remaining polymer structure. Atomic force microscopy analysis used the same sample preparation process to capture the polymer morphology and surface roughness. Additional electro-optic investigations were carried out using a helium-neon laser ($\lambda = 633\,\text{nm}$) and photo detector connected to a personal computer to measure the electro-optical properties as a function of applied voltage.

RESULTS AND DISCUSSION

H-PDFLC samples constructed from a 50:50 weight mixture of FLC and monomer showed radical differences from samples prepared from a 40:60 weight mixture. In the 50% FLC samples, optical polarizing microscopy clearly reveals the ferroelectric liquid crystal rich and polymer rich planes when placed between crossed polarizers as shown in Figure 3(a). As the sample is rotated 45° between crossed polarizers the grating contrast of liquid crystal and polymer planes remains relatively constant as shown in Figure 3(b). The lack of visible change in grating contrast between Figure 3(a) and 3(b) shows the polarization insensitive (or independent) nature of the grating, indicating there is not a preferential alignment for the FLC droplets. Further investigation of this grating structure (polymer morphology) is imaged by both SEM and AFM to extract information about the polymer morphology and surface roughness. A SEM image of the polarization

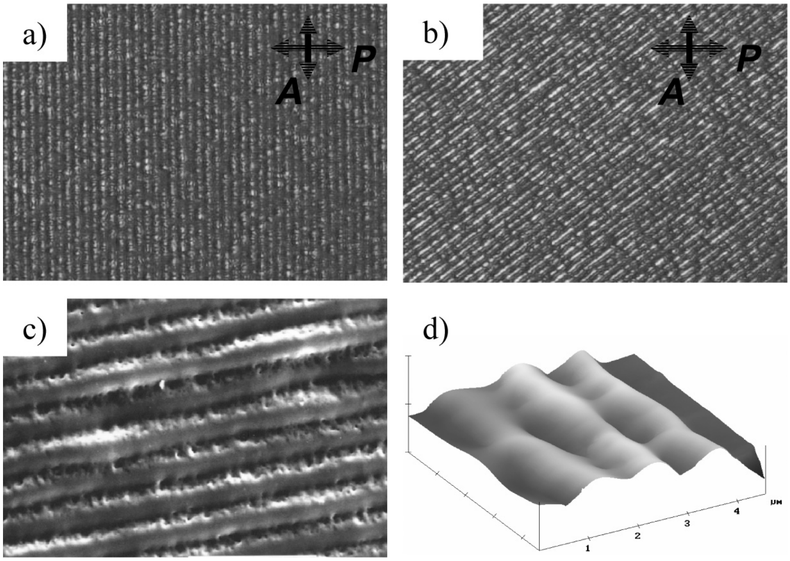


FIGURE 3 Optical polarizing microscopy of a polarization insensitive FLC H-PDLC grating (a) 90° between crossed polarizers, (b) 45° between crossed polarizers, (c) scanning electron microscopy image showing the droplet morphology, and (d) atomic force microscopy image showing the surface roughness created from the grating formation. (See COLOR PLATE XLIII)

independent grating is shown in Figure 3(c). The image reveals the polymer structure with voids where the ferroelectric liquid crystal droplets were before being removed with a solvent for imaging purposes. We anticipate that this type of droplet morphology creates a frustrated alignment of ferroelectric liquid crystal that causes the H-PDFLC gratings to be polarization insensitive. Atomic force microscopy also confirms the morphological features showing the droplet morphology and revealing a rough surface texture caused by the phase separation of the FLC and polymer as shown in Figure 3(d).

Contrary to the polarization insensitive gratings shown in Figure 3(a)–(d), the 40% FLC grating produces a completely different grating texture as shown by the optical polarizing microscopy images in Figure 4(a) and (b). When the grating is placed between crossed polarizers under and optical polarizing microscope the grating appears black with little contrast between the liquid crystal rich and polymer rich planes shown in Figure 4(a). As the sample is rotated 45° between crossed polarizers, the contrast increases to reveal the grating planes shown in Figure 4(b). This sharp contrast between these two images

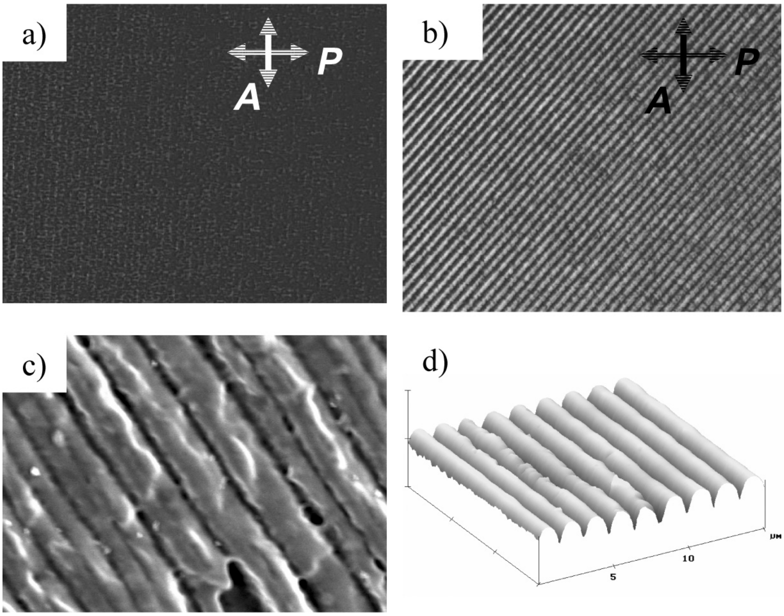


FIGURE 4 Optical polarizing microscopy of a polarization sensitive FLC H-PDLC grating (a) 90° between crossed polarizers and (b) 45° between crossed polarizers, (c) scanning electron microscopy image showing the channel morphology, and (d) atomic force microscopy image showing the clean phase separation between FLC and polymer planes. (See COLOR PLATE XLIV)

indicates that there is a preferential alignment of the ferroelectric liquid crystal parallel to the polymer walls resulting in a polarization sensitive (or dependant) grating. The FLC alignment is therefore orthogonal to the direction that most nematic based H-PDLCs align [10]. Scanning electron microscopy shows a magnified view of the grating structure after the FLC has been removed. The polymer morphology of this grating structure shows a smooth channel-like with a clean phase separation of FLC and monomer, as shown in Figure 4(c). Atomic force microscopy also shows the clean channel-like morphology over long range order of the grating structure in Figure 4(d). These smooth and well-separated systems are also seen in low functionality nematic based H-PDLCs [11] and in POLYCRYPS [17].

Quantitatively the polarization sensitivity of the H-PDFLC gratings was measured by recording the laser power of the transmitted beam for both s-polarization and p-polarization when the grating vector is parallel to the optics table. The graph in Figure 5 shows

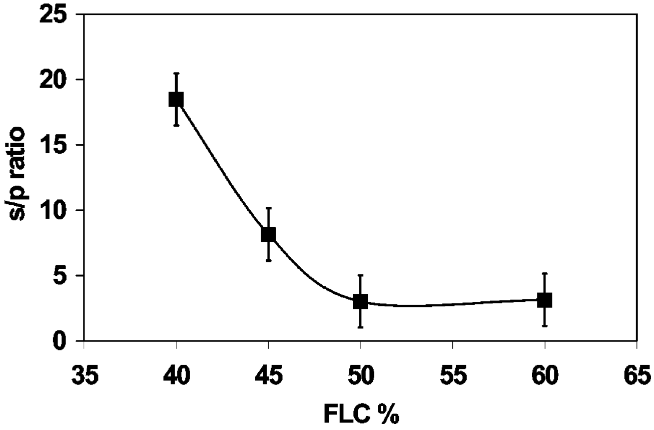


FIGURE 5 Polarization selectivity (s/p ratio) as a function of increasing FLC % in the FLC H-PDLC.

the polarization sensitivity ratio (s/p), or polarization contrast as a function of weight % of FLC. In addition to the 40% and 50% FLC samples, 45% and 60% FLC samples were fabricated to show the trend in polarization sensitivity as a function of weight % of FLC. As the weight % of FLC is increased from 40% to 60% the polarization sensitivity dramatically decreases to making the H-PDFLC samples more polarization independent. This is due to the transition from the channel morphology into the droplet morphology as the ratio of FLC to monomer is increased.

Polarization sensitivity was also measured as a function of film thickness for the 40% FLC (polarization dependant) and 50% FLC (polarization independent) gratings. As film thickness was increased from 5 μm to 25 μm the polarization sensitivity (s/p ratio) decreased for the 40% FLC sample as shown in Figure 6. This shows that we are able to tailor the polarization sensitivity in the 40% FLC gratings making them polarization independent by increasing the film thickness. In the 50% FLC gratings, the polarization sensitivity remains constant as the film thickness is increased to 25 μm shown in Figure 6. This further supports the notion of non-preferential alignment of FLC in the droplet morphology when the weight ratio of FLC is increased.

Diffraction efficiency was also investigated for the 50% FLC grating using incident s- and p-polarized light from a helium-neon laser to show the polarization independence. A graph of diffraction efficiency vs. film thickness is shown in Figure 7. As film thickness

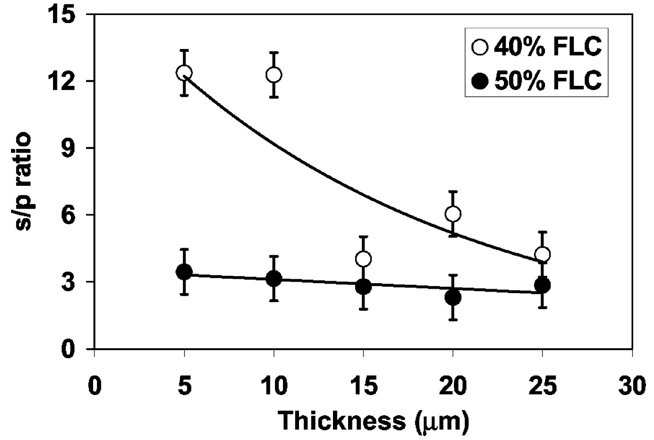


FIGURE 6 Polarization selectivity as a function of sample thickness for the polarization sensitive (40% FLC) and insensitive (50% FLC) H-PDLC. The lines in the plot are used to show the general trend as sample thickness is increased.

is increased, both s- and p- polarizations produce similar diffraction efficiencies showing the polarization independent diffractions for the 50% FLC grating. The 25 μm sample shows a strong light scattering appearance.

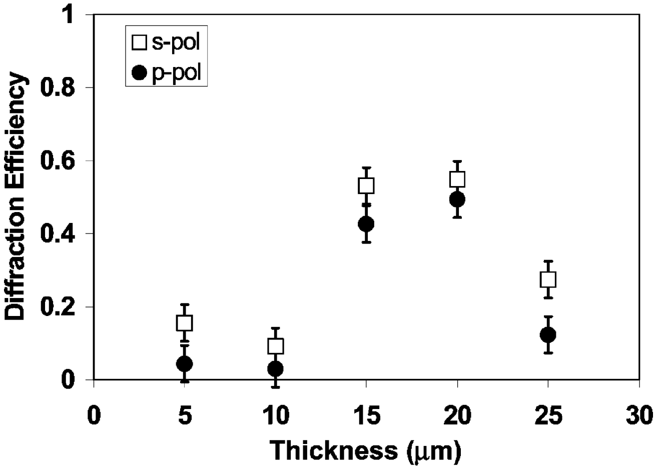


FIGURE 7 A plot of diffraction efficiency for both incident s- and p-polarizations with a polarization independent FLC H-PDLC grating.

The polarization selectivity results suggest to us that the preferred FLC alignment in the polarization sensitive gratings align parallel to the polymer walls, which is a different situation than in nematic based H-PDLCs [10]. The interaction of the fluorinated FLC therefore appears to be much different than in nematic based H-PDLCs. Since the cell gap is 2.5 times larger than the helical pitch, we do not achieve bistability for our FLC H-PDLC gratings.

In the case of the polarization insensitive gratings that produce a droplet morphology, the FLC alignment is hard to predict inside the droplets using only microscopy techniques. However, nuclear magnetic resonance studies are planned.

CONCLUSIONS

In conclusion we have shown a method to tailor the polarization dependence of H-PDFLC gratings by controlling the alignment of the FLC. We have shown through various microscopy tools that that polarization dependence is dictated by the polymer and FLC morphology resulting from the photo induced phase separation in the holographic exposure. The two distinct morphologies that were investigated were the channel and droplet morphologies producing polarization dependant and independent electro-optic properties respectively. Although we focus on the basic morphological features of the polymer network here, we are currently evaluating these materials for fast switching applications. The electronic performance parameters will be a subject of future study, as well as more basic studies on the mechanisms of the FLC alignment.

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