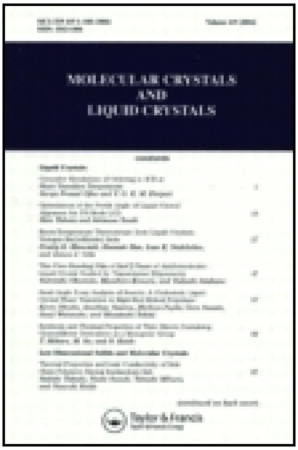

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Morphological Studies of Holographically Formed Polymer Dispersed Ferroelectric Liquid Crystals Using Elevated Temperature Exposure

James N. Eakin [a] , Gregory P. Crawford [a] & Marc D. Radcliffe [b]

[a] Division of Engineering, Brown University, Providence, USA

[b] 3M Display and Graphics Laboratory, Minnesota, USA

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Morphological Studies of Holographically formed Polymer Dispersed Ferroelectric Liquid Crystals Using Elevated Temperature Exposure

James N. Eakin
Gregory P. Crawford
Division of Engineering, Brown University, Providence, USA

Marc D. Radcliffe
3M Display and Graphics Laboratory, Minnesota, USA

In this contribution we describe a method of controlling the polarization dependence in holographically formed polymer dispersed liquid crystals using a ferroelectric liquid crystal mixture and a diacrylate monomer. By elevating the temperature of the prepolymer and liquid crystal mixture prior to the holographic exposure, we can control the polymer morphology and therefore the resulting alignment of the ferroelectric liquid crystal. The two distinct polymer morphologies that we manufacture and investigate are droplet and channel like. We investigate these grating structures using optical polarizing microscopy and scanning electron microscopy. We support our polarization dependence results with electro-optic characterization to see if ferroelectrics have added benefits of faster electro-optic response verses nematics in holographically formed polymer dispersed liquid crystal geometries.

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

INTRODUCTION TO H-PDLCs

Holographically formed polymer dispersed liquid crystals (H-PDLCs) are formed from a photo induced phase separation counter diffusion process that is initiated by the inference of two coherent laser beams [1,2]. When a photosensitive mixture of liquid crystal and monomer is exposed to an amplitude interference pattern, the high intensity

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Address correspondence to James N. Eakin, Division of Engineering, Brown University, Providence, RI 02912 USA. E-mail: James_Eakin@brown.edu

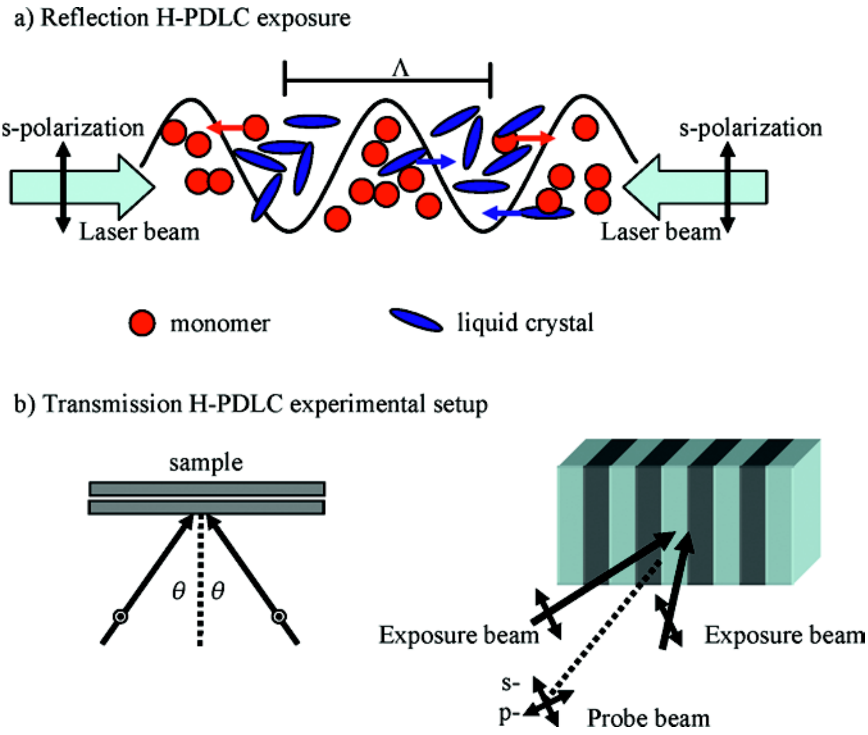

FIGURE 1 A schematic illustration illustrating a two beam reflection holographic setup showing the intensity modulation with monomer in the high intensity regions and liquid crystal in the low intensity regions (a) and experimental setup of the exposure beams and the probe beam for transmission H-PDLCs.

regions of the amplitude modulation initiate polymerization of the monomer and forces out the non-reactive liquid crystal to the dark regions of the interference pattern as shown in Figure 1. After the exposure process (~30 seconds) the grating is permanently “locked in” to produce stratified alternating liquid crystal rich and polymer rich planes. The periodicity (or pitch Λ) of the grating is determined by Bragg’s Law:

$$\Lambda = \frac{\lambda_w}{2\sin\theta}$$

where λ_{w} is the wavelength of the exposure beams, and θ is the half angle between the beam pairs. In a reflection mode H-PDLCs the two beams interfere from opposite sides of the sample to create planes of liquid crystal and polymer parallel to the glass substrates [3,4]. In transmission mode H-PDLCs, the two beams interfere from the same side of the sample to produce alternating planes of liquid crystal and polymer perpendicular to the glass substrates [3,4].

When H-PDLCs are formed between glass substrates that have a transparent conducting electrode layer such as indium tin oxide (ITO) the optical properties of these active gratings switch from a diffractive element to a transparent element by applying an electric field across the film. The basic principle of operation of H-PDLCs relies on an index mismatching and matching case between the liquid crystal and polymer [3,4]. Liquid crystal materials are chosen such that the extraordinary index (n_e) is mismatched with the polymer (n_p) and the ordinary index of the liquid crystal (n_o) is matched with n_p. When the H-PDLC film is illuminated with a laser, the light experience the refractive index modulation caused by the liquid crystal rich regions (a combination of n_e and n_o) and polymer rich planes (n_p). If a sufficiently large electric field is applied across the film (5–10 V/μm) and the liquid crystal molecules posses a positive dielectric anisotropy ($\Delta\varepsilon > 0$) the liquid crystal molecules will reorient parallel to the direction of the electric field. In this case, $n_o \sim n_p$ and the film appears optically transparent [3,4].

The attractive nature of these electrically switchable gratings has enabled researchers to find many different applications for these diffractive elements including candidates for reflective display technologies [5], add-drop filters for telecommunications [6], lasing media for optically pumped lasers [7–9] and multi-dimensional switchable lattices for photonic crystals and quasi-crystals [10–13]. These composite films, which typically use nematic liquid crystal materials, exhibit electro-optic results that are polarization sensitive because of a controlled and preferential alignment of the liquid crystal between the polymer planes [14]. This paper focuses on using ferroelectric liquid crystal materials prepared at an elevated temperature exposure. Using this process we find that the nature of the output polarization is tailorable. Many groups have demonstrated similar exposure methods using nematic liquid crystals exposed in the isotropic phase. These process known as polymer liquid crystal polymer slides (POLYCRYPS), creates a complete phase separation between the liquid crystal and polymer [15–17].

EXPERIMENTAL

Holographically formed polymer dispersed ferroelectric liquid crystal transmission gratings were formed from a mixture of fluorinated ferroelectric liquid crystal (*3M Company*) and diacrylate monomer

(PN393, *EM Industries*). The ferroelectric liquid crystal mixture exhibited a wide SmC* phase from room temperature to 64.8°C, a spontaneous polarization (P_s) of 25.8 nC/cm^2, a tilt angle of 23.7° and a helical pitch of $\sim 2\,\mu$m. The diacrylate monomer, PN393, was selected because of its low glass transition temperature ($T_g \sim -20$°C) and high solubility at room temperature in the fluorinated FLC mixture. When above the T_g, PDLCs are known to switch at low voltages [18]. Equal weight amounts of prepolymer and FLC were combined together to form a homogenous mixture of prepolymer and FLC. A drop of the prepolymer and FLC mixture was sandwiched between two pieces of glass having an indium tin oxide (ITO) transparent conducting electrode layer and an index matching layer on the inner surfaces. The outer glass surfaces employed an antireflection coating to reduce spurious reflections during the holographic exposure. Glass fiber spacers were used to maintain a constant cell thickness of 5 μm. between the two substrates. The prepolymer and ferroelectric liquid crystal mixture was exposed to a two beam transmission holographic setup using an Ar^+ laser (*Coherent Inc.*) operating at $\lambda = 351$ nm. Both beams in the holographic setup were s-polarized and had equal power (25 mW) with a beam diameter of 1 cm. The half angle between the two beams was measured at 3° to produce a holographic grating pitch of 2 μm.

Holographically formed polymer dispersed ferroelectric liquid crystal samples were exposed at various temperatures in the SmC* phase (25–40°C) to investigate the effects of polymer grating morphology and ferroelectric liquid crystal alignment in the context of potential opto-electronic applications. Optical polarizing microscopy provided initial qualitative results of the polarization dependence by imaging the holographic gratings as they were rotated between crossed polarizers. H-PDFLC gratings were also imaged with scanning electron microscopy (SEM) to investigate the polymer structure formed from the holographic exposure. Samples were prepared for SEM analysis by a freeze fracturing the grating and extracting the FLC with a solvent evaporation to image the polymer morphology and FLC voids. Prior to the SEM study, quantitative measurements of polarization dependence were record by illuminating the grating with a helium-neon laser ($\lambda = 632.8$ nm) and using a photodetector to measure intensity of the first order diffraction peak for incident s- and p- polarized light.

RESULTS AND DISCUSSION

Holographically formed polymer dispersed ferroelectric liquid crystal (H-PDFLC) gratings exposed at room temperature formed a considerably different grating structure than H-PDFLCs exposed at elevated temperatures in the SmC* phase. An optical polarizing microscopy image of the H-PDFLC grating exposed at room temperature shows the stratified grating of ferroelectric liquid crystal and polymer planes at 90° between crossed polarizers in Figure 2(a). The discontinuous light grey areas of the grating image are FLC rich with the dark grey areas being polymer rich. As the H-PDFLC grating is rotated 45° between crossed polarizers the grating contrast between the FLC and polymer remains relatively constant as shown in Figure 2(b). The lack of grating contrast shows the polarization insensitive (or independent) nature of the H-PDFLC grating formed from a room temperature holographic exposure. The polarization independent gratings suggest there is not a well defined alignment of the FLC within the encapsulating polymer as in the case of nematic based H-PDLCs [14].

Scanning electron microscopy further probes the grating structure by imaging the polymer morphology of this grating shown in Figure 3. The formation of FLC domains (a very rough and corrugated morphology) between the polymer rich planes further supports the idea that there is no preferential alignment of the FLC. We believe that due to the grating pitch and cell gap constraints a frustrated alignment of FLC occurs inside the droplets making the grating exhibit polarization independent properties.

Optical polarizing microscopy images of an H-PDFLC grating at formed at an elevated temperature exposure (40°C) are shown in Figure 4(a) and (b). Note that the 40°C is still in the SmC* phase and 20 degrees below the Smectic A* phase. When the grating is placed at 90° between crossed polarizers the grating appears black

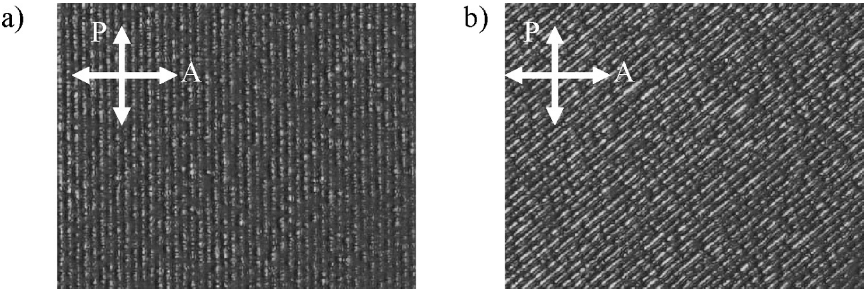

FIGURE 2 Optical polarizing microscopy of a polarization insensitive FLC H-PDLC grating (a) 90° between crossed polarizers, (b) 45° between crossed polarizers.

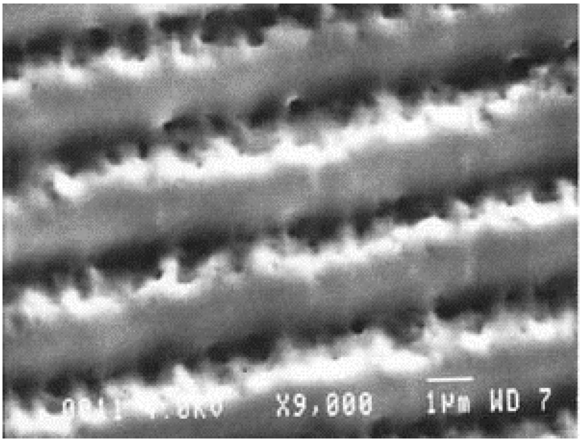

FIGURE 3 Scanning electron microscopy image of a polarization insensitive grating showing droplet morphology.

with very little visible contrast between the FLC and polymer rich planes shown in Figure 4(a). As the grating is rotated 45° between crossed polarizers the contrast between the FLC and polymer rich improves significantly to reveal the FLC rich planes (grey) and the polymer rich planes (black) in Figure 4(b). This drastic change in contrast suggests that the FLC aligns parallel to the polymer planes (confirmed later by probing the sample with s- and p- polarization. This is contrary to nematic based H-PDLCs with high polarization selectivity where the liquid crystals align perpendicular to the polymer walls. The preferential alignment that results from this elevated temperature exposure is a polarization dependant (sensitive) grating.

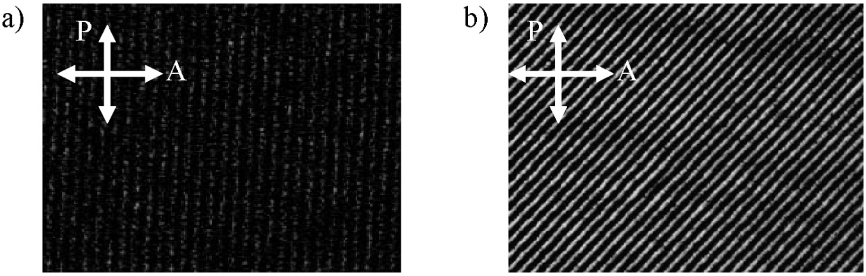

FIGURE 4 Optical polarizing microscopy of a polarization insensitive FLC H-PDLC grating (a) 90° between crossed polarizers, (b) 45° between crossed polarizers.

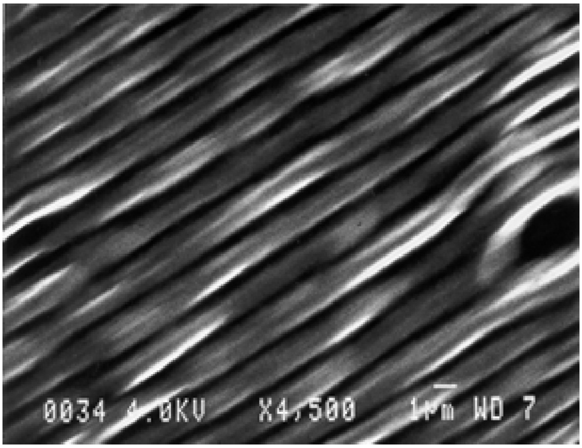

FIGURE 5 Scanning electron microscopy image of a polarization sensitive grating showing channel morphology.

Further investigation of this grating structure shows a scanning electron microscopy image in Figure 5. The polymer morphology formed from the elevated temperature exposure reveals a 'clean' phase separation between the FLC and monomer as indicated by the smooth polymer walls and empty channels. We attribute the polarization dependence and preferential alignment of the FLC to this complete phase separation that produces a non-droplet morphology. This type of polymer morphology has been previously reported in H-PDLCs using low functionality monomers [19] and also in POLYCRYPS [15–17].

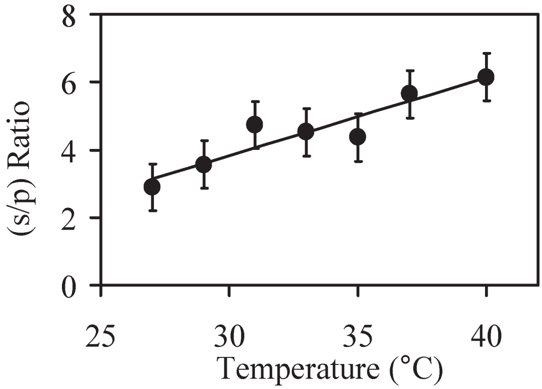

FIGURE 6 Polarization selectivity (s/p) ratio for elevated temperature exposures of H-PDLFC gratings.

Polarization selectivity measurements were recorded by illuminating the polarization insensitive and polarization sensitive H-PDFLC gratings with a helium-neon laser ($\lambda = 632.8\,\text{nm}$) and measuring the transmitted intensity of the zero order beam with a photodetector. A ratio of transmitted intensities for incident s- and p- incident polarizations were used as a metric to define the polarization selectivity (s/p) for the two types of gratings. In the case of a "perfect" polarization independent grating $s/p = 1$. A plot of the recorded polarization selectivity ratios for different temperature exposures are shown in Figure 6. As the exposure temperature increases from room temperature to 40°C the polarization selectivity (s/p ratio) increase. This is due to the change in morphology from droplet to channel like. We also believe that the increase in temperature causes a better phase separation to occur which in turn creates a preferential alignment of the FLC.

CONCLUSIONS

We have shown a method to control the polarization dependence of H-PDLC grating using ferroelectric liquid crystals and an elevated temperature exposure process. By changing the exposure temperature in the SmC* phase we can produce a grating structure having either a droplet or nearly channel-like morphology. The droplet morphology produces a polarization independent holographic grating apparently due to the non-preferential alignment of FLC domains between polymer planes. The channel-like morphology produces a polarization dependent holographic grating at elevated temperatures that causes the FLC to align parallel to the polymer walls. While the results of this paper focused mainly on polymer morphology, we will continue to evaluate these two types of gratings using electro-optic characterizations to determine dynamic responses for the different confined FLC geometries. We believe this process is attractive for applications since we can control the polarization selectivity of the sample. It is a subject of future study to directly probe the FLC configuration with solid state nuclear magnetic resonance techniques, and correlate the FLC structure and polymer morphology to the electro-optic performance parameters (efficiency, threshold voltages, and dynamic response time). Also, in future investigations, we will work with different ferroelectric liquid crystal mixtures to determine if the polarization tailorability results described above are associated with FLCs in general or are materials specific.

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