

POLICRYPS-based electrically switchable Bragg reflector

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Abstract: The formation and characterization of a switchable volume reflective element fabricated from a polymer liquid crystal (LC) polymer slice (POLICRYPS) structure by holographic photopolymerization at high temperature (65 °C) using a photosensitive/nematic liquid crystal prepolymer mixture is reported. The submicron Bragg structure formed consists of periodic continuous polymeric walls separated by periodic LC channels. The phase separated NLC self-aligns in a homeotropic alignment between the polymer walls as indicated by polarizing optical microscopy analysis (Maltese cross). The resulting periodic grating structure results in a Bragg reflection notch upon illumination with white light due to the periodic variation in refractive index. Electro-optical experiments realized through in-plane electrodes and temperature experiments confirm that the multilayer structure acts as a Bragg mirror whose reflection efficiency can be controlled by either a small (~3V/μm) electric field or temperature.

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1. Introduction

Holographic photopolymerization (HP) is a simple, fast and attractive way to fabricate one-, two- and three-dimensional (1D, 2D, 3D) complex structures with length scale periodicity commensurate with the optical regime [1–4]. For these applications, the recording material must be optimized for efficient diffraction with low scattering and maximum information storage. Photopolymer materials are inexpensive, easily processed, can record low-loss, high-diffraction-efficiency optical elements, and have large data storage capability [5,6]. Combining the properties of HP and liquid crystals (LC) by mixing before photopolymerization enables the fabrication of switchable periodic structures. Upon photopolymerization induced by a periodic intensity pattern, two distinct phases, polymer and LC-rich can be formed whose ultimate local and periodic morphology is related to the chemistry, wavelength of irradiation, and interference geometry. The final morphology is dictated by a complex balance between polymerization kinetics, phase separation, and diffusion. The Bragg diffraction properties arising due to the periodic refractive index profile can be modulated with an electric field. Two different kinds of switchable gratings grew from this premise including holographic polymer dispersed liquid crystals (H-PDLCs) [7–10], composed of periodic LC nano/micro-domains (droplets) separated by cross linked polymer regions and POLICRYPS [11–13], slices of pure NLC (instead of droplets) separated by polymer walls. The molecular director of the latter case can be uniformly aligned relative to the polymeric walls during the fabrication process and thus much larger refractive index contrast can be obtained. In general a large surface to volume ratio is introduced by the small droplets [14] in the HPDLC case which leads to large field strengths (15-20 V/micron) needed to switch the optical properties. Improvements to the field strengths can be obtained by introducing specialty monomers and additives into the system [14]. A second drawback is light scattering in the blue portion of the visible spectrum due to the droplet morphology. It is worth mentioning that another approach for reducing the scattering losses is to align the LC during formation by utilizing reactive mesogenic monomers [15,16]. The absence of individual NLC droplets (present in H-PDLC) in POLICRYPS structures enables field strengths of a few V/ μm to reorient the NLC director on a millisecond timescale. The confinement and subsequent alignment of NLC molecules into uniform channels also prevents light scattering and allows fabrication of structures with high optical quality as diffraction efficiencies as high as 98% have been measured. H-PDLCs have been extensively

studied for the realization of both Bragg transmission and reflection gratings [17–20]. For transmission gratings, extensive concepts exploiting the ability to dynamically diffract between two states have been explored. For reflection gratings, it is possible to take advantage of the strong wavelength selectivity and efficient diffraction of a single beam for applications ranging from high resolution reflective spatial light modulators to dynamic filtering. POLICRYPS transmission gratings have been extensively studied and have shown relevance to switchable phase modulators [21], all-optical diffraction gratings [22] and tunable optical filters [23]. This geometry offers a versatile suite of wall geometries, either planar or curved, allows different orientation states (perpendicular or parallel) depending on chemistry and cure conditions, and can be utilized to produce multi-dimension high resolution patterning [24]. To date, however, reflection mode POLICRYPS have not been obtained due to the large differences in Bragg spacing between transmission and reflection geometries and photochemical complexities. Reported here is the first demonstration of a Bragg reflector utilizing the POLICRYPS fabrication technique.

2. Materials and Method

NOA61 (Norland Optical Adhesive), LC BL038 (Merck) and a visible photoinitiator (Irgacure 784) were utilized in the weight ratio of 70%, 28%, and 2%.

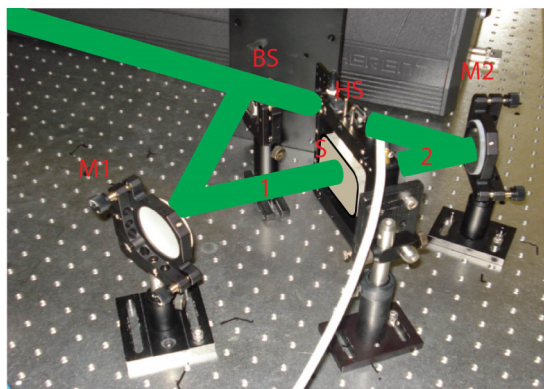


Fig. 1. Holographic setup for the realization of POLICRYPS structures in reflection geometry: BS, beam splitter; M1, M2 mirrors, HS hot stage; S, sample.

The holographic setup illustrated in Fig. 1 uses a CW laser emitting at $\lambda = 532\text{nm}$ where the beam is expanded, collimated by means of a telescopic beam expander (spatial filter + collimating lens) and divided into two parts of almost equal intensity by a beam splitter. The two beams (1 and 2) are reflected from two mirrors (M1 and M2) and overlap in a counterpropagating geometry at the entrance plane of the sample cell giving rise to an interference pattern (the interference fringes are perpendicular to the cell surfaces) whose spatial period is approximately 200 nm. The reactive mixture was sandwiched between glass slides (without any chemical treatment) spaced $10\ \mu\text{m}$ apart using glass spacers and exposed to the interference pattern for 10 minutes at $170\text{mW}/\text{cm}^2$. Unlike the typical HPDLC process, photopolymerization is performed at elevated temperature ($70\ \text{°C}$) to exploit the higher diffusivity of the NLC molecules in the isotropic state. This enables a final morphology devoid of individual small, random dispersed LC droplets. The temperature is controlled by a hot-stage which is used to slowly cool ($0.2\ \text{°C}/\text{min}$) the exposed reflection grating to room temperature by means of a controlled ramp once the curing process has ended.

3. Optical and electro-optical characterization

As shown in the schematic representation of Fig. 2(a), the reflective POLICRYPS structure is composed of continuous polymeric layers interspersed between phase separated homeotropically aligned NLC layers.

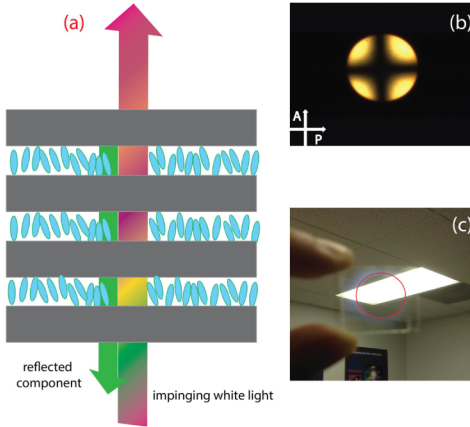


Fig. 2. Schematic of the NLC configuration in reflective POLICRYPS structures (a), a conoscopic image of the sample (b), and an image looking through the sample (c)

This geometry was confirmed by inspection of the sample under conoscopic imaging conditions realized by placing a conventional microscope between crossed polarizers and including a condensing and a Bertrand lens (BL). At the back-focal plane of the BL, a dark Maltese cross [Fig. 2(b)] was observed indicating that the NLC molecules were homeotropically aligned within the phase separated LC layers. As further evidence [Fig. 2(c)], the grating area (red circle) shows no scatter and is transparent indicating the absence of a scattering NLC droplet morphology. The periodic structure formed acts as a Bragg mirror with a modulation of the refractive index between pure polymer ($n_p \approx 1.54$) and the ordinary index of the NLC ($n_o \approx 1.5$). The Bragg condition can be expressed as:

$$2n_{\text{eff}}\Lambda \sin \vartheta = m\lambda_B \quad (1)$$

where n_{eff} is the effective refractive index of the structure, Λ is the periodicity, ϑ is the angle between the propagating beam and the sample, m is an integer and λ_B is the Bragg wavelength. In our case since $\vartheta = 90^\circ$ (normal incidence), $n_{\text{eff}} \approx 1.52$ and $m = 1$, Eq. (1) can be expressed as $2n_{\text{eff}}\Lambda = \lambda$.

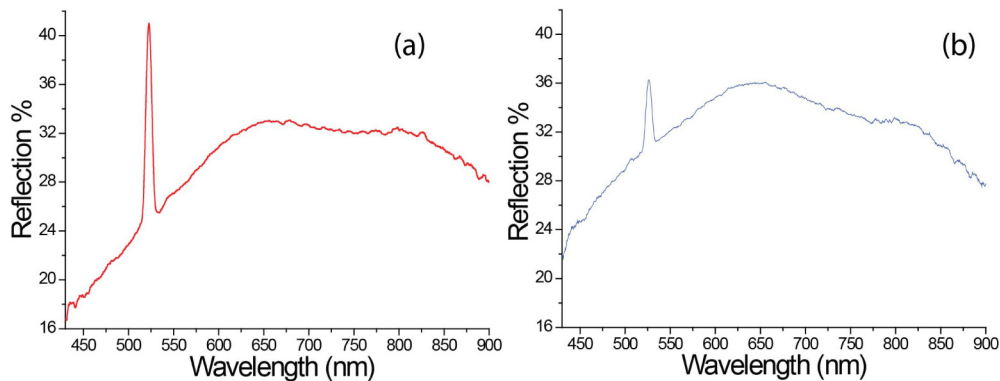


Fig. 3. Reflection spectrum of the sample at room temperature (a) and beyond (b) the NLC clearing temperature (70°C) (b).

The reflection spectrum of the sample [Fig. 3(a)] shows a sharp and narrow ($\approx 7\text{nm}$) peak centered at $\lambda_B = 523\text{nm}$ suggesting a periodicity of $\Lambda \approx 170\text{nm}$. The grating diffraction efficiency (η) can be explained by using the coupled-wave theory, for both transmission and reflection gratings, employing an effective medium approach to model the refractive index

modulation. Anisotropic coupled-wave theory has yielded excellent agreement with experimental polarization and electro-optical properties of these gratings [25]. In this framework, η depends mainly on grating thickness L , probe wavelength λ , electric field E and temperature T and refractive index contrast of the grating, Δn_g . In our case, the reflection efficiency of the sample is quite modest ($\approx 16\%$) since $\Delta n_{gr} = n_p - n_o = 1.54 - 1.5 = 0.04$ of the structure is small. To confirm this behavior, the sample was heated above the NLC clearing temperature (70°C). In this condition, the NLC (isotropic phase) exhibits a refractive index of ~ 1.53 and consequently Δn_{gr} is reduced to 0.01. As a consequence, the amplitude of the reflection peak is attenuated and exhibits a reflection efficiency of $\sim 4\%$ [Fig. 3(b)]. We have performed some early explorations on the stability of such a system and have not observed any degradation in electro-optical or optical behavior when subjected to temperature cycles across the nematic-isotropic phase transition (70°C).

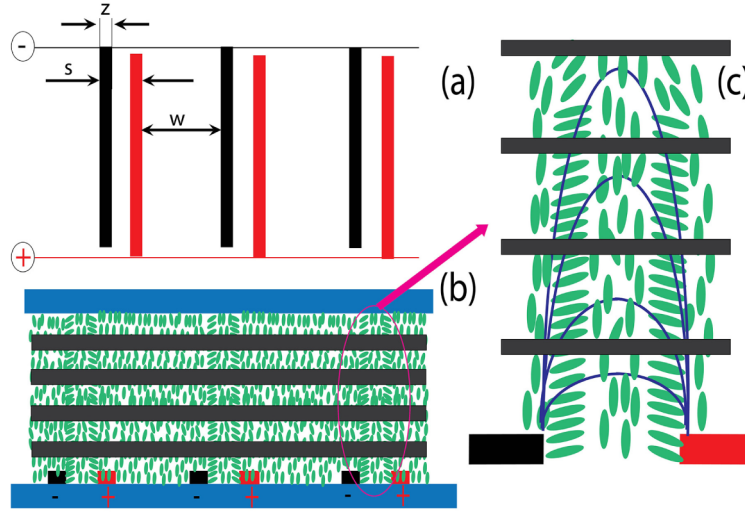


Fig. 4. Schematic of the electrodes in the in-plane switching configuration (a). Sketch of the NLC molecules under the influence of the in-plane electric field (b) along with a detail of the electric field distribution affecting only the NLC molecules in proximity to the electrodes(c).

The sample does not exhibit electric-field switching as initially formed as the LC molecules (positive dielectric anisotropy) are already aligned parallel to the field direction across the cell (electric field applied through the bulk of the cell by means of ITO coated glass substrates). To further prove this LC orientation and to show that e-field modulation is possible (proof-of-concept), a sample (same experimental conditions) was fabricated with in-plane electrodes. The schematic of the electrode configuration is reported in Fig. 4a. The electrodes are aluminum (width = $z = 5\mu\text{m}$; distance = $s = 20\mu\text{m}$; interdistance = $w = 60\mu\text{m}$) formed through a standard photolithographic process reported elsewhere [26].

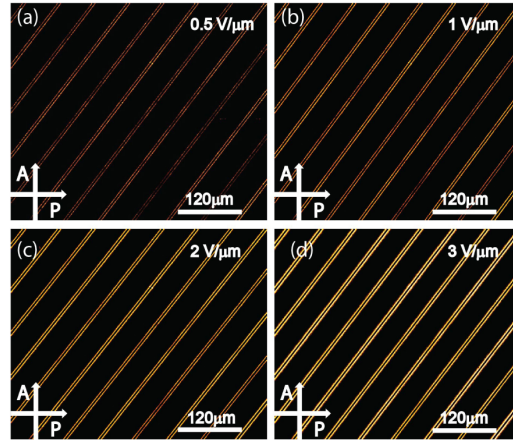


Fig. 5. POM images of the sample under the influence of an in-plane electric field.

Figs. 5(a)-5(d) show polarized optical microscope (POM) images of the sample at different values of the electric field. Bright stripes with increasing intensity (from a-d) confirm that the application of an external voltage (square voltage, 1KHz) induces a reorientation of the NLC molecules along the electric field distribution. The electric field affects only the NLC molecules in proximity to the electrodes (see schematic in Figs. 4 (b) and 4 (c)). This can be explained by considering that the strength of the electric field is proportional to s^{-2} (where s is the distance between the electrodes). In this case, $s = 20\mu\text{m}$, and for this reason the quite modest electric field ($3\text{ V}/\mu\text{m}$) affects only the NLC molecules in proximity to the electrodes as the strength of the electric field is not strong enough to reorient the NLC molecules in the middle between the two electrodes (dark area or homeotropic alignment between the two close bright strips, Figs. 5(a)-5(d)). The unaffected area can be reoriented by increasing 2-3 times the amplitude of the electric field. This condition affects irreversibly the electro-optical properties of the sample. Optimization of the electrode pattern for in-plane switching is well known in LCD technologies. Related opportunities include FFS (Fringing Field Switching) techniques but optimization of the In-Plane structure and approach were not the focus of the current study. We simply used the geometry to independently prove that the NLC molecules were in a homeotropic orientation.

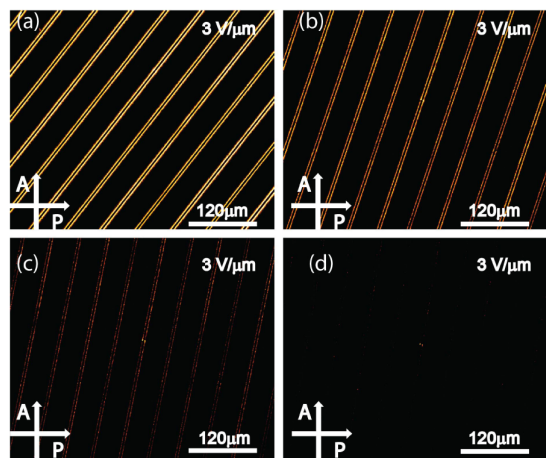


Fig. 6. POM images of the structure under the influence of an in-plane electric field ($3\text{V}/\mu\text{m}$) for different angles between the analyzer and the optical axis of the sample.

For impinging white (non-collimated) light, a noticeable difference between bright [Fig. 6(a)] and dark [Fig. 6(d)] states is obtained by rotating the sample between crossed polarizers while keeping the external voltage ($3\text{V}/\mu\text{m}$) applied. This observation is clear proof that the NLC confined between the polymer layers does not exhibit a droplet-based morphology (e.g. H-PDLC) but instead is experimental evidence that the NLC exhibits a pure nematic phase and the sample behaves as a uniaxial retardation plate with its optical axis aligned parallel to the polymer layers.

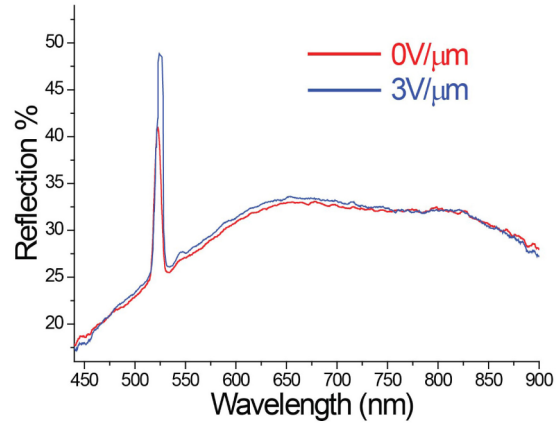


Fig. 7. Reflection spectrum of the sample without (red curve) and with (blue curve) an applied electric field.

In this geometry, Fig. 7 shows that an electric field induces an enhancement of the reflection peak amplitude ($\approx 10\%$) due to an increase of Δn_{gr} . Noteworthy, despite the reflection efficiency is not very high, the spontaneous vertical alignment of the NLC represents a tremendous opportunity for new applications such as vertically aligned displays. As such, the low reflection efficiency in this geometry confirms the specific orientation. According to the anisotropic coupled-wave theory (Ref. 25), using a $\Delta n_{\text{gr}} = 0.2$ (achievable, for example, with simple E7 NLC) there are means to obtain higher reflection efficiencies. Alternative methods to potentially increase the diffraction efficiency include using a NLC with a negative dielectric anisotropy or by chemically modifying the pre-polymer in order to force the NLC molecules to stay planar aligned in the initial state. Study of both approaches is currently underway. The focus of this paper wasn't on maximizing the specific reflection efficiency, but instead to show it is possible to use the POLICRYPS methodology to fabricate a reflection grating system (of appropriate periodicity).

4. Conclusion

To summarize, an electrically switchable Bragg reflector has been fabricated using a composite mixture of pre-polymer and nematic liquid crystal through a holographic photopolymerization process. The periodic grating structure is composed of polymeric layers with phase separated, homeotropically aligned NLC layers (POLICRYPS) formed through this one-step in situ process. Electro-optical characterization of these switchable reflective POLICRYPS structures, performed through an in-plane electrode geometry indicates control of the reflection efficiency with a moderate electric field ($3\text{ V}/\mu\text{m}$). Exploration of reflective POLICRYPS samples prepared with different LC materials and phases (liquid crystalline polymers, cholesteric, ferroelectric, azo-LC) is currently underway.

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