

## Optically Switchable Liquid Crystal Photonic Structures

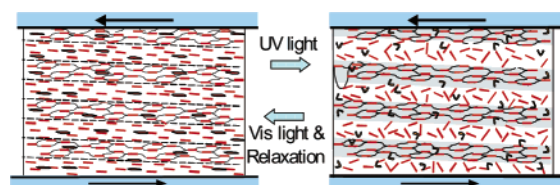
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Advances in photonic devices depend on the development of active structured optical materials and patterned optical systems.<sup>1</sup> Success with passive photonics propelled interest in active materials and tunable properties.<sup>2,3</sup> Promising routes include liquid crystals (LCs).<sup>4</sup> Recent work has explored the use of self-assembled templates<sup>5</sup> and structures in patterned materials.<sup>6</sup> Spatial light modulators<sup>7</sup> and lasers,<sup>8</sup> for example, have been fabricated with liquid crystal-based, structured hybrid optical materials. Current research has relied on the introduction of azobenzene dyes<sup>9</sup> and liquid crystalline azobenzene (AzoLCs) materials into LC hosts for holographic recording and photo-optic properties in patterned optical matrices.<sup>10,11</sup> AzoLCs undergo a reversible trans–cis photoisomerization when exposed to certain wavelengths. When blended with a host nematic LC, the conformational change of the azoLC disrupts the order of the surrounding LCs, changing the optical properties of the ensemble.<sup>12</sup> Sufficient concentrations of Azo-LC can induce a nematic–isotropic transition in bulk LC. When the AzoLC-doped blend is incorporated into an optical structure, this allows for phototuning of the spectral properties. Such blends can be incorporated into arbitrary optical structures through the use of holographic photopolymerization.<sup>13</sup> Observation of optically reversible photoinduced reflectivity in a holographically patterned polymer stabilized liquid crystal film is reported in this communication.

Holographic patterning offers feature sizes and dimensional control appropriate to working with optical wavelengths. Significant control over morphology and, hence, optical properties, as well as parallel fabrication, make it an excellent technique when speed and throughput are critical factors. A simple example of a holographic structure is the Bragg reflector, a periodic multilayer or striated film resembling a quarter wave stack or diffraction grating. This report will concern holographic Bragg reflectors where the grating vector is normal to the film and thus the films exhibit wavelength selective reflectivity and a complimentary reduction in transmission. These reflectors are patterned by interfering two beams from a solid-state 532 nm laser source (Coherent, Verdi) to create a standing wave pattern within an LC/LC-photopolymer syrup in a cell between two transparent electrodes (both indium tin oxide (ITO) coated glass) with a 15 micron spacer, as in the case of Sutherland et al.<sup>14</sup> The photopolymer syrup is a combination of the diacrylate liquid crystal monomer (1,4-phenylene bis{4-[6-(acryloyloxy)hexyloxy]benzoate}), trifunctional monomer TMPTA, and liquid crystal (Merck, ML-1009) used by Kato and co-workers<sup>15</sup> and is supplied by Kent Optronics Inc. (KOI, Kent, OH). The photoinitiator used in these experiments is Rose Bengal with the co-initiator *n*-phenyl glycine (NPG, Aldrich). The transparent electrodes are coated prior to assembly with a polyimide thin film and rubbed to provide an alignment texture. The cell is assembled such that the



**Figure 1.** Diagram of several layers of a holographically patterned, polymer stabilized, liquid crystal structure. The azoLC molecules are represented as darker. UV light triggers photoisomerization of the azoLC and disrupts the nematic order of LCs in the free regions only. The transition generates an index profile within the structure. The change is reversible with exposure to visible light.

rubbing directions are opposed to induce planar alignment in the prepolymer nematic liquid. The exposure process does not disrupt the orientation of the LC, and the films show a uniform transparency between cross polarizers consistent with a nematic monodomain texture. During the exposure, regions of high intensity within the film undergo photoinduced polymerization to form an LC-polymer network; monomer from the dark regions diffuses in and reacts creating regions of polymer stabilized LC and coaligned regions with less polymer content and relatively free liquid crystal domains, as shown in Figure 1. The Bragg wavelength of the written grating is controlled by the angle of intersection of the beams. For this experiment 635 nm was chosen so as not to significantly overlap either the absorption of the azobenzene or the 532 nm excitation wavelength. This corresponds to a bilayer thickness of 210 nm in the patterned structure or roughly 70 bilayers in the cell. After patterning, the cell remains transparent. When a sufficient voltage is applied across the ITO electrodes, the free LC regions are realigned with the nematic director normal to the film and the polymer-stabilized regions are not. This induces a periodic modulation in the index of refraction through the film. The film becomes reflective for light in a narrow range of wavelengths corresponding to the Bragg wavelength and polarized in the rubbing direction.

Photo-optic properties are imparted to the Bragg reflector through the incorporation of a photochromic LC, 4-butyl-4-methoxyazobenzene (BMAB, BEAM co., Winterpark, FL) in the prepolymer syrup at 7 wt %. When the trans, rodlike, isomer of this LC absorbs a UV photon, it triggers a reversible conformational change to the kinked, cis, state. The cis isomer affects the host nematic as an impurity, disrupting the local order and lowering the clearing temperature. As shown in Figure 1, the polymer-stabilized regions show relatively little change in order or optical properties, while the free regions become disordered. This order change generates a photoinduced refractive index modulation. The result is a reflective notch similar to the electro-optic action of the samples. In Figure 2 the transmission spectra of unexposed and exposed samples are shown clearly demonstrating the induced reflectivity.

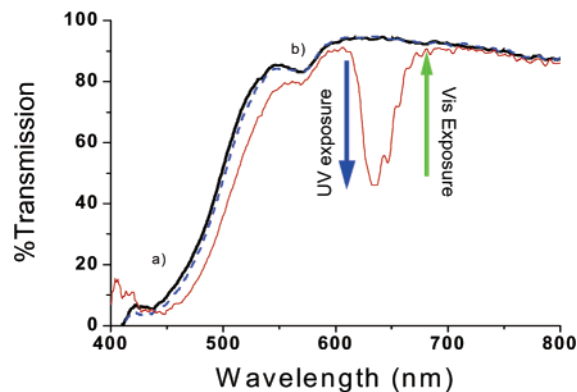
The sample exhibits a peak diffraction efficiency of 58% for light polarized along the rubbing direction, at 635 nm, after 490 s

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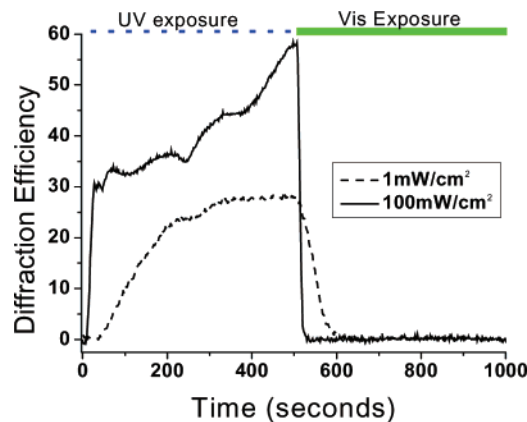


**Figure 2.** Transmission curves of an azoLC sample in the unexposed (solid) and exposed (grey) states as well as after recovery (dashed). Arrows indicate the cycle of changing features. (a) Indicates the Azo-LC absorption and (b) is the location of the residual Rose Bengal absorption.

of exposure to Ar<sup>+</sup> laser radiation at 363.8 nm (UV) of 100mW/cm<sup>2</sup> intensity. According to Sutherland,<sup>16</sup> for symmetric layers of LC and stabilized LC with nematic order in the stabilized regions and isotropy in the LC regions, the expected diffraction efficiency (DE) is 97%. The peak is asymmetric and shows multiple lobes indicating a substantial degree of disorder or chirp in the microstructure, which could serve to lower the observed DE below the predicted value. Furthermore, the symmetry of the layers could also limit the peak reflectivity. The diffraction efficiency is small for the orthogonal polarization (3% for the experiment reported in Figure 2). This is inconsistent with the simple model of isotropic/nematic bilayers and suggests an anisotropic rearrangement of the directors, such as planar disorder. The form of the induced index contrast and the director orientations will be the subject of future investigations. The process is reversed by subsequent exposure to solid-state laser radiation at 532 nm (vis), as shown in Figure 2 for 100mW/cm<sup>2</sup> intensity and 200 s. The optical properties of the unexposed sample are recovered.

Dynamic characteristics of the photo-optic properties of the system can be observed as well. Transmission spectra were collected at 0.5 s intervals during the exposure cycle. The DE of the grating (the change in transmission below the baseline) was extracted from the collected spectra. DE is plotted as a function of time in Figure 3. Periods of UV and visible exposure are indicated in the graph. One trace represents lower exposure intensities than the other for both sources. Data presented were taken after many exposure cycles. Samples can be cycled continuously when exposed to the lower intensity UV exposure, but response decreases for cycled high intensity. Full response is observed for high intensity when a 12–24 h interval elapses between runs, however. The speed of the transition is clearly intensity dependent as is the ultimate DE reached. Interestingly, the higher UV exposure intensity shows two distinct time scales. This could indicate two reorganization regimes within the cell, perhaps due to differences in the polymer content of regions of the nematic texture. More highly polymerized areas could rearrange in response to the cis-AzoLC population more slowly, for example. This behavior will be the subject of future exploration.

In conclusion, a photoresponsive, holographically patterned Bragg reflector in a polymer-stabilized liquid crystal has been



**Figure 3.** Diffraction efficiency is plotted as a function of time for an exposure cycle at two excitation powers. The regions of UV and vis exposure are indicated. Two distinct response time scales can be seen in addition to power dependent rates and degrees of change.

prepared by the incorporation of a photoresponsive azobenzene derived liquid crystal. The device is optically clear in the unexposed state and exposure to UV light develops an index profile within the material according to the holographic pattern. The profile is developed through disruption of local order within the LC structure, which selectively affects the areas within the structure with little polymer content. The diffraction efficiency of the Bragg reflector increases depending on the exposure dose and reaches a stationary value that depends on the intensity. This is correlated with the production of a cis-AzoLC population within the material. The transition is optically reversible by exposure to visible light. Significant diffraction efficiency is induced within the device making it practical for applications. Future studies will include patterning multidimensional photonic crystals and nonperiodic, resonant and quasi-crystalline morphologies for optical applications. Alternate LC photoisomers, such as thiolindigo derivatives, will be explored to enhance the wavelength range of the photo-optic properties.

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