

# Optically switchable gratings based on azo-dye-doped, polymer-dispersed liquid crystals

Yan Jun Liu, Yue Bing Zheng, Jinjie Shi, Hua Huang, Thomas R. Walker, and Tony Jun Huang\*

Department of Engineering Science and Mechanics, The Pennsylvania State University,  
University Park, Pennsylvania 16802, USA

\*Corresponding author: junhuang@psu.edu

Received April 28, 2009; revised June 4, 2009; accepted June 14, 2009;  
posted June 26, 2009 (Doc. ID 110750); published July 30, 2009

We report a holographically fabricated, optically switchable grating using azo-dye-doped, polymer-dispersed liquid crystals (LCs). Our experiments show that upon photoirradiation, the diffraction of the grating was decreased significantly. We believe that this switching behavior is due to two factors—nematic–isotropic phase transition of LCs and thermal expansion of the grating structure. © 2009 Optical Society of America  
OCIS codes: 050.2770, 160.2900, 160.3710, 230.1150.

Holographic polymer-dispersed liquid crystals (H-PDLCs) [1] have been developed for a wide range of photonic applications [2,3]. In an H-PDLC structure, liquid crystals (LCs) exist within polymeric matrices as periodically arranged droplets of diameters  $\leq 200$  nm. The optical properties of the entire structure allow it to be electrically switched. Owing to the high surface-to-volume ratio of nanoscale LC droplets, a high electric field (10–20 V/ $\mu\text{m}$ ) is often required to drive H-PDLC devices [4,5]. However, the all-organic nature of H-PDLC devices makes them vulnerable to high electric fields and thereby fore-stalls practical applications. To address this challenge, the requisite driving voltages in H-PDLC devices have to be decreased. Although existing approaches [5–9] are effective in decreasing driving voltage, they tend to cause other complications. For instance, adding a small amount of surfactant may induce undesirable heating effects [10].

The limitations of electrically driven H-PDLC devices call for alternative solutions, such as driving with light instead of electricity. To realize light-driven H-PDLC devices, one may utilize the photo-switching effects of photoresponsive dyes. Among the photoresponsive dyes reported thus far, azobenzene derivatives are commonly used in LC-based photonic materials. Owing to the azobenzene derivatives' reversible *trans-cis* isomerization by photoirradiation [11], one can manipulate not just optical properties, but the optical anisotropy of the surrounding LCs as well. However, for most azobenzene derivatives, UV light is needed to trigger the photoswitching, which usually degrades the physical properties of the LCs [12]. To avoid this issue, it is favorable to choose an azo dye whose *trans-cis* isomerization can be triggered by visible light. Methyl Red (MR) appears to be a good candidate in this case, since its absorption band of *trans* isomer is typically in the blue–green range [13], the effect of which is negligible on the LCs.

In this Letter, we demonstrate significantly enhanced photoswitching effects in azo-dye-doped H-PDLC transmission gratings. In our approach, the light absorption of azo dyes caused the LC molecules to undergo a nematic–isotropic (N–I) phase transi-

tion, which changed the refractive index experienced by the incoming light. Figure 1 illustrates the experimental setup and working mechanism of the switch. We irradiated the grating with a *p*-polarized, pulsed Ar<sup>+</sup> laser beam (514.5 nm). The transmittance of the grating was monitored with an unpolarized white-light beam (HR4000CG-UV-NIR, Ocean Optics) that was incident upon the grating with an angle of 25°. To fabricate the H-PDLC gratings, we made a syrup of LC/prepolymer mixture from the following: 40.33 wt. % monomer, dipentaerythritol penta-/hexa-acrylate (DPPHA); 6.41 wt. % cross-linking monomer, *N*-vinylpyrrolidone (NVP); 0.79 wt. % photoinitiator, Rose Bengal (RB); 0.81 wt. % coinitiator, *N*-phenylglycine (NPG); 6.76 wt. % surfactant, oleic acid (OA); 1.47 wt. % azo dye, MR; and 43.41 wt. % LC E7. Drops of the mixture were sandwiched between two pieces of glass. The thickness was controlled to be  $\sim 10$   $\mu\text{m}$  using plastic microbeads.

The azo-dye-doped H-PDLC gratings were fabricated using a conventional laser holography setup. Two collimated writing beams from an Ar<sup>+</sup> laser (488 nm) intersected at an angle of  $\sim 40^\circ$ . Each beam had a diameter of 2 cm and a power of  $\sim 50$  mW/cm<sup>2</sup>. The exposure time was 5 min. After exposure, the

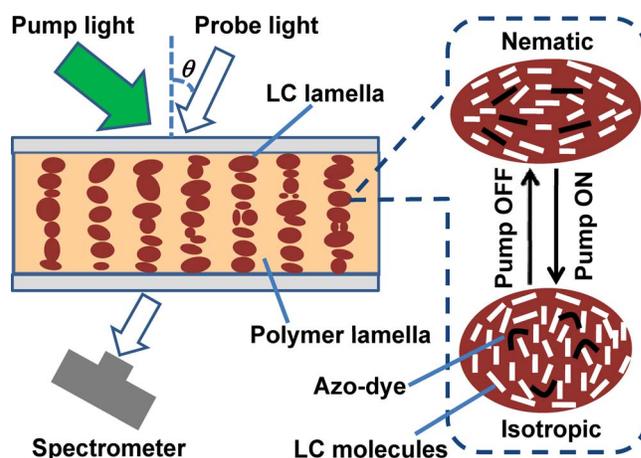


Fig. 1. (Color online) Schematic of the experimental setup and working mechanism. The magnified part shows the working mechanism of the optically switchable process.

samples were cured for another 5 min under a UV lamp. As reported by Bunning *et al.* previously [14], polarization-sensitive gratings can be realized at certain exposure intensities. Generally, the conversion of monomer molecules into a polymeric network is accompanied by a contraction of the composites, known as polymerization shrinkage [9,15]. When the polymeric network shrinks, the LC droplets are compressed, and the rod-shaped LC molecules align along the long symmetric axis of the droplet (a preferential direction). The diffraction is thereby sensitive to the polarization of the incident light.

To confirm the polarization-sensitive nature of the grating, we measured the angle-dependent diffraction of the grating for both *p*- and *s*-polarized light from an He-Ne laser beam (632.8 nm, Fig. 2). Differential scattering was observed previously in the stretched LC droplets [16]. In our experiment, the diffraction of *p*-polarized light was  $\sim 25\%$  higher than that of *s*-polarized light, indicating that the long axis of each LC droplet preferentially aligned parallel with the grating vector. This prediction was confirmed by a scanning electron microscope (SEM) image of the grating with the LCs removed (the inset in Fig. 2). The SEM image shows that most of the LC droplets are ellipsoidal and their long axes are parallel to the grating vector. The observed  $\sim 25\%$  difference in diffraction between *p*- and *s*-polarized light was mainly attributed to the relatively high exposure intensity purposely designed in our experiment. Exposure intensity plays an important role in the phase separation between LCs and polymers: higher/lower exposure intensity yields polarization-sensitive and insensitive gratings [2,17].

Figure 3(a) shows the changes in transmittance under different pumping intensities with an incident angle of  $25^\circ$ . There is a clear trough near 700 nm, which is induced by the grating diffraction. With the pumping intensity increasing from 0 to 40 mW, the trough became much flatter, indicating decreased dif-

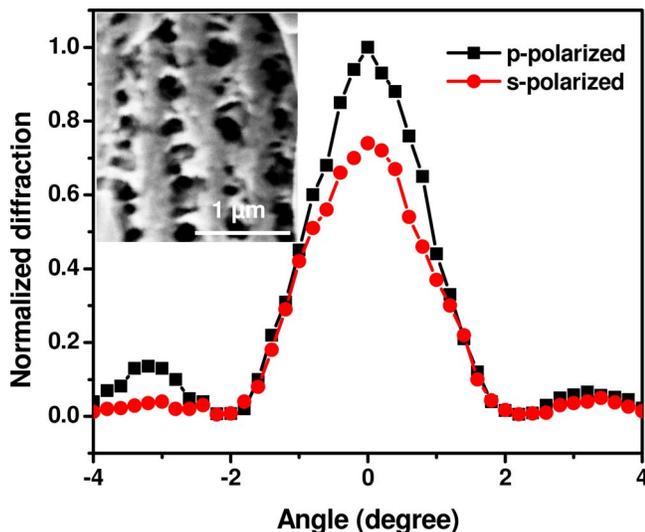


Fig. 2. (Color online) Angle-dependent diffraction of the optically switchable transmission-mode grating for *p*- and *s*-polarized light. The inset shows an SEM image of the grating.

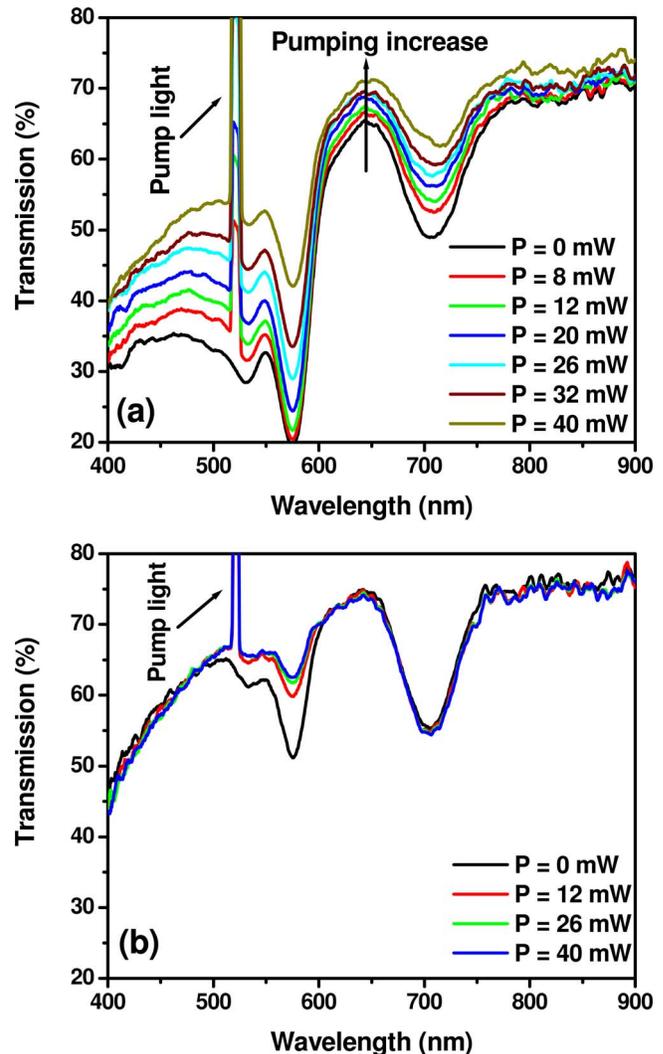


Fig. 3. (Color online) Changes in transmittance under different pumping intensities for (a) an azo-dye-doped H-PDLC grating and (b) an undoped one.

fraction. In addition, increased transmission between 400 and 600 nm was observed owing to the enhanced *cis* population. Turning off the pumping light, the trough returned to the initial states. For comparison, we conducted a control experiment in which the azo dye was absent and other experimental conditions remained the same [Fig. 3(b)]. The results indicated that the transmittance changed less than 3%, confirming that the azo dye was critical to the observed optical switching behavior. Figure 4 shows the time-dependent response of the gratings under different pumping intensities (13, 24, and 36 mW). When the pumping intensity was increased, the response speed became faster. At 36 mW, the rising time was about 2 s, and the falling time was longer than 10 s owing to the thermal-releasing effect.

Fuh *et al.* have reported optical switching from H-PDLC gratings that contained G-206 dye [18]. They observed that when a pumping light was on, the diffraction increased; in contrast, we observed that the transmission increased. We believe that this discrepancy was due to the difference in the grating morphologies. In our work, the LC droplets were el-

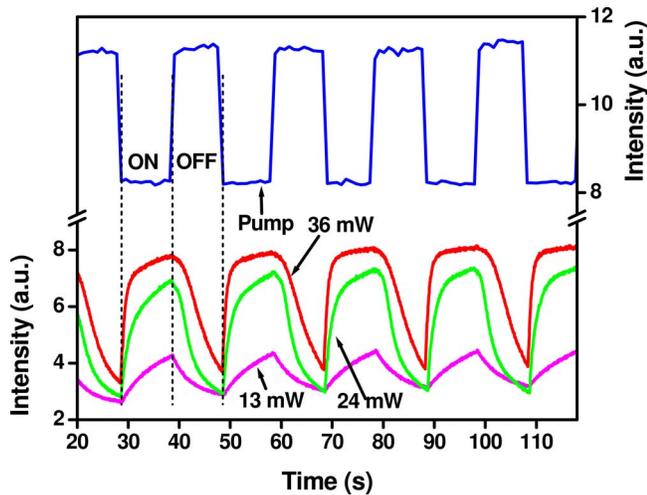


Fig. 4. (Color online) Photoresponse of the azo-dye-doped H-PDLC gratings at different pumping intensities. The upper curve corresponds to the laser pulse, and the lower curves correspond to the response of the grating to different pumping intensities (13, 24, and 36 mW). The “ON” and “OFF” processes are labeled.

lipoidal, and their long symmetry axes were along the direction of the grating vector; however, in the report of Fuh *et al.* [18], although the LC droplets were ellipsoidal, their long symmetry axes were perpendicular to the grating vector. Thus, in our case the index of LCs experienced by the probe beam was close to the extraordinary refractive index of LC,  $n_e$ , while in the case of Fuh *et al.* [18], it was close to the ordinary refractive index of LC,  $n_o$ , with a smaller index difference between the LC and the polymer lamella. As a result, in the case of Fuh *et al.* [18], once switched, the refractive index of the LCs changed slightly, inducing weak photoswitching effects. By comparison, the observed photoswitching effects in our work were much stronger (per the transmission trough) and thus more promising in practical applications.

The optical switching phenomenon observed in our experiments could be attributed to the N–I transition of the LCs as well as the thermal expansion of the grating. When the pumping light was on, the azo dye absorbed the green light and transformed from *trans* to *cis*, inducing the phase transition of the LCs from nematic to isotropic. The empirical effective index for a nematic and isotropic LC layer can be estimated to be  $n_N = [(n_o^2 + n_e^2)/2]^{1/2}$  and  $n_I = [(n_o^2 + n_o^2 + n_e^2)/3]^{1/2}$ , respectively. For E7 used in our experiment, these values were  $n_N = 1.64$  and  $n_I = 1.60$ . The refractive index of the polymer matrix was 1.53. Therefore the decreased index modulation resulted in the low diffraction efficiency. In addition, the grating structure absorbed light and was thus subject to thermal expansion, especially in the polymer-rich regions. This thermal expansion subsequently squeezed the LC droplets, making the LC droplets deform from ellipsoids to more-spherical shapes. As a result, more and more LC molecules reoriented parallel to the short axes of the ellipsoidal LC droplets near the boundaries. These two effects acted constructively to

induce a decreased index experienced by the incident light, regardless of light polarization. As a result, the transmittance of the trough increased significantly. In our experiments, the measured diffraction efficiency of the grating using a *p*-polarized He–Ne laser beam changed from 68% to 32% as the pumping intensity changed from 0 to 40 mW.

In conclusion, we demonstrated an optically switchable grating based on azo-dye-doped H-PDLC materials. Under relatively high exposure intensities, ellipsoidal LC droplets formed with their long axes aligning parallel with the grating vector. This grating morphology accounted for the enhanced optical switching observed in our experiments. The physical mechanisms for the switching effects include the N–I phase transition of LCs induced by the *trans-cis* isomerization of the azo dyes, as well as the thermal expansion of polymer-rich regions during light absorption.

This research was supported by the U. S. Air Force Office of Scientific Research (AFOSR) (grant FA9550-08-1-0349), the National Science Foundation (NSF) (grants ECCS-0801922 and ECCS-0609128), and the Penn State Center for Nanoscale Science.

## References

1. T. J. Bunning, L. V. Natarajan, V. P. Tondiglia, and R. L. Sutherland, *Annu. Rev. Mater. Sci.* **30**, 83 (2000).
2. Y. J. Liu, X. W. Sun, J. H. Liu, H. T. Dai, and K. S. Xu, *Appl. Phys. Lett.* **86**, 041115 (2005).
3. Y. J. Liu, X. W. Sun, P. Shum, H. P. Li, J. Mi, W. Ji, and X. H. Zhang, *Appl. Phys. Lett.* **88**, 061107 (2006).
4. Y.-H. Fan, Y.-H. Lin, H. Ren, S. Gauza, and S.-T. Wu, *Appl. Phys. Lett.* **84**, 1233 (2004).
5. Y. J. Liu, X. W. Sun, H. T. Dai, J. H. Liu, and K. S. Xu, *Opt. Mater.* **27**, 1451 (2005).
6. M. De Sarkar, N. L. Gill, J. B. Whitehead, and G. P. Crawford, *Macromolecules* **36**, 630 (2003).
7. J. Klosterman, L. V. Natarajan, V. P. Tondiglia, R. L. Sutherland, T. J. White, C. A. Guymon, and T. J. Bunning, *Polymer* **45**, 7213 (2004).
8. M. De Sarkar, J. Qi, and G. P. Crawford, *Polymer* **43**, 7335 (2002).
9. L. V. Natarajan, C. K. Shepherd, D. M. Brandelik, R. L. Sutherland, S. Chandra, V. P. Tondiglia, D. Tomlin, and T. J. Bunning, *Chem. Mater.* **15**, 2477 (2003).
10. P. S. Drzaic, *Liquid Crystal Dispersions* (World Scientific, 1995).
11. A. Urbas, V. Tondiglia, L. Natarajan, R. Sutherland, H. Yu, J.-H. Li, and T. Bunning, *J. Am. Chem. Soc.* **126**, 13580 (2004).
12. C.-H. Wen, S. Gauza, and S.-T. Wu, *Liq. Cryst.* **31**, 1479 (2004).
13. G. J. Lee, D. Kim, and M. Lee, *Appl. Opt.* **34**, 138 (1995).
14. R. L. Sutherland, L. V. Natarajan, V. P. Tondiglia, and T. J. Bunning, *Chem. Mater.* **5**, 1533 (1993).
15. J. Qi, M. DeSarkar, G. T. Warren, and G. P. Crawford, *J. Appl. Phys.* **91**, 4795 (2002).
16. I. Amimori, J. N. Eakin, G. P. Crawford, N. V. Priezjev, and R. A. Pelcovits, *SID Int. Symposium Digest Tech. Papers*, **33**, 834 (2002).
17. Y. J. Liu, B. Zhang, Y. Jia, and K. S. Xu, *Opt. Commun.* **218**, 27 (2003).
18. A. Y.-G. Fuh, M.-S. Tsai, L.-J. Huang, and T.-C. Liu, *Appl. Phys. Lett.* **74**, 2572 (1999).