Enhanced diffraction properties of photoinduced gratings in nematic liquid crystals doped with Disperse Red 1

By Hongjing LI,*1 Jianhao WANG,*2 Changshun WANG,*1,† Pengfei ZENG,*1 Yujia PAN*1 and Yifei YANG*1

(Communicated by Koichi SHIMODA, M.J.A.)

Abstract: Diffraction properties of photoinduced gratings recorded by overlapping two coherent beams at 532 nm in nematic liquid crystals doped with Disperse Red 1 were investigated with a probe beam at 632.8 nm. The grating was formed due to the alignment of dye molecules that led to the reorientation of the liquid crystal phase. The diffraction efficiency of the photoinduced grating was found to increase rapidly when the sample temperature was close to the clearing point in the nematic phase and a nearly 30-fold enhancement of the first-order diffraction efficiency was obtained. The pretransitional enhancement of the diffraction efficiency was discussed in terms of the reorientation of liquid crystals, optical nonlinearity effects and the onset of critical opalescence near the nematic-isotropic phase transition. Moreover, a peak shift of diffraction efficiency towards the lower temperature was observed with the increase of recording light intensity, which was attributed to laser induced photochemical disordering.

Keywords: photoinduced grating, nematic liquid crystals, azo dye, diffraction efficiency, critical opalescence, photochemical phase transition

Introduction

Photosensitive liquid crystals are promising materials that can combine a high refractive index modulation, typical of liquid crystals, with high photosensitivity, due to the presence of photochromic molecules such as azobenzene and derivatives. Photoinduced gratings based on azo dye doped nematic liquid crystals have attracted great interests due to their promising applications in display technology, optical storage, optical limiting and nonlinear optical devices.1)–15) Disperse Red 1 (DR1), a kind of push-pull azo dye8)9) doped liquid crystals are regarded as one of the most promising materials for its application in dynamic holographic display because of its fast response time of few milliseconds and no need for external electric field.10)–12) However, the lower diffraction efficiency is not beneficial to the development and its practical application. The azo dye molecules can undergo a reversible trans-cis-trans photoisomerization under irradiation with light of an appropriate wavelength and the molecular geometrical change during this photoisomerization process can lead to the photoinduced anisotropy of azo chromophores, which exert intermolecular torques to align liquid crystals perpendicular to the polarization of incident light.10)–23) The reorientation of liquid crystals caused by photoisomerization process of azo dye molecules plays an important role in the refractive index modulation of photoinduced grating. On the other hand, the temperature effect on the refractive indices of liquid crystals has to be considered for its application, as the liquid crystal performance is closely related with temperature especially near the phase transition temperature.24)–28) The orientation of nematic liquid crystals is altered by thermal expansion which causes the nematic liquid crystal to flow and imposes a realigning torque on the

*1 State Key Lab of Advanced Optical Communication Systems and Networks, Department of Physics and Astronomy, Shanghai Jiao Tong University, Shanghai, China.
*2 Shanghai Key Laboratory of Green Chemistry and Chemical Processes, Department of Chemistry, East China Normal University, Shanghai, China.
† Correspondence should be addressed: C. Wang, State Key Lab of Advanced Optical Communication Systems and Networks, Department of Physics and Astronomy, Shanghai Jiao Tong University, Shanghai, 200240, China (e-mail: cswang@sjtu.edu.cn).
Abbreviation: DR1: Disperse Red 1; 5CB: pentylcyanobiphenyl; ITO: indium-tin oxide; PVA: polyvinyl alcohol; DSC: differential scanning calorimetry; CW: continuous wave.
nematic liquid crystal molecules and the optic axis. Lucchetti et al. and Ramos-Garcia et al. observed a critical enhancement of the nonlinear optical response of dye-doped liquid crystals by approaching the clearing point in liquid crystal cell with no surface treatment. Liquid crystal cell with alignment treatment is a prerequisite for a vast number of basic studies of material properties of liquid crystals. In this paper, we report the diffraction enhancement of photoinduced gratings in DR1 doped nematic liquid crystals near the nematic-isotropic phase transition temperature with homogeneous alignment. A peak shift of diffraction efficiency towards the lower temperature can be observed with an increasing of recording light intensity.

Materials and methods

The liquid crystals used were pentylcyanobiphenyl (5CB) doped with traces of DR1 molecules at a concentration of about 1 wt. %. The mixture was magnetically stirred at room temperature in the dark until the DR1 was dissolved. The homogenous mixture was injected into an empty cell by a capillary. The sample was then sandwiched between two indium-tin oxides (ITO) glass substrates with 50 µm thick spacers. The two ITO glass substrates were precoated with polyvinyl alcohol (PVA) and rubbed in the same direction to obtain homogeneous alignment which was confirmed by polarizing microscope. The absorption spectrum of the sample at room temperature (27 °C) is shown in Fig. 1. It was measured using the spectrophotometer equipped with a polarizer before the sample. The rubbing direction of the sample was parallel to the polarization direction of the recording beam. The intensities of the first-order diffraction with temperature variation were simultaneously detected by a photodetector and recorded by a digitizing storage oscilloscope (Tektronix DPO2014).

The photochemical processes occurred in DR1 doped liquid crystals were investigated with He-Ne laser at 632.8 nm as the probing light, which is far from the absorption band of the sample, and CW Nd:YAG laser at 532 nm with intensity of 260 mW/cm² as the pumping light. The sample was placed between two crossed polarizers in the path of the probe light and the pumping light was set to linearly polarized at ±45° with respect to the polarizers. The rubbing direction of the sample was parallel to the temperature-controlled chamber with glass window to enable the recording beams transmitted. The heating rate of the chamber was precisely controlled at 0.5 °C/s by a temperature controller (HCS302, Instec Co.). The rubbing direction of the sample was parallel to the polarization direction of the recording beam. The photochemical processes occurred in DR1 doped liquid crystals were investigated with He-Ne laser at 632.8 nm as the probing light, which is far from the absorption band of the sample, and CW Nd:YAG laser at 532 nm with intensity of 260 mW/cm² as the pumping light. The sample was placed between two crossed polarizers in the path of the probe light and the pumping light was set to linearly polarized at ±45° with respect to the polarizers. The rubbing direction of the sample was parallel to the polarization direction of the pumping light. The experimental setup was illustrated in Fig. 2(b). The transmittance of probe light going through the sample was measured with a photodetector connected to the digital oscilloscope. Any changes in transmittance in response to the trans-cis photoisomerization of azo dye molecules in the sample could be measured by exposing the sample to pumping light.

Results and discussion

When the recording light intensity at room temperature (27 °C) was increased to 50 mW/cm², the first-order diffraction appeared and disappeared after turning off the recording beams, i.e. dynamic holography was performed. Figure 3 shows the first-order diffraction efficiency as a function of heating time for the sample with the recording intensity of

![Absorption spectrum of nematic liquid crystals doped with 1 wt. % DR1. Inset: chemical structures of the compounds.](image)
The chamber was heated for 36 s at 0.5 °C intervals from 27 °C to 45 °C. A nearly 30-fold enhancement of the first-order diffraction efficiency was obtained when the chamber temperature was heated up to 34.8 °C. As the chamber temperature exceeded 34.8 °C, the diffraction efficiency decreased sharply to a stable value, which was smaller than that at room temperature. With a further increase of chamber temperature, the diffraction efficiency did not create any noticeable change. The typical self-diffraction patterns with chamber temperature variation are shown in Fig. 4.

In the experiment, DR1 molecules were excited by recording beams and then performed photoisomerisation process. The photoinduced cis isomers in the bright regions of the light interference pattern are thermally excited back to trans isomers. Trans isomers end up with their optical axes perpendicular to the light polarization. The liquid crystals in the bright regions will be reoriented perpendicular to the unchanged liquid crystals in the dark regions because of the molecular interactions between DR1 molecules and liquid crystals. In order to study the temperature dependence of the diffraction efficiency, the 0th-order diffraction efficiency as a function of heating time is shown in Fig. 3. It is noticed that 260 mW/cm².
the 0th-order diffraction efficiency is also seriously affected on the same temperature range and follows closely the behaviour of the first-order diffracted signal. It is well known that the transmitted power reaches its maximum value in the isotropic phase where light scattering is minimal. We can deduce the maximum first-order diffraction efficiency and the minimum 0th-order diffraction efficiency both occurs near the clearing point in nematic phase. The photoinduced grating based on the reorientation of liquid crystals should arise due to the modulation of the sample refractive index from $n_0$ in the bright fringes to $n_e$ in the dark fringes of the interference pattern. However, the optical anisotropy of nematic liquid crystals decreases as the sample temperature approaches the phase transition temperature. Therefore, the reorientation of liquid crystals cannot explain the diffraction efficiency enhancement near the phase transition temperature. The enhancement of diffraction efficiency indicates large variation of refractive index can be obtained. Because the condition $A^2 \gg \lambda d\chi$ holds, the diffraction is in the Raman-Nath regime. Under the condition the first-order diffraction efficiency at 34.8 °C is approximated by $\eta \sim (\pi \Delta n d/\lambda)^2$ yielding $\Delta n \sim 9.8 \times 10^{-4}$. When the sample temperature is close to the clearing point in the nematic phase, the optical nonlinear effects of the sample are complicated due to the large variation of liquid crystal performance. The diffraction efficiency enhancement occurring in the sample near the phase transition is a critical effect, which is similar to the critical opalescence in fluid from a less ordered to a more ordered phase owing to a sudden increase in the fluctuations. Light scattering of the probe and recording beams become strong as the sample temperature approaches to the nematic-isotropic phase transition temperature. However, light scattering occurs in any possible angles while the diffraction can be observed only at angles which satisfy Bragg’s equation. Besides, we found the diffraction in the experiment is sensitive to laser polarization while light scattering of the sample has no large variation with rotating laser polarization. Based on the experimental results, light scattering is not a prominent effect on the enhancement of diffraction efficiency near the phase transition. Figure 5 shows the polarizing photomicrographs of the sample. The sample was exposed to the CW Nd:YAG laser for 20 s at three different temperatures. As the sample temperature approaches to the nematic-isotropic phase transition temperature, the nematic microspheres gradually immerse in the isotropic phase.\(^{27}\)

This process is accompanied by strong fluctuation of density and order parameter that could lead to large refractive index variation of the sample and enhance the diffraction efficiency of photoinduced gratings in DR1 doped liquid crystals.\(^{29}\)

Figure 6 shows the first-order diffraction efficiencies as a function of heating time with different recording light intensities. There is a peak shift of diffraction efficiency towards the lower temperature with the increase in recording light intensity. The larger diffraction efficiency and shorter heating time to diffraction efficiency peak can be obtained by larger recording intensity. With increasing recording light intensity, the torque resulted from photoisomerization process azo dye become strong to reorient liquid crystals. When the recording light intensity increases from 65 mW/cm\(^2\) to 260 mW/cm\(^2\), the maximum diffraction efficiency increases from 3.8% to 8.2%. The variation of diffraction efficiency is enhanced with increasing light intensity when the sample is close to the clearing point in the nematic phase. As shown in Fig. 6, the variation of heating time for diffraction efficiency peaks between 65 mW/cm\(^2\) and 260 mW/cm\(^2\) is about 5 s. As described previously, the heating rate of the chamber was controlled at 0.5 °C/s. The temperature variation for diffraction efficiency peaks between 65 mW/cm\(^2\) and 260 mW/cm\(^2\) is about 2.5 °C, indicating the increasing recording light intensity might result in the sample temperature variation. The sample temperature was precisely controlled by the temperature controller. Due to the large absorption at 532 nm, the fraction of cis states of azo dye molecules increases with the increase of the recording light intensity. The reaction of azo dye molecules reduces the order parameter of the nematic phase. We investigated the photochemical processes of the sample at different temperatures. By monitoring the change in optical transmittance of the sample in response to pump light exposure (Fig. 2(b)), we could assess the perturbation of the liquid crystal order by the trans-cis photoisomerization of azo dye molecules in the sample.\(^{31}\) In Fig. 7, the result shows the photochemical disordering is increased at elevated temperatures below the clearing temperature of liquid crystal. This effect is similar to the thermal effect.

**Conclusions**

We have investigated the diffraction enhancement of photoinduced gratings in DR1 doped liquid crystals with homogeneous alignment. The first-order
diffraction efficiency as a function of heating time can reach nearly 30-fold enhancement when the sample temperature is close to phase transition temperature. Laser induced photochemical disordering is discussed to explain the peak shift of diffraction efficiency with the increase of recording light intensity. The temperature dependent diffraction properties of photoinduced grating in DR1 doped liquid crystals may be the good candidate for application in thermo-optical sensor, optical switching and light beam modulation.

**Acknowledgements**

This work was supported by the National Natural Science Foundation of China (No. 11574211) and the fund of State Key Laboratory of Advanced Optical Communication Systems and Networks.

**References**

1) Lee, C.-R., Mo, T.-S., Cheng, K.-T., Fu, T.-L. and Fuh, A.Y.-G. (2003) Electrically switchable and thermally erasable biphotonic grating in dye-doped liquid crystal films. Appl. Phys. Lett. 83, 4285–4287.

2) Lucchetti, L. and Tasseva, J. (2012) Optically recorded tunable microlenses based on dye-doped liquid crystal cells. Appl. Phys. Lett. 100, 181111.

3) Tong, X., Wang, G., Yavrian, A., Galstian, T. and Zhao, Y. (2005) Dual-mode switching of diffraction gratings based on azobenzene-polymer-stabilized liquid crystals. Adv. Mater. 17, 370–374.
4) Miroshnichenko, A.E., Brasselet, E. and Kivshar, Y.S. (2008) Light-induced orientational effects in periodic photonic structures with pure and dye-doped nematic liquid crystal defects. Phys. Rev. A 78, 053823.

5) Lee, M.-R., Wang, J.-R., Lee, C.-R. and Fuh, A.Y.-G. (2004) Optically switchable biphotonic photorefractive effect in dye-doped liquid crystal films. Appl. Phys. Lett. 85, 5822–5824.

6) Cipparrone, G., Mazzulla, A. and Simoni, F. (1998) Orientational gratings in dye-doped polymer-dispersed liquid crystals induced by the photorefractive effect. Opt. Lett. 23, 1505–1507.

7) Wei, D., Iljin, A., Cai, Z., Residori, S. and Bortolozzo, U. (2012) Two-wave mixing in chiral dye-doped nematic liquid crystals. Opt. Lett. 37, 734–736.

8) Poprawa-Smoluch, M., Baggerman, J., Zhang, H., Maas, H.P.A., Cola, I.D. and Brouwer, A.M. (2006) Photoisomerization of disperse red 1 studied with transient absorption spectroscopy and quantum chemical calculations. J. Phys. Chem. A 110, 11926–11937.

9) Toro, C., Thibert, A., Boni, L.D., Masunov, A.E. and Hernandez, F.E. (2008) Fluorescence emission of Disperse Red 1 in solution at room temperature. J. Phys. Chem. B 112, 929–937.

10) Li, X., Chen, C.P., Gao, H.Y., He, Z.H., Xiong, Y., Li, H.J., Hu, W., Ye, Z.C., He, G.H., Lu, J.G. and Su, Y.K. (2014) Video-rate holographic display using azo-dye-doped liquid crystal. J. Disp. Technol. 10, 438–443.

11) Sabet, R.A. and Khoshchina, H. (2010) Real-time holographic investigation of azo dye diffusion in a nematic liquid crystal host. Dyes Pigments. 87, 95–99.

12) Khoshchina, H., Goodarzi, H., Kundijam, S.A. and Sabet, R.A. (2012) The study of dynamic behaviour of transient grating in azo dye doped nematic liquid crystal. Mol. Cryst. Liq. Cryst. 560, 62–66.

13) De Sio, L., Serak, S., Tabiryan, N., Ferjani, S., Veltri, A. and Umeton, C. (2010) Composite holographic gratings containing light-responsive liquid crystals for visible bichromatic switching. Adv. Mater. 22, 2316–2319.

14) Gao, H., Jiang, Y., Zhou, Z., Gu, K. and Gong, D. (2006) The dependence of orientational optical nonlinearity in dye-doped liquid-crystal films on the polarization direction of the recording beams. IEEE J. Quantum Electron. 42, 651–656.

15) Fuh, A.Y.-G., Liao, C.-C., Hsu, K.-C., Lu, C.-L. and Tsai, C.-Y. (2001) Dynamic studies of holographic gratings in dye-doped liquid-crystal films. Opt. Lett. 26, 1767–1769.

16) Statman, D. and Janossy, I. (2003) Study of photoisomerization of azo dyes in liquid crystals. J. Chem. Phys. 118, 3222–3232.

17) Janossy, I. and Szabados, L. (1998) Optical reorientation of nematic liquid crystals in the presence of photoisomerization. Phys. Rev. E 58, 4598–4604.

18) Chen, A.G. and Brady, D.J. (1992) Surface-stabilized holography in an azo-dye-doped liquid crystal. Opt. Lett. 17, 1231–1233.

19) Khoo, I.C., Li, H. and Liang, Y. (1994) Observation of orientational photorefractive effects in nematic liquid crystals. Opt. Lett. 19, 1723–1725.

20) Becchi, M., Janossy, I., Shankar Rao, D.S. and Statman, D. (2004) Anomalous intensity dependence of optical reorientation in azo-dye-doped nematic liquid crystals. Phys. Rev. E 69, 051707.

21) Zetsu, N., Ogawara, T., Mizoshita, N., Nagono, S. and Seki, T. (2008) Photo-triggered surface relief grating formation in supramolecular liquid crystalline polymer systems with detachable azobenzene units. Adv. Mater. 20, 516–521.

22) Kim, Y., Senyuk, B. and Lavrentovich, O.D. (2012) Molecular reorientation of a nematic liquid crystal by thermal expansion. Nat. Commun. 3, 1133.

23) Khoo, I.C., Li, H. and Liang, Y. (1993) Optically induced extraordinarily large negative orientational nonlinearity in dye-doped liquid crystal. IEEE J. Quantum Electron. 29, 1444–1447.

24) Li, J., Gauza, S. and Wu, S.T. (2004) Temperature effect on liquid crystal refractive indices. J. Appl. Phys. 96, 19–24.

25) Li, J., Gauza, S. and Wu, S.T. (2004) High temperature-gradient refractive index liquid crystals. Opt. Express 12, 2002–2010.

26) Lucchetti, L., Gentili, M. and Simoni, F. (2005) Pretransitional enhancement of the optical nonlinearity of thin dye-doped liquid crystals in the nematic phase. Appl. Phys. Lett. 86, 151117.

27) Ramos-Garcia, R., Lazo-Martinez, I., Guizar-Ituribide, I., Sanchez-Castillo, A., Boffety, M. and Ruck, P. (2006) Colossal nonlinear optical effect in dye-doped liquid crystals. Mol. Cryst. Liq. Cryst. 454, 179–185.

28) Wang, Y.J. and Carlisle, G.O. (2002) Optical properties of disperse-red-1-doped nematic liquid crystal. J. Mater. Sci. Mater. Electron. 13, 173–178.

29) Schadt, M., Schmitt, K., Kozinkov, V. and Chigrinov, V. (1992) Surface-induced parallel alignment of liquid crystals by linearly polymerized photopolymers. Jpn. J. Appl. Phys. 31, 2155–2164.

30) Simoni, F., Lucchetta, L. and Francescangeli, O. (2001) On the origin of the huge nonlinear response of dye-doped liquid crystals. Opt. Express 9, 85–90.

31) Tong, X. and Zhao, Y. (2009) Multiple photochemical processes in liquid crystalline azo dye-doped liquid crystals. Chem. Mater. 21, 4047–4054.

(Received Feb. 25, 2016; accepted June 14, 2016)