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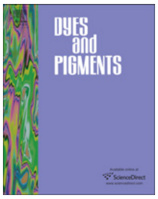

Real-time holographic investigation of azo dye diffusion in a nematic liquid crystal host

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ABSTRACT

The diffusion anisotropy of C.I. Disperse Red 1 (2-(ethyl(4-((4-nitrophenyl)azo)phenyl)amino)ethanol), in a nematic liquid crystal mixture (1294-1b) was studied using real-time diffraction-monitoring. The trans-cis photoisomerization of the dye molecules and the diffusion of photoexcited isomers were identified as essential components in the mechanisms of grating formation and relaxation, respectively. The results were used to investigate the diffusion parameters of dye molecules in both parallel and perpendicular directions to the director.

1. Introduction

Nematic liquid crystals (NLC) are well known for their nonlinear optical behavior and strong birefringence [1,2]. Recently it was discovered that the light-induced orientational nonlinearity of liquid crystals can be increased by several orders of magnitude by the addition of a small number of dye molecules [3–5]. Of various types of dyes, azo dyes have attracted special attention due to the large conformational change that occurs during trans-cis isomerization and they have been investigated as an active component for a variety of applications such as lithography, optical switches, data storage [6] and real-time holography [7,8].

In this context, the nematic liquid crystal mixture (1294-1b) is a high birefringence ($\Delta n = 0.318$) NLC mixture that comprises fourteen components (isothiocyanates) with a wide temperature interval of the nematic phase (3° N 155° Iso.) [9,10]. These properties make this particular nematic liquid crystal a very good candidate for electro-optical applications. In real-time diffraction-monitoring, which can be used to determine the dynamic behavior of a holographic grating, relaxation time measurements are used to gather information about the mechanisms involved in the grating relaxation. These measurements have attracted attention because they can characterize the diffusion parameters of dye molecules in the NLC host. In this work, the diffusion anisotropy of 2-(ethyl (4-((4-nitrophenyl)azo)phenyl)amino)ethanol (C.I. disperse Red 1; DR1) in the NLC mixture (1294-1b) at room temperature was investigated using the technique mentioned above.

2. Experimental work

The measurement cells were homogeneous (HG, planar) LC cells with 2° tilt angle. LC cells with two different cell gaps (6.2 and 50 μm) were used. The NLC mixture (1294-1b) and the LC cells were purchased from AWAT PPW Company (Poland). The dye-doped NLC mixture was prepared by dissolving about 0.5% weight of 2-(ethyl (4-((4-nitrophenyl)azo)phenyl)amino)ethanol, (C.I. disperse red 1, DR1) from Aldrich (dye content %95 and wavelength of maximum absorption $\lambda_{max} = 502$ nm) without any purification in the nematic liquid crystal mixture (1294-1b). The chemical formula of the DR1 dye is illustrated in Fig. 1.

LC cells with a polyamide alignment layer for HG (planar) alignment were filled with the dye-doped NLC mixture by capillary forces. The alignment layers of the LC cell force the mesogenic molecules to line up with their long molecular axis parallel to the alignment layer and thus parallel to the glass plates of the LC cell. The absorption spectrum of the sample as shown in Fig. 2, was measured by Shimadzu spectrophotometer model UV 2450, and according to its results, an argon laser (Ar^+ laser) beam at 514 nm

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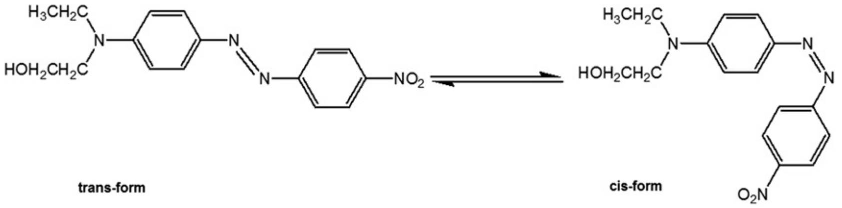

Fig. 1. Molecular structure of C.I. disperse Red 1, 2-(ethyl(4-((4-nitrophenyl)azo)phenyl)amino)ethanol in trans and cis forms.

wavelength was used. The ordinary refractive index of the LC mixture measured by an Abbe refractometer (Bellingham + Stanly 60/ED) at room temperature for this wavelength as $n_o = 1.499$. The Ar^+ laser beam was split into two coherent beams of equal intensities (about 50 mW/cm^2) as the writing beams. These two beams intersect the sample at variable angle θ. The range of the angle of intersection between the pump beams were between 0.5 and 4.1°. A linearly polarized 1 mW He-Ne laser ($\lambda = 632$nm) was also used as the probe beam. The holographic grating formed in the sample was in Raman-Nath regime and multi-order diffraction of the probe beam was observed during the experiment. First order diffracted signal from the probe beam was detected by Photomultiplier tube (P.M.T) type E.M.I 9816B and monitored by a digital storage oscilloscope (Tektronix 300 MHz, model TDS3032B) when one or both of the writing beams were switched off/on. The intensity gradient created in this setup was always parallel to the *y*-axis as shown in Fig. 3.

Dynamic behavior of the grating relaxation was investigated using the real-time diffraction-monitoring technique in two geometries at room temperature. In the first geometry all the writing and probe beams were s-polarized and the director was parallel to the *z*-direction. In this geometry the intensity modulation was in the *y*-direction, and so the diffusion direction was perpendicular to the director, $\vec{n}$. In the second geometry, all the writing and probe beams were p-polarized and direction of the director was parallel to the *y*-axis. So in this configuration the light modulation direction and diffusion direction were parallel to the director. Considering the small θ values for the second geometry, it is acceptable that in both geometries the polarization direction of the writing and probe beams were parallel with the director. So the only difference between these two geometries was the translational diffusion direction which is perpendicular (parallel) to the director in the first (second) geometry.

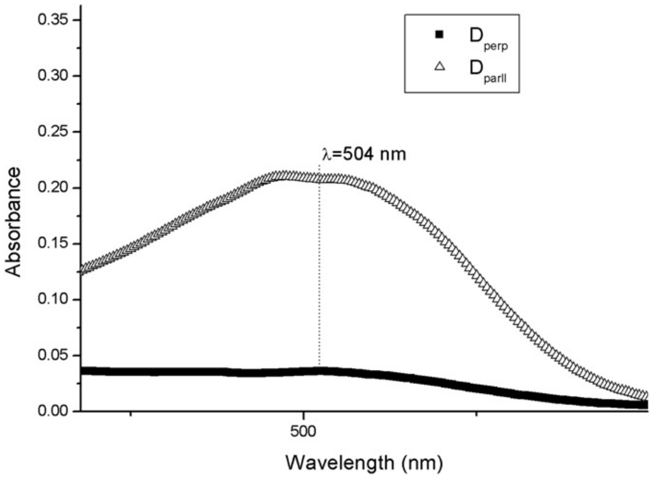

Fig. 2. Absorbance of the dye-doped LC sample ($d = 50$ μm).

3. Results and discussion

Periodic isomerization of DR1 molecules can cause refractive index modulation via molecular reorientation in the nematic liquid crystal host [11]. When exposed to light having a wavelength within the absorption spectrum of dye molecules, after several trans-cis-trans isomerization cycles, dye molecules tend to reorient perpendicular to the electric field of the light. Liquid crystal molecules will also reorient because of the molecular interactions between DR1 and NLC molecules. So, the refractive index seen by the propagating beam will differ. Moreover, the existence of the cis species can change the refractive index due to a change in the order parameter of the liquid crystals [12,13]. So in DR1 doped NLC medium, a refractive index grating can be induced when the sample is illuminated by a periodic modulated intensity produced in the overlapping area of two coherent laser beams, called writing beams. When the writing beams are switched off the refractive index grating vanishes due to the orientational relaxation of LC molecules, uniform redistribution of cis and trans azo dye molecules as well as thermal relaxation of cis molecules in the host medium. Therefore, the relaxation mechanism includes the behavior of NLC and DR1 molecules.

Time constant related to the orientational relaxation of LC molecules is given by Erickson-Leslie theory (Equation (1))[11]:

$$\tau_{\mathrm{LC}} = \frac{\gamma}{2K}\left[\frac{1}{\frac{\pi^2}{d^2}+\frac{4\pi^2}{\Lambda^2}}\right] \tag{1}$$

in which γ/K is the visco-elastic coefficient of pure liquid crystal, d is the sample thickness and Λ is the grating period. Also the relaxation time corresponding to the diffusion of excited dye molecules is given by (Equation (2))[12,14,15]:

$$\tau_{\mathrm{dye}} = \frac{1}{\left(D_y\frac{4\pi^2}{\Lambda^2}+\frac{1}{T_{\mathrm{cis}}}\right)} \tag{2}$$

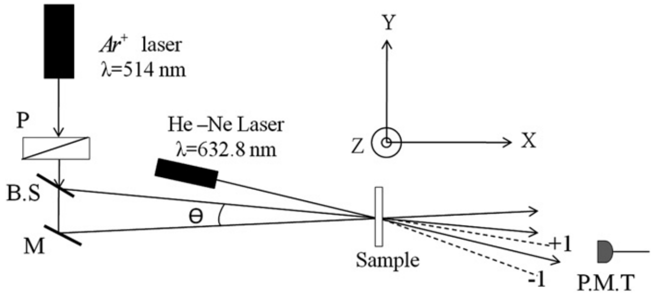

Fig. 3. Experimental real-time diffraction-monitoring technique setup to study the dynamic behavior of laser induced grating. P, Polarizer; B.S, Beam Splitter; M, Mirror, P.M.T, PhotoMultiplier Tube.

in which D_y is the diffusion coefficient of dye molecules in LC host in the *y*-direction and T_{cis} is the intramolecular relaxation time; that is, the lifetime of the cis state in the presence of host molecules. Using Eq. (2), inverse of the relaxation time ($1/\tau$) is related to the inverse of the square of the grating period ($q^2 = (2\pi/\Lambda)^2$) as (Equation (3)):

$$\tau^{-1} = D_y q^2 + T_{cis}^{-1} \tag{3}$$

Grating period, Λ, in these equations is $\Lambda = \lambda/(2n_{ave}\sin(\theta/2))$, where λ is the wavelength of the writing beams, n_{ave} is the mean refractive index of the liquid crystal ($n_{ave} = (2n_o + n_e)/3$) and θ is the angle of the intersection of the writing beams [16].

According to these mechanisms, it is expected that the relaxation and formation of the optical grating will be different for the cases where one or both of the writing beams are switched off/on.

Using the real-time diffraction-monitoring technique, the dynamic behavior of the first order diffracted probe beam from the laser induced grating, in the samples with thicknesses 6.2 and 50 μm, was investigated when one or both of the writing beams were switched off/on. The results are shown in Fig. 4.

By switching on both of the writing beams simultaneously, a huge increase of the cis type dye molecules occurs in the bright regions; and due to the interaction of dye molecules with electric field of light, the reorientation of dye and NLC molecules begin. This causes an increase of refractive index difference between dark and bright regions and it is followed by the diffusion of cis isomers from bright to dark regions and makes a small decrease in the diffraction efficiency of probe beam and appears as an overshoot in the plot. However no overshoot is observed in the formation dynamics of the grating in the thicker sample. This can be related to the reduction of the surface effects in thick samples and so an increase in the reorientation angle as well as reorientation time of NLC molecules in the bright regions.

On the other hand, by switching off both of the writing beams simultaneously, periodic illumination on the sample vanishes. Then, diffusion of the cis isomers follows by their thermal relaxation and orientational relaxation of the NLC molecules begins. By the reorientation of LC molecules to their initial order and also uniform distribution of cis isomers, the relaxation of laser induced refractive index grating occurs.

Similar mechanisms are also involved in grating formation and relaxation when one of the writing beams is switched on/off in the presence of the other beam. By switching on the second writing beam in the presence of the first beam, the intensity grating will be created in a region which was already uniformly illuminated (so the population of cis isomers have reached to an equilibrium state). In this case, by switching on the second beam, the orientational relaxation of LC in the recently created dark regions as well as population difference of cis isomers between dark and bright regions causes the formation of a refractive index grating in the sample.

On the other hand, by switching off the second beam in the presence of the first beam, the sample is uniformly illuminated again. Population of the cis isomers begins to increase in the regions which have been dark and this causes a reorientation of LC molecules. Simultaneously, the diffusion of cis isomers from bright to dark regions leads to a decrease in the refractive index difference between dark and bright regions, and the grating vanishes. It is clear that the grating relaxation mechanisms when one or both of the writing beams are switched off are the same. So as indicated in Fig. 4, the holographic grating relaxation behavior is similar in both cases.

Using the experimental results, the relaxation time (τ) of the grating was measured for various grating periods (Λ) when both of the writing beams were switched off in two different geometries. The results show that the relaxation time constants for different geometries are different so that for the second geometry they are shorter than those of the first geometry. Also the relaxation time constants for different grating periods decrease with the decrease of Λ and are independent on the sample thickness as can be seen in Fig. 5.

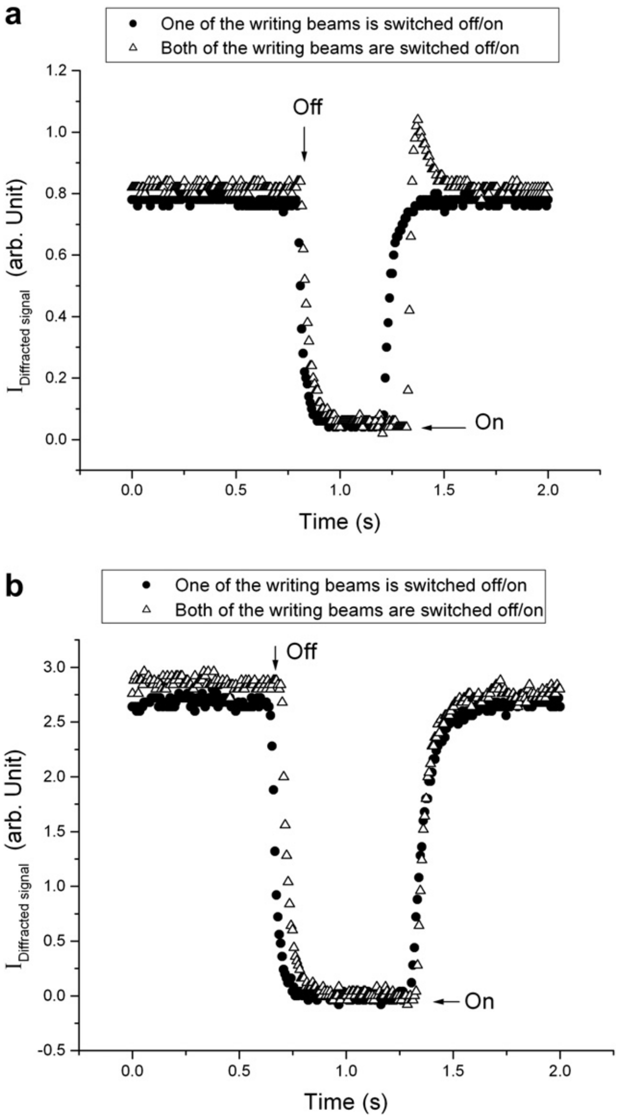

Fig. 4. Dynamic behavior of the first order diffracted probe beam for two samples with thicknesses (a) 6.2 μm and (b) 50 μm.

Using the experimental results and according to the Eq. (3), the inverse of the relaxation time, τ^{-1}, were plotted versus q^2 and using “OriginPro 8” software linearly fitted for each thickness separately (see Fig. 6). The results of the linear fits show that there exists a difference between the interceptions of the plots for the two geometries in one sample, which cannot be explained by orientational relaxation mechanisms. It can be concluded from these observations that the reorientational relaxation of the LC molecules, which is related to the sample thickness, cannot be the dominant relaxation mechanism in our system.

So the diffusion mechanism, which gives Equation (2), for the relaxation time constant, seems to be the dominant mechanism for the relaxation of the grating in this medium, and the slope of the linear fit to the experimental results shows the diffusion coefficient

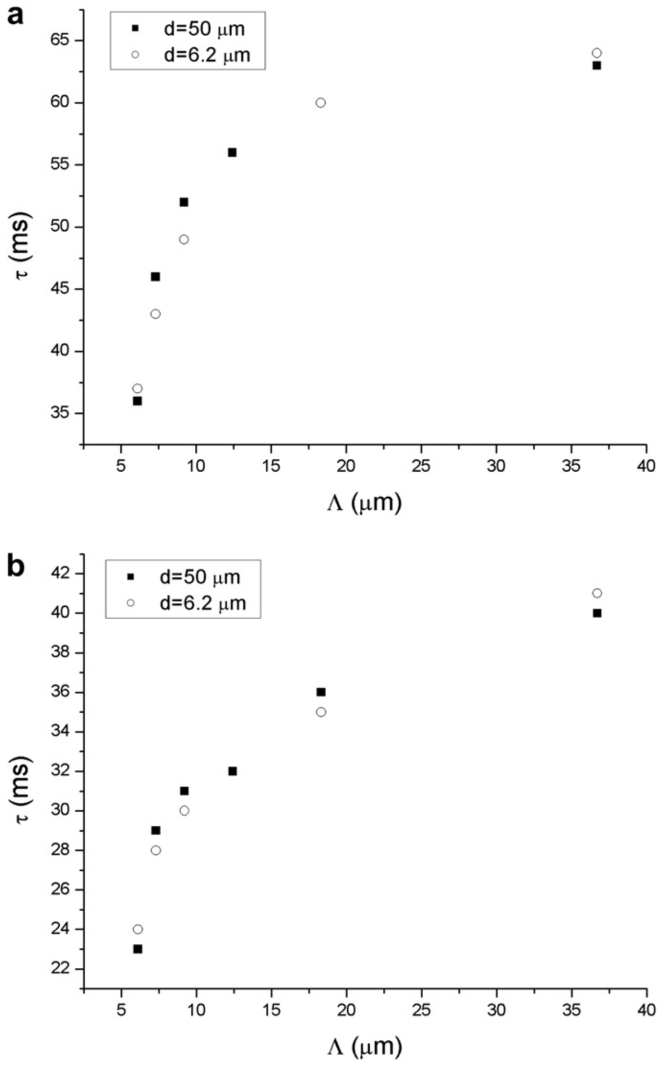

Fig. 5. Relaxation time, measured when both of the writing beams are switched off, versus grating period, when diffusion direction (intensity modulation direction) is (a) perpendicular and (b) parallel to the director.

in a certain direction. According to our results, the diffusion coefficient for the second geometry in which the diffusion direction is parallel with the director is more than that of the first geometry in which the diffusion direction is perpendicular to the director. The interception of the linear fit also shows the inverse of the intramolecular relaxation time of the cis isomers which can be different due to the different interactions between the host molecules and the azo dye molecules in these two geometries.

So, the experimental results can be used to calculate the translational diffusion coefficient as well as intramolecular relaxation time for the directions perpendicular and parallel to the director, which are approximately the same for both thicknesses, as follows:

$$D_{\perp} = 0.0110\ \mu\text{m}^2\ \text{ms}^{-1}, T_{\text{cis}\perp} = 67\ \text{ms}$$

$$D_{\parallel} = 0.0154\ \mu\text{m}^2\ \text{ms}^{-1}, T_{\text{cis}\parallel} = 39.5\ \text{ms}.$$

The uncertainty in the measurement of the diffusion coefficients was approximately estimated as 10%. This uncertainty was related to the systematic errors and depended on the accuracy of the equipments and procedures. Comparing the results, it would be obvious that there is small diffusion anisotropy of dye molecules.

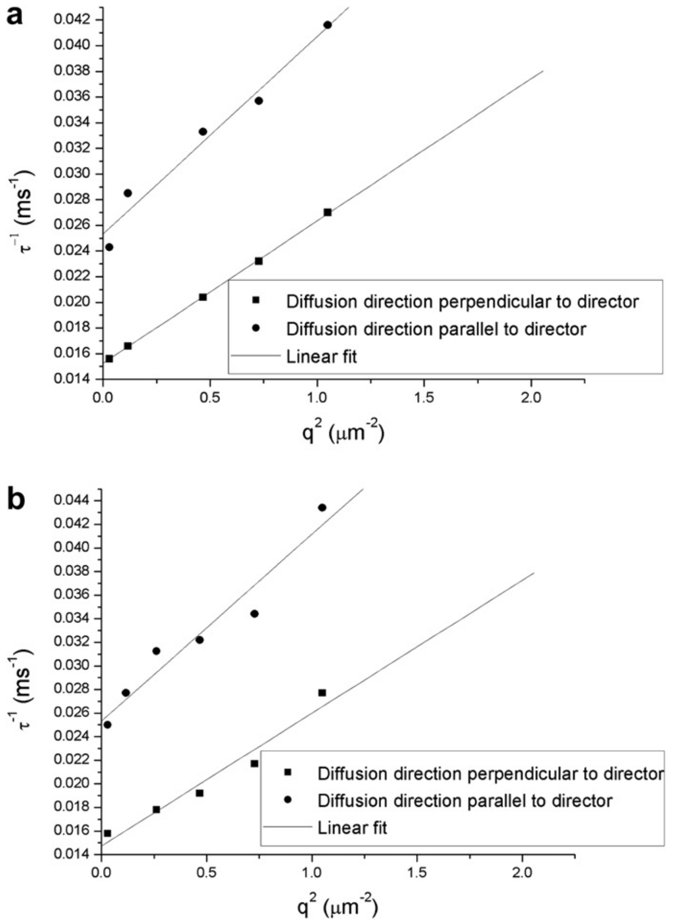

Fig. 6. Inverse of the relaxation time versus the inverse of q^2 for thicknesses (a) 6.2 μm and (b) 50μm (the solid lines represent linear fits).

So the relaxation of the refractive index grating, when the diffusion direction is parallel with the director, is faster than the other geometry. This more rapid relaxation could be due to the easier movement of photoexcited dye molecules when the diffusion direction is parallel with the director, which also leads to the shorter intramolecular relaxation time of the cis state.

4. Conclusion

The dynamics of the formation and relaxation of the refractive index grating were investigated in DR1 doped nematic liquid crystal mixture (1294-1b). Experimental results corresponding to the formation and relaxation of the grating, when one or both of the writing beams were switched off/on, show that the reorientation of LC molecules, the increase of the cis isomers and the diffusion of the cis isomers are the mechanisms involved in the formation and relaxation of the grating. Experimentally obtained relaxation time of the grating for the various recording angles indicates that the relaxation time is independent on the sample thickness. Therefore, diffusion is accepted as the dominant mechanism for the grating relaxation. Comparing of the results obtained from linear fitting of the experimental data with Equation (3), the diffusion coefficients of DR1 dye molecules in the NLC host (in two different geometries in which diffusion direction is parallel or perpendicular to the director) are determined. The observed diffusion anisotropy is related to the molecular mobility anisotropy of dye molecules in the LC host.

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