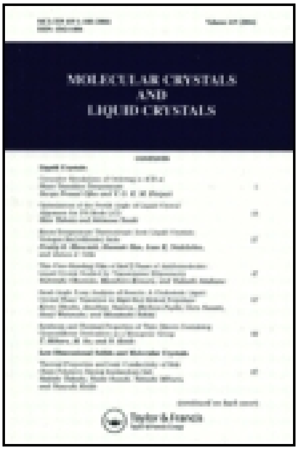

Molecular Crystals and Liquid Crystals

Photoisomerization in Photoaligned Azo Dyes Exhibiting Photostability

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Photoisomerization in Photoaligned Azo Dyes Exhibiting Photostability

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Here in this investigation, the molecules exhibiting photoisomerization in solutions is also photostable is observed. On the other hand molecules not showing photoisomerization behavior in solutions is not shown such kind of stability. Surprising behavior in which after writing laser is turned off, there is going to be increase in phase retardation (or order parameter) which is under deep consideration. Detail investigation is in progress to reveal the behavior of chemical structures when light is shined on them. Proposed investigation is crucial for selecting suitable azo dyes for photoalignment studies and also for many commercial applications which depends on many factors like stability, order parameter etc.

Keywords: birefringence; cis-trans; photoisomerization; stability

1. INTRODUCTION

The field of LC photoalignment is very rapidly developing and a vast amount of the new materials, techniques and LCD prototypes based on photoalignment (PA) technology have appeared recently [1,2]. The effect of LC photoalignment is a direct consequence of the appearance of the photoinduced optical anisotropy and dichroic absorption in thin amorphous films, formed by molecular units with anisotropic

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Address correspondence to Gurumurthy Hegde, Post-Doctoral Research Assistant, Department of E.C.E., The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong. E-mail: murthyhegde@gmail.com absorption properties. Despite of these potential advantages the application of PA to LCD production is hampered by the lack of good materials. Nevertheless azodye materials remain among the best candidates for technological importance. The structure of the azo dyes plays crucial role in exhibiting excellent photoalignment. Although many azo dyes shows good photoalignment properties but exact physical mechanisms behind this is not well understood. Photoisomerisation phenomena is one such tool to find out the behavior of the azo dyes inside the molecule. If a material showing good photoalignment quality means it should exhibit high order parameter, stability, high anchoring energy, uniform alignment and many more factors [3–5]. Order parameter is another important parameter which tells about materials property. It is to be mentioned in the literature that order parameter and photoinduced birefringence are directly proportional in a photoaligning substrate [6].

Here in this investigation, materials shows photoisomerization in solutions also shows photo stability in solid forms which is very important for application is concerned.

2. EXPERIMENTAL

The photosensitive azo dyes SD1, CD-1, and BY was used in this investigation. Figure 1a shows the chemical structures of these dyes. Chemical structure of these three dyes is very similar except –COONa-, COOH groups in respective places. UV/vis absorption spectra exhibits similar absorption wavelength for SD-1 and CD-1 dyes (~394 nm) but exhibits higher wavelength for BY (~418 nm) in Figure 1b.

The azo dyes are dissolved in N,N-dimethylformamide at an optimal concentration (for absorbance study in solution requires very small concentration and in all the 3 dyes absorbance maxima is kept at 1.5) for photoisomerization studies. Intensity used for photoisomerization studies is 7mW/cm^2. UV light of wavelength 365 nm is shined on the sample. Whereas for birefringence studies, 10% of the azo dye was dissolved in N,N-dimethylformamide (thickness of the azo dye layer is around 50 nm) and then spin-coated on ITO-coated glass substrate at 3000 rpm during 30 sec. The coated substrate was cured for 15 min at T = 145°C. This procedure provides a thin homogeneous solid dye film onto ITO-glass surface.

For accurate insitu measurement of small thin film phase retardation δ, a setup (Fig. 2) has been constructed. The photoinduced birefringence in photoaligning azo dye was investigated with a He-Ne laser at 632 nm as the probe light, which is far from the absorption

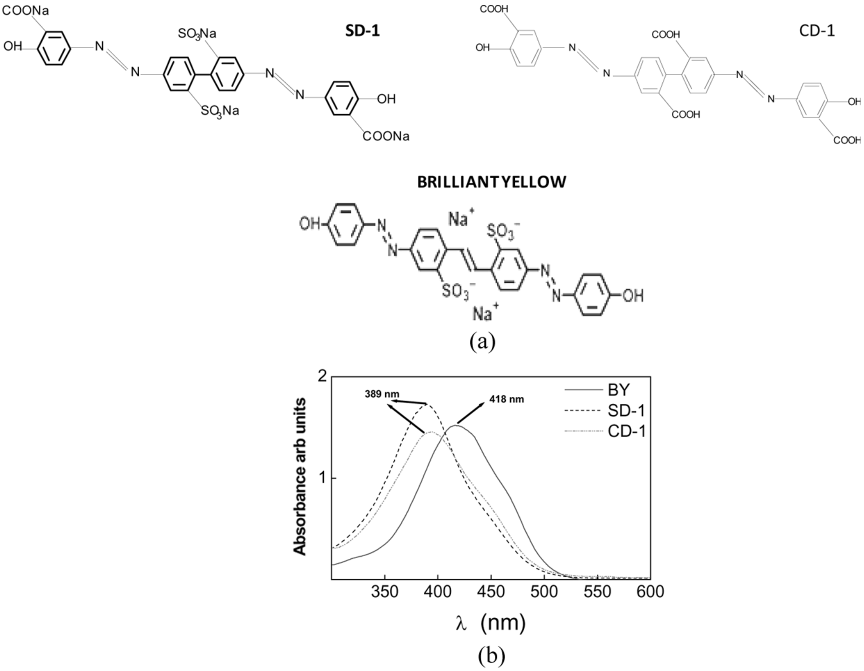

FIGURE 1 (a) Shows chemical structure of the azo dyes SD1, CD-1, and BY used for this experiment. (b) Shows the UV/Vis absorption spectrum before shining the light. SD-1 and CD-1 shows similar wavelength whereas BY exhibiting higher wavelength.

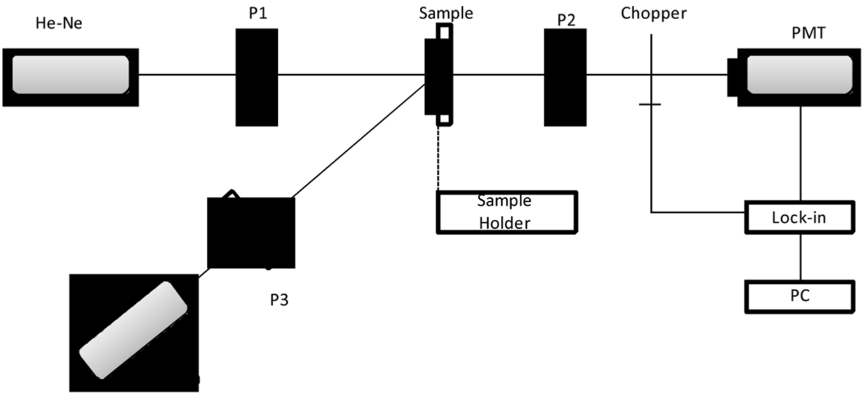

FIGURE 2 Experimental set up used for birefringence study. P1, P2, and P3 are the polarisers. P1 and P2 were crossed polarisers. Solid samples with nano scale thickness are used for this study. Writing laser was Ar-Ion laser.

band of the photochromic azo groups and the pump beam for inducing of optical anisotropy in azo dye film was provided by Ar-Ion laser, which has a linear polarized light at the output with the power $W = 10\,\mathrm{mW/cm^2}$. The sample was placed between two crossed polarizer P1 and analyzer P2 in the path of He-Ne laser. Writing the substrate is done by shining polarized light (P3) of wavelength 457 nm (Ar-Ion laser). A light signal appeared from analyzer due to the birefringence induced in the sample under the action of pump light. The coming signal was measured with a photo detector, then processed by a lock-in amplifier and recorded using computer. All measurements are performed at room temperature.

3. RESULTS AND DISCUSSION

It is well-known that molecules can undergo trans-cis-trans isomerization under irradiation of light with an appropriate wavelength and be oriented by a linearly polarized light [7,8]. An exception to this in which materials in solid state orienting perpendicular to the polarized light and no photochemical effects is reported by Chigrinov and co-workers [9]. They proposed diffusion model to explain this phenomena. According to them, the azo dye molecules, which have their absorption oscillators (chomophores) parallel to the light polarization, will most probably get an increase in energy which results in their reorientation from their initial position. This results in an excess of chromophores in a direction where the absorption oscillator is perpendicular to the polarization of the light. In anyway linearly polarized light aligns azobenzene molecules in such a way that the direction of their optical transition is perpendicular to the polarization of the light. This alignment process results in polarization anisotropy and thus the photoinduced birefringence [10]. But when experiment is performed for these kinds of molecules in solutions, they do show photoisomerization.

Figures 3–5 shows the results obtained using UV/vis absorption spectroscopy for measuring cis-trans isomerization in solutions for three different dyes. Before shining the UV molecules is in energetically more stable trans state. Upon shining UV light of wavelength ~365 nm, molecules are excited to cis state which is evident if there is decrease in absorbance value. Figures 3 and 4 shows decrease in absorbance values whereas for Figure 5 absorbance values remain the same. Once molecules excited to cis state because of its unstable nature it will come back to trans state after switching off of the radiation. With this point one can safely conclude that Figures 3 and 4 surely shows photoisomerization behavior whereas Figure 5 is not

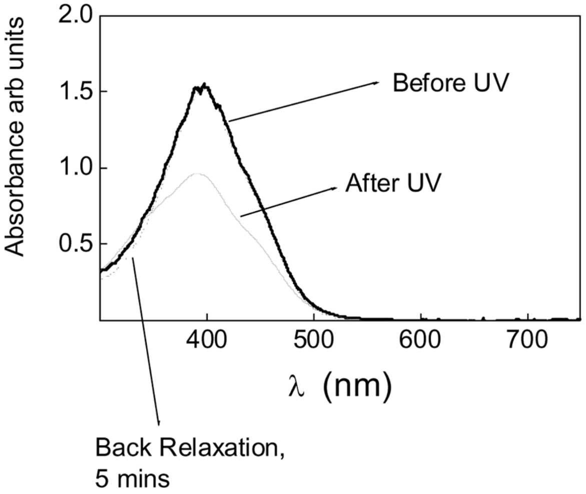

FIGURE 3 UV/vis absorption spectroscopic data shows photoisomerization behavior for SD-1 solution. Before shining the light of wavelength 365 nm material is in trans form. After shining UV, absorbance decrease which is the clear indication of trans to cis state. If material is left for 5 minutes, it will come back to original trans configuration as shows in the figure.

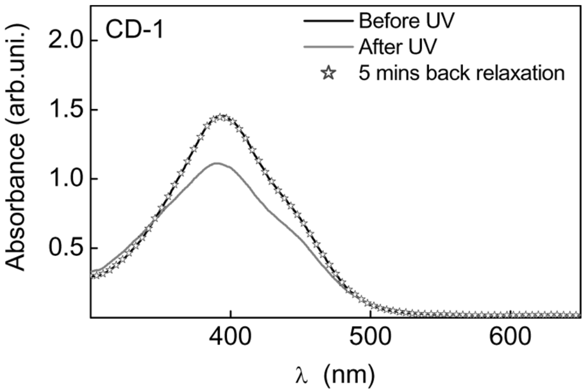

FIGURE 4 UV/vis absorption spectroscopic data shows photoisomerization behavior for CD-1 solution. Even in this one also, before shining the light of wavelength 365 nm material is in trans form. After shining UV, absorbance decrease which is the clear indication of trans to cis state. If material is left for 5 minutes, it will come back to original trans configuration as shows in the figure.

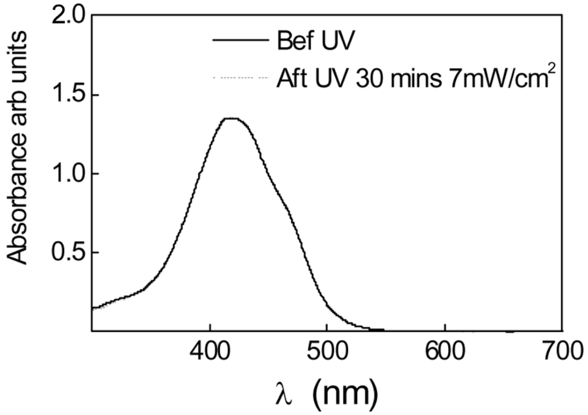

FIGURE 5 UV/vis absorption spectroscopic data shows no photoisomerization behavior for BY solution. Before shining the light of wavelength 365 nm material is in trans form. After shining UV, there is no influence of light on the solution so that no change in absorbance values. Even after 30 minutes also there is no influence on the solution.

showing photoisomerization behavior. Because after switching off the radiation, SD-1 and CD-1 molecules will return to original state but BY is independent of radiation shined. This is surprising behavior since all the three molecules are having similar chemical structures but exhibits different behavior.

Next step is to find out the photoinduced birefringence of these materials which is very essential for photoalignment behavior is concerned. Initial studies about these dyes [11] showed excellent photoaligning behavior. The purpose of our experimental investigations on these dyes is to measure UV light induced birefringence, which is proportional to an order parameter of a photoaligning substance. The photo-induced phase retardation $\delta = \frac{2\pi\Delta nd}{\lambda}$ *(d ≈ azo dyes layer thickness,* $\lambda = 632.8\,nm$*),* measured in experiment is directly proportional to the relative order parameter s of the azo dyes layer:

$$\delta = \frac{2\pi\Delta nd}{\lambda} = ks \tag{1}$$

where k is a coefficient proportional to the anisotropy of the molecular polarizability of the azo dye molecule [6,12].

The dependence of the phase retardation versus exposure time for SD-1, CD-1, and BY with the pump Ar-Ion laser is shown on Figures 6–8. The monotonous increase of the photo-induced phase

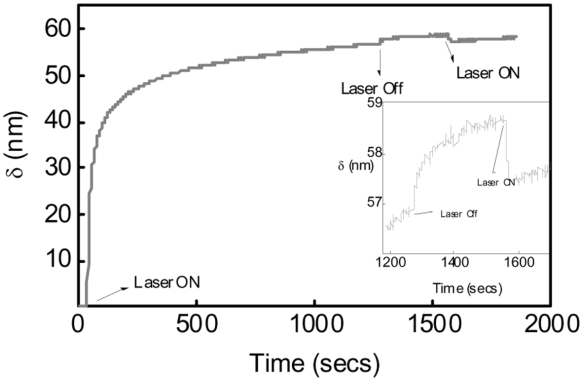

FIGURE 6 The photoinduced birefringence δ of the azo dye SD-1 with time. Experimental results show that phase retardation increases first and saturates with irradiation of Ar-Ion light. When light is switched off there is an increase in phase retardation which correlates with order parameter. Inset shows the clear indication of increase in order parameter when writing laser is turned off.

retardation δ from zero level at $t = 0$ (isotropic state) up to the saturation value δ_0 (anisotropic state) was observed. Surprisingly when laser light is switched off, there is increase in phase retardation value (or inotherwards increase in order parameter) is observed for Figure 6 (see the inset of the Fig. 6 for better visualization). This is the surprising effect suggests that the highly stable system for many applications. Figures 7 and 8 shows the dependence of phase retardation on

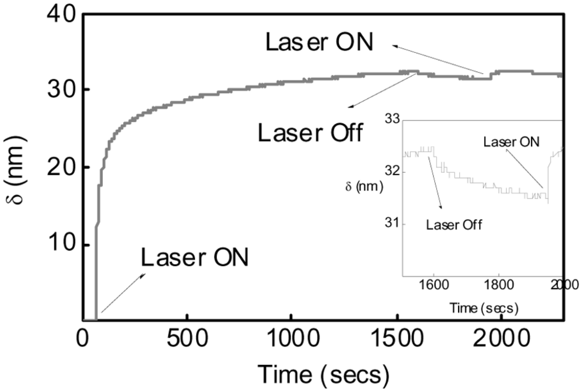

FIGURE 7 The photoinduced birefringence δ of the azo dye CD-1 with time.

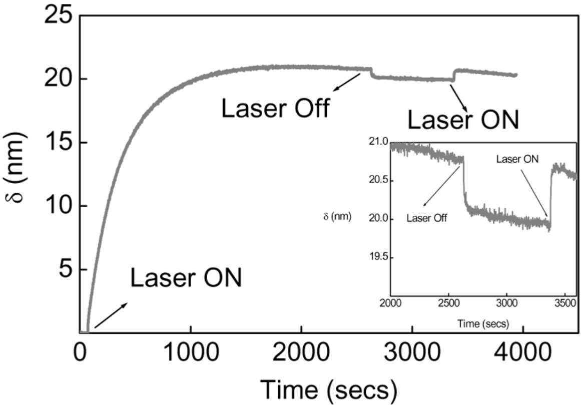

FIGURE 8 The photoinduced birefringence δ of the azo dye BY with time.

exposure time for CD-1 and BY with the pump Ar-Ion laser. Here there is no increase in phase retardation value once writing laser is switched off.

Figure 9 shows the polarized absorption spectra (absorbance or optical density) of SD-1 (a), CD-1 (b), and BY (c) before (curve1) and after (curves 2 and 3) the UV radiation. Before the irradiation the absorption of the azo dye layer does not depend on the polarization of the light, used in measurements. After the irradiation by linearly polarized light, the absorption of the light with the polarization direction parallel to the polarization direction of the activated light ($D_{||}$) decreases (curve 2) while that one with orthogonal polarization direction ($D_{\perp}$) increases (curve 3) [13]. Notice that order parameter which is calculated using these values (the ratio between $D_{\perp}$ and $D_{||}$) shows higher value for SD-1 and CD-1, lower value for BY. Since from our experiments BY is not showing photoisomerization behavior in solution whereas SD-1 and CD-1 does.

Although we don't know the exact reason but we speculate the following. According to the diffusion model proposed for SD-1 by Chigrinov and coworkers (equally holds good for CD-1 also) [9], azo dye molecules when optically pumped by a polarized light beam, the probability for the absorption is proportional to the $\cos^2 \theta$, where θ is the angle between absorption oscillator of the azo dye molecule and the polarization direction of the light. Therefore, azo dye molecules which have their absorption oscillators (chromophores) parallel to the light polarization will most probably get an increase in internal energy which results in more energetic rotational motion through internal energy transfer. This may be the reason for increased trend

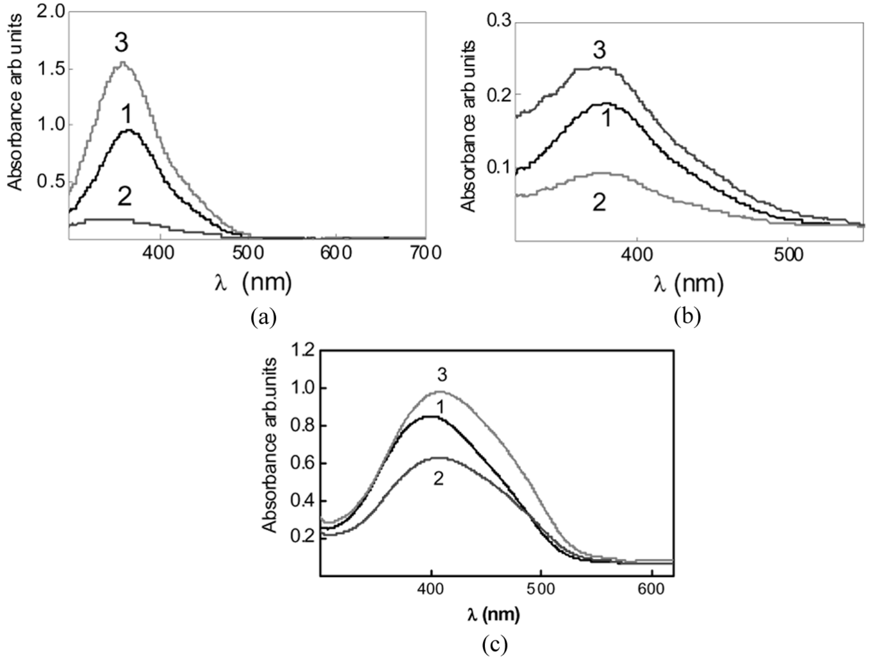

FIGURE 9 Absorption spectra of SD-1 (a), CD-1 (b), and BY (c) layer before the polarized UV exposure (curve 1). Curves 2 and 3 show the polarized absorption spectra after the exposure by a polarized UV light in the direction parallel ($D_{\|}$) and perpendicular ($D_{\perp}$) to the activating light polarization accordingly [13]. One can clearly see that SD-1 shows high order parameter compare to CD-1 and BY (Order parameter = ratio between $D_{\perp}$ and $D_{\|}$).

observed in present investigation. After entire molecules or most of the molecules oriented, intermolecular interactions will lock their positions in place and prevent re-diffusion and randomization even after light is turned off which results in long stability for the molecule. Noteworthy that SD-1 contains $NaSO_3$ groups in the biphenyl core may influence adhesion of dye molecules to the glass substrates, character of photoiosmerization and so ordering peculiarities in thin films. On the other hand, in solution, molecules have enough space to move around whereas in solid, they are tightly packed. This kind of film, if light is shined, perhaps there is going to be some kind of photo reorientation happens in the system so that reversing back to the original state is not possible even after light is turned off. Order parameter supports our argument since increasing in order parameter value is observed for SD-1 and CD-1 which shows photoisomerization whereas decrease in order parameter value is observed for BY which is not showing photoisomerization behavior.

Present study investigates the new effect of dependence of photoinduced birefringence and photoisomerization of the mentioned dyes which is crucial for selecting suitable dyes for commercial applications.

4. CONCLUSIONS

So in conclusion, the molecules exhibiting photoisomerization in solutions is also photostable is observed. On the other hand molecules not showing photoisomerization behavior in solutions is not shown such kind of stability. Surprising behavior in which after writing laser is turned off, there is going to be increase in phase retardation (or order parameter) which is under deep consideration. Detail investigation is in progress to reveal the behavior of chemical structures when light is shined on them. Proposed investigation is crucial for selecting suitable azo dyes for photoalignment studies and also for many commercial applications which depend on many factors like stability, order parameter etc.

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