



Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl20>

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Version of record first published: 18 Oct 2010

To cite this article: Eunje Jang, Hak-Rin Kim, Yu-Jin Na & Sin-Doo Lee* (2004): Stability of Optical Reorientation of Nematic Liquid Crystals Doped with Azo-Dyes in Polymer Networks, *Molecular Crystals and Liquid Crystals*, 422:1, 11-19

To link to this article: <http://dx.doi.org/10.1080/15421400490501950>

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STABILITY OF OPTICAL REORIENTATION OF NEMATIC LIQUID CRYSTALS DOPED WITH AZO-DYES IN POLYMER NETWORKS

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We report on the stability of the optical reorientation of doped nematic liquid crystals (LCs) with azo-dyes in polymer networks. The photo-reactive polymer networks formed within the doped LC medium play a critical role in achieving the stable optical reorientation of the LC originating from the trans-cis transformation of the dye molecules. Moreover, the photo-reactive polymer layer on the substrate surface is required to produce the surface memory effect of the dye-doped LC. The optically induced memory is well retained in the dye-doped LC only in the presence of the polymer network medium.

Keywords: liquid crystals doped with azo-dyes; optical reorientation; polymer networks; surface memory effect

INTRODUCTION

Liquid crystals (LCs) containing azo-dyes have recently attracted great attention for optical applications such as optical data storage and optical switching devices [1–3] since azo-dye molecules are highly photo-sensitive and the large birefringence of the LC medium magnifies the optical reaction of azo-dyes. If the azo-dye molecules are exposed to resonant light, they undergo trans-cis photo-isomerization which induces the reorientation of the LC molecules in the bulk.

In the LCs with azo-dyes, the dye molecules can be either coated on the substrate surfaces of the LC cell [4] or simply doped in the LC material [5,6]. In the case that the azo-dyes are coated on the substrate surfaces,

This work was supported in part by the Ministry of Information and Communication of Korea through Advanced Backbone IT Technology Development Project and ISRC 2003-X-4730.

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the photo-isomerization process of the dye molecules on the surface predominantly governs the LC alignment which propagates into the bulk. However, in the case of dye-doped LCs, the LC reorientation is dictated by the optical torque generated by the photo-isomerization of the azo-dyes in the bulk as well as the anisotropic aligning forces produced from the azo-dyes adsorbed on the substrate surface. It should be noted that the reorientation of the LC molecules by the optical torque in the bulk is transient while that by the surface effect is relatively stable.

The surface memory effect of the dye-doped LC on a polymer-coated surface was observed previously [7]. Recently, it has been also reported that the memory effect occurs on the polymer wall of a dye-doped polymer-dispersed liquid crystal (PDLC) [8]. The alignment of the doped PDLC with azo-dyes was found to be stable without appreciable relaxation due to surface interactions between the LC and the dye molecules at the LC droplets dispersed in the polymer matrix. However, the PDLC has the intrinsic scattering loss, resulting from random orientation of the LC droplets as well as the distortions of the LC director inside the droplets, which is not suitable for practical applications. Therefore, it is very important to understand the stability of the surface memory and the optical reorientation process of the LCs containing dye molecules under various conditions such as polymer networks and polymer-dispersed droplets.

In this work, we report on the stability of the optical reorientation of a nematic LC doped with azo-dyes in polymer networks. In order to understand the optical memory and the reorientation process, three types of the sample cells were studied; the first (I) was made with two substrates having polyvinyl alcohol (PVA) layers rubbed for the LC alignment, the second (II) with one substrate having the rubbed PVA layer and the other having a photo-reactive polymer layer solidified under ultraviolet (UV) light, and the third (III) with two substrate having PVA layers in contact with a mixture of a doped LC with dyes and the photo-reactive polymer. Upon the exposure of ultraviolet (UV) light to the third cell, networks of the photo-reactive polymer were formed within the dye-doped LC medium and a strong optical memory effect with no relaxation was observed.

EXPERIMENTAL

In our study, a nematic liquid crystal of ZLI-2293 (E. Merck Industries), azo-dyes of Methyl Red (MR, Sigma-Aldrich), and a photo-reactive, i.e., UV-curable polymer of NOA65 (Norland Products Inc.) were used. Two kinds of the dye-doped LCs were prepared; for the first (I) and second (II) sample cells, a mixture of 99 wt.% of ZLI-2293 and 1 wt.% MR was used. For the third (III) cell, a mixture of 98 wt.% of ZLI-2293, 1 wt.% of

MR, and 1 wt.% of NOA 65 was used to form polymer networks upon the UV exposure. The mixtures were injected into the sample cells above the clearing temperature of the LC. Note that the PVA layers prepared on the substrates were unidirectionally rubbed so as to promote homogeneous alignment of the LC. The cell gap of each cell was maintained using glass spacers of $6\text{ }\mu\text{m}$ thick. Sample III was exposed to UV light, generated from a Xe-Hg lamp, having the power of 10 mW/cm^2 to form the polymer networks in the bulk.

Figure 1 shows the schematic diagram of the optical reorientation of the LC molecules in Sample III (having polymer networks) by the trans-cis transformation of azo-dyes upon the irradiation of an input (pump) beam of 488 nm. Before pumping, the initial planar alignment of the LC molecules is produced on the rubbed PVA layers. Note that the MR molecules are in their stable trans-form and in rod-shape like the LC molecules. Thus, the MR molecules tend to orient along the LC director via the guest-host effect. This is consistent with anisotropic absorption measurements. During pumping, the MR molecules undergo the trans-cis isomerization that induces the optical reorientation of the LC molecules in the polymer networks. After the pump beam is off, the LC reorientation gained during pumping will remain because of rotational hindrance of the LC molecules within the polymer networks.

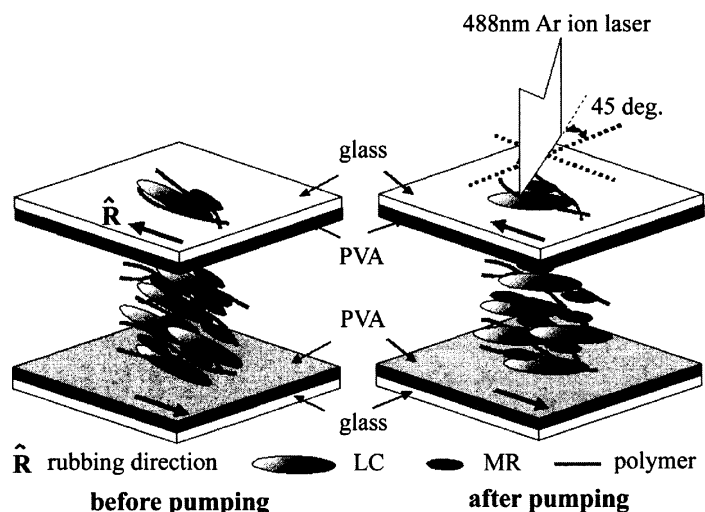


FIGURE 1 The schematic diagram of the optical reorientation of the LC molecules in Sample III (having polymer networks) by the trans-cis transformation of azo-dyes upon the irradiation of an input (pump) beam of 488 nm.

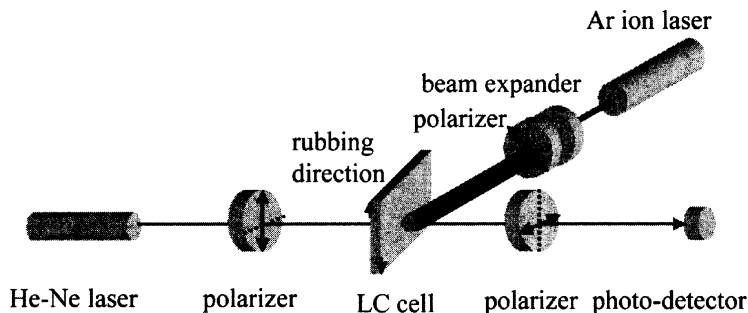
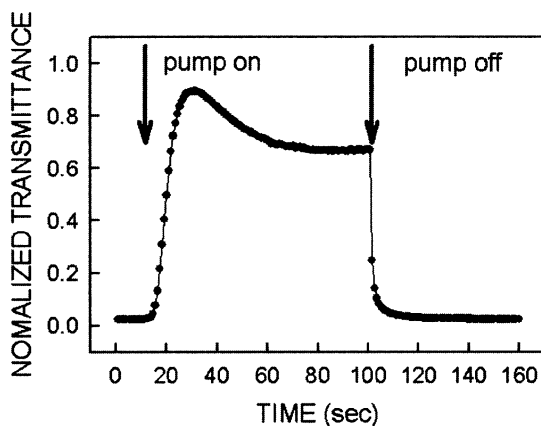


FIGURE 2 Experimental setup for measuring the photo-excitation and relaxation kinetics of the LC reorientation under a pump beam polarized linearly at an angle of 45° with respect to the rubbing direction.

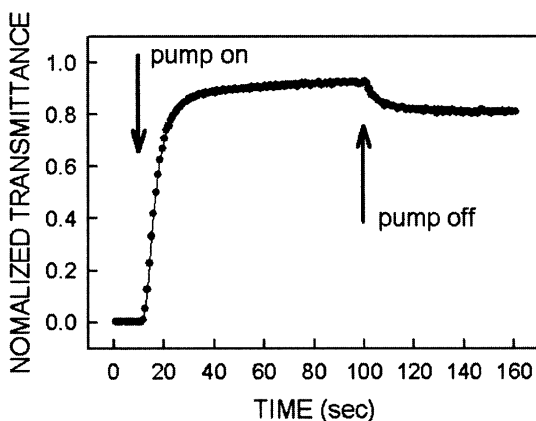
Figure 2 shows the experimental setup for measuring the photo-excitation and relaxation kinetics of the LC reorientation under a pump beam polarized linearly at an angle of 45° with respect to the rubbing direction so that the maximum optical torque is produced [9]. As a pump beam source, an Ar-ion laser with wavelength of 488 nm and the power of 100 mW/cm^2 was used. The reorientation dynamics of the LC molecules in each sample cell was monitored using a He-Ne probe laser with wavelength of 632.8 nm. The rubbing direction of the sample cell was parallel to one of crossed polarizers and the transmitted intensity through the cell was measured with a photodiode in conjunction with a digitizing oscilloscope.

RESULTS AND DISCUSSION

We first describe the nature of the LC reorientation induced by the structural transformation of the azo-dye molecules under a pump beam in sample I and sample II. The dynamics of the optical reorientation and relaxation of the LC molecules in Sample I and Sample II were shown in Figures 3(a) and 3(b), respectively. It is clear that when the pump beam was off, no optical memory effect was observed in Sample I having two rubbed PVA layers although the LC reorientation was produced by the isomerization process of the azo-dyes during pumping as shown in Figure 3(a). In contrast, in Sample II with one rubbed PVA layer and one solidified NOA 65 layer, a strong optical memory effect was present but decayed to some extent in the bulk when the pump beam was off as shown in Figure 3(b). This may be attributed to strong surface memory for the dye-doped LC alignment on the solidified NOA65 layer in Sample II unlike the PVA layer. Microscopic measurements revealed that a finite angle between the easy axis on the UV-solidified NOA65 layer and the rubbing direction on



(a)



(b)

FIGURE 3 The transmitted intensity of the probe beam through the dye-doped LC cell as a function of time: (a) Sample I with two rubbed PVA layers and (b) Sample II with one rubbed PVA layer and one solidified NOA 65 layer by the UV exposure.

the PVA layer was generated. This comes from the difference in the interactions of the azo-dyes between the PVA and the NOA65 in addition to the surface morphology.

In Figure 4, the reorientation dynamics of the dye-doped LC in Sample III having polymer networks were shown. Before pumping, the LC molecules were uniformly aligned along the rubbing direction on the PVA layer as shown in Figure 1. In this case, the transmitted intensity of the probe

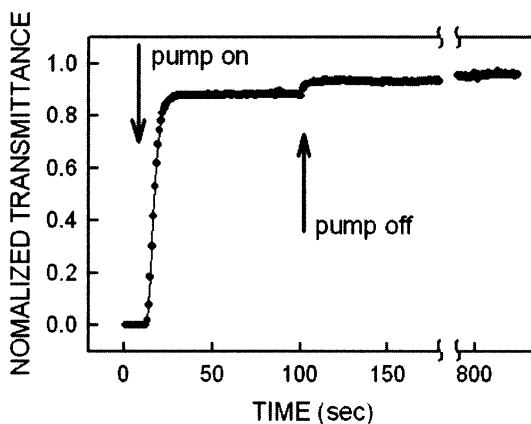


FIGURE 4 The transmitted intensity of the probe beam through the dye-doped LC cell having polymer networks with two rubbed PVA layers (Sample III) as a function of time.

beam through Sample III was zero. During pumping by a linearly polarized beam of the Ar-ion laser, the photo-excited MR molecules were generated and thus the optical torque was exerted on the LC molecules so that the optical reorientation perpendicular to the pump polarization direction was produced. As a result, the transmitted intensity of the probe beam increased and became to saturate in time as shown in Figure 4. When the pump beam was off, the saturated intensity through Sample III slightly increased due to the relaxation of the azo-dyes from the photo-isomerized cis form into the stable cis-form after pumping. In contrast to Sample I with no polymer networks, Sample III clearly shows the existence of strong optical memory without relaxation in time as shown in Figure 4 although the two sample cells had rubbed PVA layers. Considering the memory effect in Sample II as shown in Figure 3(b), it may be concluded that the optical memory in dye-doped LCs is dictated by the surface memory for the LC alignment as well as the optical reorientation of the LC molecules in polymer network environment. Note that the presence of the azo-dyes in the cis-form disturb the LC alignment in the bulk as well as on the substrate surfaces. Another point is that in the low concentration (1 wt.%) regime of the NOA65, the optical scattering is negligible and the polymer networks stabilize the LC alignment induced by the photo-isomerization of the azo-dye molecules.

Figure 5 shows microscopic textures of the optically reoriented LC (Sample III) observed with a polarizing microscope under crossed polarizers. The textures were taken at 1 hour after the pump beam was off.

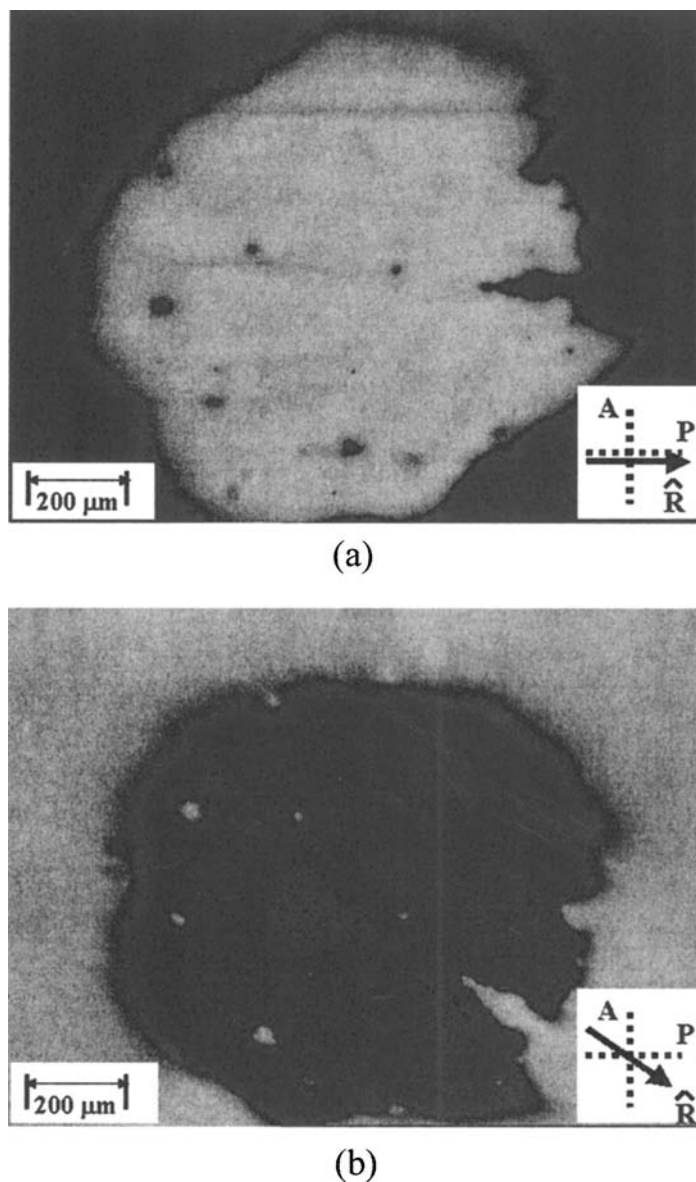


FIGURE 5 Microscopic textures of the optically reoriented LC (Sample III) observed with a polarizing microscope under crossed polarizers: (a) the texture observed for the rubbing direction on the PVA layer along polarizer and (b) the texture for the rubbing direction rotated 35° with respect to the polarizer.

Figures 5(a) and 5(b) correspond to the texture observed for the rubbing direction on the PVA layer along polarizer and that for the rubbing direction rotated 35° with respect to the polarizer, respectively. The white area in a circular shape in Figure 5(a) represents the optically reoriented LC region by the pump beam that was linearly polarized along the direction of 45° to the initial LC director. The white state became completely dark state when the sample cell was rotated by an angle of 35° to the polarizer as shown in Figure 5(b). In other words, the optically induced easy axis of the dye-doped LC on the PVA layer in the polymer networks is uniformly rotated by an angle of 35° with respect to the direction of the pump polarization. This is consistent with anisotropic absorption results of the MR molecules at the wavelength of 488 nm.

Finally, the optical memory effect in Sample III remains at least several months in the range of our observation in the case that the duration of pumping was 90 seconds. It should be noted that the retention time for the optical memory depends on the concentration of the photo-reactive polymer, the structure of the polymer networks, the concentration and the photosensitivity of the doped dye, and the optical power used for recording.

CONCLUSION

We presented results for the dynamics of the optical reorientation and relaxation of the nematic LCs doped with azo-dyes that undergo the photo-isomerization. The optical memory effect with no relaxation was demonstrated in a dye-doped LC with polymer networks formed from photo-reactive polymers. Unlike dye-doped PDLC systems reported previously, our sample cell with polymer networks, stabilizing the LC alignment induced by the photo-isomerization process, has negligible scattering loss due to a very low concentration of the photo-reactive polymer in the dye-doped LC medium. The work presented here would provide a basis for further research on other dye-doped LC systems as well as for various applications.

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