

# Multiple Photochemical Processes in Liquid Crystalline Azo Dye-Doped Liquid Crystals

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We present a detailed study on the multiple photochemical processes that can occur in a nematic liquid crystal (BL006) doped with a liquid crystalline azobenzene compound (LC azo dye) as a result of the photoinduced isomerization of the chromophore. On the basis of the photo-optical response (transmittance change upon illumination) and the electro-optical response (transmittance change upon application of a voltage) as well as polarizing microscopic observations, two regimes of behaviors can be distinguished upon UV exposure inducing the trans–cis isomerization. In the regime of low LC azo dye concentrations ( $\leq 7$  wt %), where the achievable amount of cis isomers are miscible with the LC host, only a photochemical disordering of the LC takes place at room temperature, with a precisely controllable degree of disordering. At elevated temperatures, but below the clearing temperature  $T_{ni}$  of the LC, the photochemical disordering can lead to the photochemical nematic–isotropic phase transition. In the regime of high LC azo dye concentrations, when the amount of cis isomers passes a certain concentration, they become immiscible with the LC, which triggers a photochemical phase separation process. Depending on the rate at which cis isomers are formed, the phase separation process can either follow the disordering or appear simultaneously with and compete against the disordering and the nematic–isotropic phase transition. In all cases, the mixture evolves over time toward two separated LC phases, with one disordered rich in cis isomer. All these photochemical processes under UV light can be reversed by visible light inducing the cis–trans back-isomerization of the chromophore. This study shows the richness of the photo-optical and electro-optical behaviors of LC azo dye-doped liquid crystals and provides a comprehensive understanding on the multiple reversible photochemical processes.

## Introduction

In a previous communication,<sup>1</sup> we reported that a nematic liquid crystal (LC) doped by a large amount (15 wt %) of a liquid crystalline azobenzene compound (referred to as LC azo dye hereafter) can display new properties related to the trans–cis photoisomerization of azobenzene upon UV and visible light exposure. The use of a LC azo dye made possible the dissolution of a large amount of the dopant in the LC without phase separation. In contrast with LCs doped with a small amount (generally <5%) of non-LC azo dyes because of the solubility constraint, the LC containing 15% of LC azo dye showed not only the well-known photochemical LC–isotropic phase transition<sup>2</sup> but also a photochemical phase separation at the micrometer-scale. We have attributed the phase separation to the presence of a high concentration of azo molecules in the cis form that is non-LC and has low solubility in the LC host. The two distinct photochemical processes were shown to be reversible and interconvertible as they are governed by the amount of cis

azo molecules.<sup>1</sup> In view of the great interest of azo dye-doped LCs and liquid crystalline polymers (LCPs) for potential optical and photonic applications,<sup>1–7</sup> this finding is of fundamental importance because the richness of

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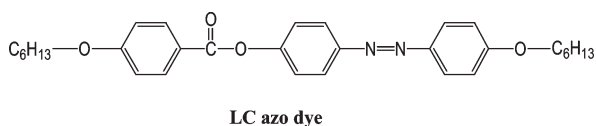
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the photochemical properties generated by high concentrations of LC azo dyes may open the door to new possibilities of exploiting this type of photoactive materials. As an example, we demonstrated that both the normal and reverse modes of photocontrolled switching of the transmittance of a probe light through crossed polarizers (optical shutters) could be achieved using the same mixture of the nematic LC (BL006) doped with 15% of the LC azo dye.<sup>1</sup>

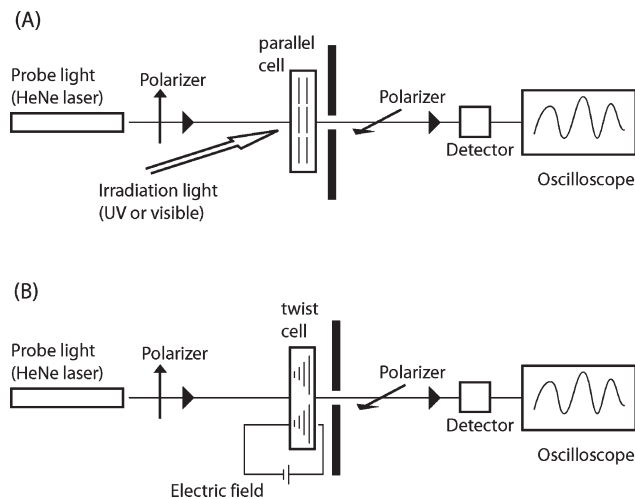
In this paper, we present a detailed and comprehensive study of the system in the regime of low and high concentrations of the LC azo dopant. Using polarizing optical microscopy, and by monitoring the change in transmittance of a probe light going through the azo dye-doped LC subjected to UV or visible light illumination (photo-optical response) or to an electric field (electro-optical response), we attempted to draw a complete picture about the transitions between the multiple photochemical LC disordering, LC-isotropic phase transition and phase separation processes in relation with the trans-cis photoisomerization of the azo dye. We emphasize that all results reported here are new and were not reported in the previous communication.<sup>1</sup>

### Experimental Section

**Materials.** The synthesis and characterization of the LC azo dye (chemical structure shown below) was already reported.<sup>1</sup> It has a broad nematic phase (between  $\sim 110$  and  $227$  °C) and can be solubilized in nematic LCs in large amount (up 25%). The used room-temperature nematic LC host, BL006 (Merck), is a eutectic mixture of several LC compounds (composition unknown) and has a clearing (nematic-isotropic) temperature of  $T_{ni} \approx 116$  °C. Their homogeneous mixtures were obtained by dissolving both BL006 and the azo dye in THF (total concentration  $\sim 3\%$ ), followed by solvent removal under reduced pressure.



**Photo-optical Measurement.** The photochemical processes occurred in the LC azo dye-doped BL006 were investigated by monitoring the change in optical transmittance of the mixture under crossed polarizers upon application of either UV ( $\lambda = 365$  nm) or visible light ( $\lambda = 440$  nm). The setup is sketched in Figure 1a. Typically, the BL006/azo dye mixture was filled in a parallel rubbed, indium-tin-oxide (ITO)-coated cell with a gap of  $5\ \mu\text{m}$  (EHC Japan); it was then placed between two crossed polarizers with the rubbing (LC orientation) direction set at  $45^\circ$  to them. The transmittance of a probe light ( $\lambda = 633$  nm from a 4 mW He-Ne laser) going through the cell was measured with a high-speed photodetector (Displaytech) connected to a digital oscilloscope (Tektronix, TDS 420A). Any changes in transmittance in response to the trans-cis photoisomerization of azo molecules in the mixture could be measured by exposing the cell to UV or visible light. The irradiation beam, generated by a spot curing system (Novacure 2100) combined with interference filters for UV and visible light (10 nm band-



**Figure 1.** Schematic illustration of the setup for (a) photo-optical and (b) electro-optical measurements of the liquid crystalline azo dye-doped liquid crystals.

width, Oriel), was applied to the cell at an angle of about  $30^\circ$  with respect to the cell normal; and by placing a nontransparent plate with a small hole ( $\sim 2$  mm diameter) in front of the photodetector, the irradiation beam had no interference on the measured transmittance. Unless otherwise stated, the mixture in the cell was equilibrated at  $140$  °C for 8 min before being cooled to room temperature for the measurement. A homogeneous LC orientation (LC molecules aligned along the rubbing direction) was obtained during the cooling.

**Electro-optical Measurement.** As shown in Figure 1b, a setup similar to the one used for photo-optical measurements was utilized to follow the changes in transmittance of the BL006/azo dye mixture upon application of a voltage through the cell. For these electro-optical measurements, perpendicular-rubbed, ITO-coated cells with a gap of  $5\ \mu\text{m}$  were used in order to reduce the dynamic response of the LC material.<sup>8</sup> In these cells, LC molecules were forced to adopt a twist orientation. A high-voltage waveform generator (WFG500, FLC Electronics) was used to apply either a square-wave ac field (1000 Hz) or pulse electric fields through the cell. The measurement of the first-order diffraction efficiency of a grating upon application of a voltage was conducted by using a setup described in a previous report.<sup>9</sup>

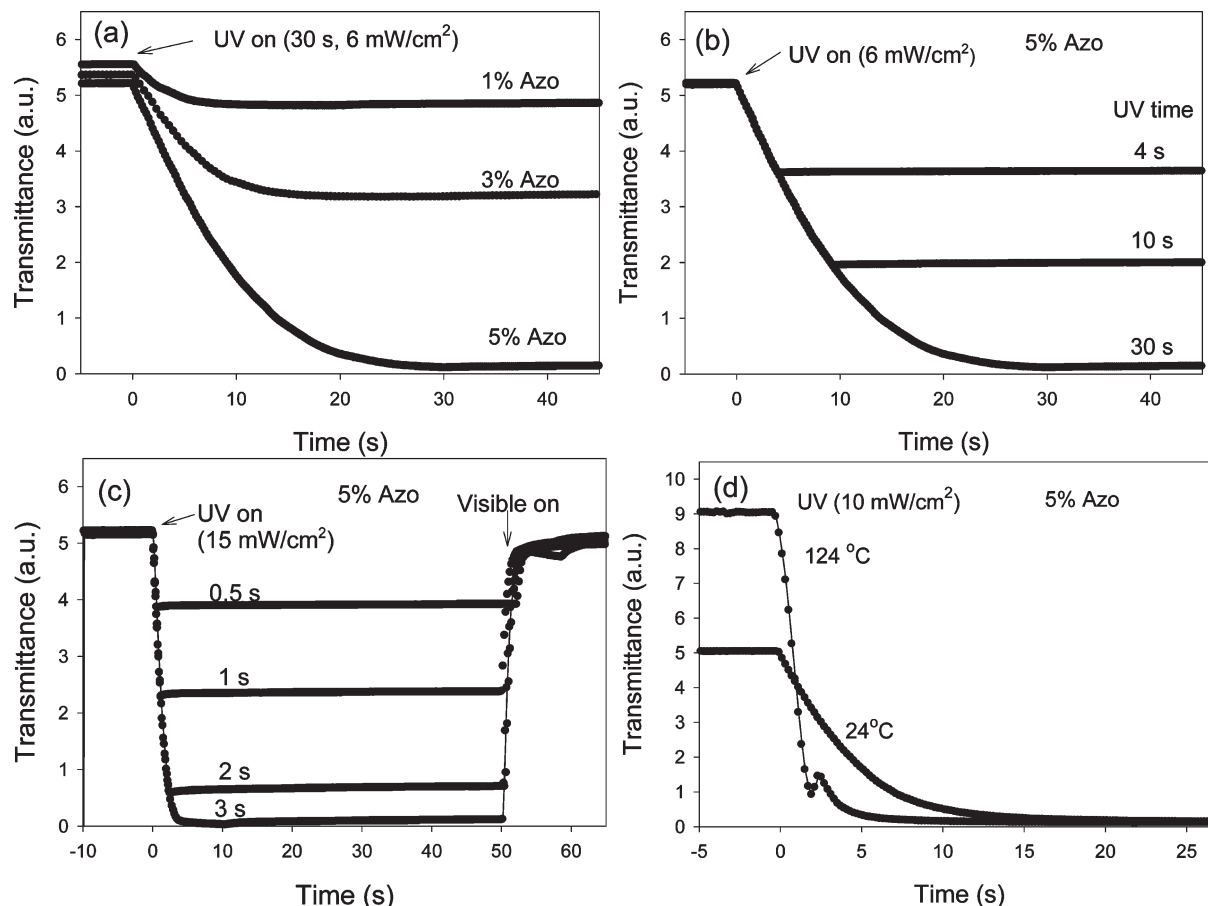
**Other Characterizations.** The BL006/azo dye mixtures have also been characterized using a number of other techniques. Particularly, UV-vis spectra (HP-8452A spectrophotometer) were recorded immediately after an irradiation in order to monitor the change in the relative amounts of trans and cis azo molecules upon UV or visible light illumination. The photochemical LC disordering, phase transition, and phase separation occurred in the mixtures were examined using a polarizing optical microscope (Leitz DMR-P) equipped with a hot stage (Instec).

### Results and Discussion

**1. From Photochemical Disorder to Nematic-Isotropic Phase Transition.** We first investigated the photo-optical behavior of BL006 doped with a low concentration of the LC azo dye. By monitoring the change in

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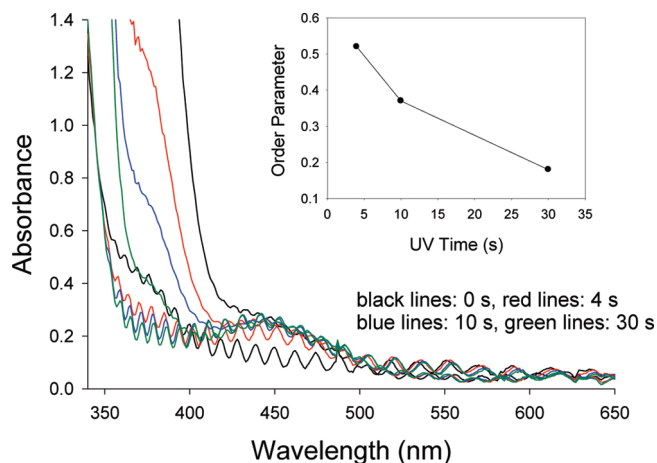
**Figure 2.** Change in transmittance vs time for (a) three mixtures containing different azo dye concentrations (1, 3 and 5%) exposed to UV light (6 mW/cm<sup>2</sup>) for 30 s; (b) a mixture containing 5% of azo dye exposed to UV light (6 mW/cm<sup>2</sup>) for different times (4, 10, and 30 s); (c) a mixture containing 5% of azo dye exposed to higher intensity UV light (15 mW/cm<sup>2</sup>) for different times (0.5, 1, 2, and 3 s), showing the stable level of transmittance after turning off the UV light and the recovery upon visible light exposure (12.5 mW/cm<sup>2</sup>); and (d) a mixture containing 5% of azo dye exposed to UV light (10 mW/cm<sup>2</sup>) at 24 and 124 °C.

optical transmittance of the mixture in response to UV exposure (Figure 1a), we could assess the perturbation of the LC order by the trans–cis isomerization of azo molecules. Figure 2 presents an example of results that show the effects of various parameters. In (a), the effect of the azo dye content is visible. With the same duration of UV exposure (30 s) and UV intensity (6 mW/cm<sup>2</sup>), the decrease in transmittance increased with the azo dye concentration (from 1 to 5 wt %). In (b), with the same azo dye concentration of 5% and UV intensity (6 mW/cm<sup>2</sup>), the achievable transmittance decrease became more important with increasing the UV exposure time. In (c), the effect of UV intensity is evident. As compared with (b), by increasing the UV intensity to 15 mW/cm<sup>2</sup>, the drop of transmittance took place much more quickly. An appealing feature of this LC azo dye, seen in (b) and (c), is that the level of transmittance decrease could easily be controlled by the UV exposure time (the decrease was stopped once UV was turned off), and that the new transmittance level remained stable in the absence of UV light (a stable cis form of the azo dye is the reason for the stability). As shown in (c), the initial transmittance level was recovered only by exposure of the mixture to a visible light (12.5 mW/cm<sup>2</sup>) that induced the reverse cis–trans isomerization for azo molecules. Such a photo-

optical behavior makes the LC azo dye-doped nematic LC an excellent system for a photocontrollable light-shutter with a tunable level of transmittance change (gray scale). The effects of the azo dye content, UV time, and UV intensity are not surprising and have all a logical explanation in term of the number of cis azo molecules upon exposure, which determines the perturbation degree of LC molecules aligned by rubbed surfaces in the cell. The data reported in (a–c) were obtained at room temperature (24 °C). The results in (d) show the effect of temperature. With all other parameters kept the same, at 124 °C, which is about 3 degrees below the clearing temperature of the mixture ( $T_{ni} \approx 127$  °C), the drop of transmittance upon UV exposure was much faster than at room temperature. The action of cis azo molecules adds up to the thermal agitation effect for the perturbation of LC molecules.

The magnitude of the transmittance decrease of the LC azo dye-doped BL006 upon UV exposure should reflect the degree of disordering imposed on the initially homogeneous alignment of LC molecules by the trans–cis isomerization. We found evidence by directly recording polarized UV–vis spectra of the cells used for photo-optical measurements. Figure 3 shows the UV–vis spectra obtained with the cell containing the mixture for

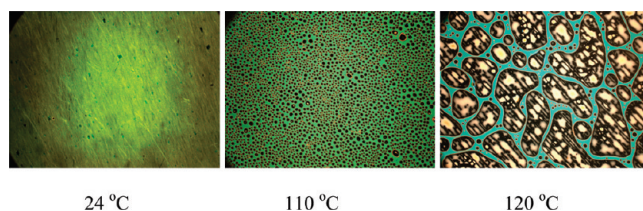




**Figure 3.** Polarized UV-vis spectra obtained with the sample in Figure 2b (in the LC cell). For each UV exposure time, the spectrum with a higher absorption around 375 nm was taken with the spectrophotometer's beam polarized parallel to the cell surface rubbing direction, whereas that with a lower absorption was obtained with the polarization perpendicular to the rubbing direction. The inset shows the estimated order parameter of trans azo molecules.

Figure 2b, with the spectrophotometer's beam polarized parallel and perpendicularly to the rubbing direction, respectively. The absorption of BL006 molecules (containing phenyl rings) was much too intense to be useful. But the dichroism of the absorption of trans azo molecules, around 370 nm, could be used as a probe, since trans azo molecules are miscible with BL006 and should have the same orientation as the host molecules. Prior to UV exposure, the dichroic ratio  $R = A_{\parallel}/A_{\perp}$  ( $A_{\parallel}$  and  $A_{\perp}$  being the parallel and perpendicular absorbance at 370 nm) could not be measured because of the too strong parallel absorption (indicative of homogeneous alignment). After 4 s of UV irradiation, the decreased LC alignment was observable from the decreased dichroism of the remaining trans azo molecules. Shown in the inset of Figure 3 is the plot of calculated order parameter  $S$ , defined as  $S = (R - 1)/(R + 2)$ , as a function of UV exposure time. The decreasing alignment of LC molecules along the rubbing direction with increasing the amount of cis azo molecules is clear. Although the initial order parameter could not be determined from the UV-vis spectra, for a homogeneously aligned nematic LC it should be about 0.6. Upon the trans-cis isomerization, the absorption of cis azo molecules centered at 450 nm became visible despite the overlap with the baseline pattern due to the interference.

With a low content of the LC azo dopant in BL006 (up to 5%) and at room temperature, despite the drop of transmittance upon UV exposure (Figure 2c), the photochemical nematic-isotropic phase transition did not occur, since remaining birefringence could still be observed on the polarizing microscope. The transmittance drop is the result of a photochemical disordering process. In other words, the reaction of azo molecules reduces the order parameter of the nematic phase. The effect is similar to the thermal effect by heating a nematic LC to close, but below, the clearing temperature. The occurrence of the

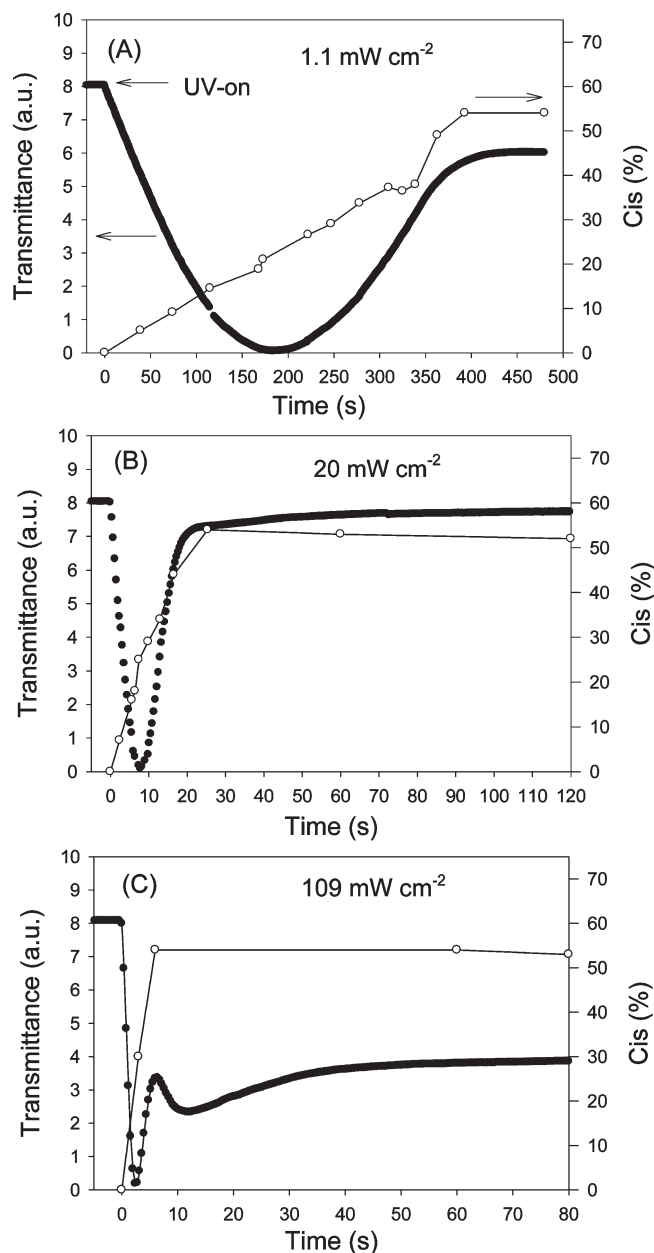


**Figure 4.** Polarizing photomicrographs of a mixture containing 5% of azo dye exposed to UV light (10 mW/cm²) for 60 s at three different temperatures (24, 110, and 120 °C) below the clearing temperature of the LC ( $\sim 127$  °C), showing the photochemical disordering and nematic-isotropic phase transition processes (picture area:  $240 \mu\text{m} \times 180 \mu\text{m}$ ).

photochemical nematic-isotropic phase transition needs the help of some thermal energy. Figure 4 shows the polarizing photomicrographs of the mixture containing 5% azo dopant and exposed to UV light for 30 s (15 mW/cm²) at three temperatures. First, at 24 °C, the birefringence of the severely (but not completely) disordered nematic phase (see Figure 2c) could be noticed; then, at 110 °C, which is about 17 °C below the  $T_{ni}$  of the mixture, the presence of an isotropic phase became clear (dark spots); and finally, at 120 °C, the nematic-isotropic phase transition was evident.

To summarize this section, in the regime of low concentrations of the LC azo dopant, the trans-cis isomerization upon UV illumination has mainly as effect the photochemical disordering of the LC host. The degree of disordering, indicated by a decrease in the order parameter, could be precisely controlled by changing a number of variables such as azo dopant concentration, UV exposure time and UV intensity that all determine the amount of azo molecules in the cis form. At elevated temperatures, but below  $T_{ni}$ , the photochemical disordering process could develop into the nematic-isotropic phase transition. During all the photochemical processes (disordering or phase transition), the mixture remained homogeneous at equilibrium. In other words, trans and cis azo molecules are miscible with the LC host.

**2. Photochemical Phase Separation Comes into Play.** In the regime of high concentrations of the LC azo dopant, the photochemical processes become even richer. Figure 5 shows the photo-optical behaviors of a mixture of BL006 doped with 18% of the azo dye exposed to UV light of different intensities. All measurements were carried out at room temperature. The new feature emerged at this high azo concentration is that the transmittance first decreased and then increased. This was observed with the three UV intensities (from the very low 1.1 mW/cm² to the high 109 mW/cm²), whereas the rate of transmittance change was greater with increasing the UV intensity. The increase in the amount of cis azo molecules in the mixture under UV light is also shown in Figure 5, with the percentage of cis isomer calculated from  $\text{cis \%} = (1 - A/A_0) \times 100$ , where  $A_0$  and  $A$  are the absorbance of trans azo molecules at 365 nm before and upon UV illumination, respectively. It is seen that regardless of the UV intensity, which determined the time scale over which the transmittance decrease and increase proceeded, the lowest transmittance



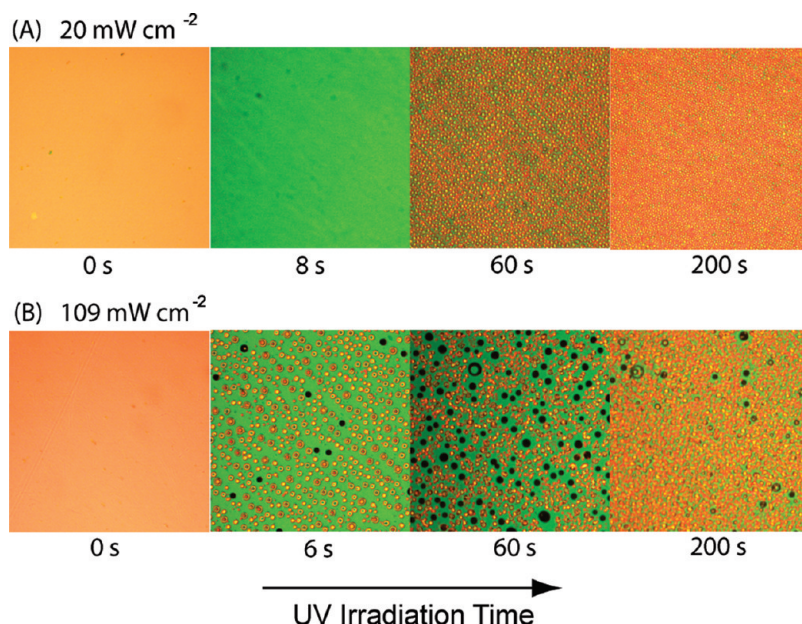
**Figure 5.** Change in transmittance vs time for a mixture containing 18% of azo dye exposed to UV light, and the concomitant variation of the amount of cis azo isomers in the mixture: (a) with a low UV intensity of 1.1 mW/cm<sup>2</sup>, (b) intermediate UV intensity of 20 mW/cm<sup>2</sup>, and (c) high UV intensity of 109 mW/cm<sup>2</sup>.

was achieved with ~20% cis isomer and the transmittance recovery was essentially completed with ~50% cis isomer in the mixture. As pointed out in our previous communication,<sup>1</sup> the recovery of transmittance with increasing the amount of cis isomer is due to a photochemical phase separation process in the mixture. When the amount of cis isomer exceeds a certain level, cis azo molecules, with a bent shape, are no longer miscible with the LC host, driving the phase separation and the appearance of a second phase in the mixture. Depending on the amount of cis isomer and the speed with which they are formed, this photochemical phase separation can couple with and compete against the photochemical disordering and phase transition processes differently. This could account

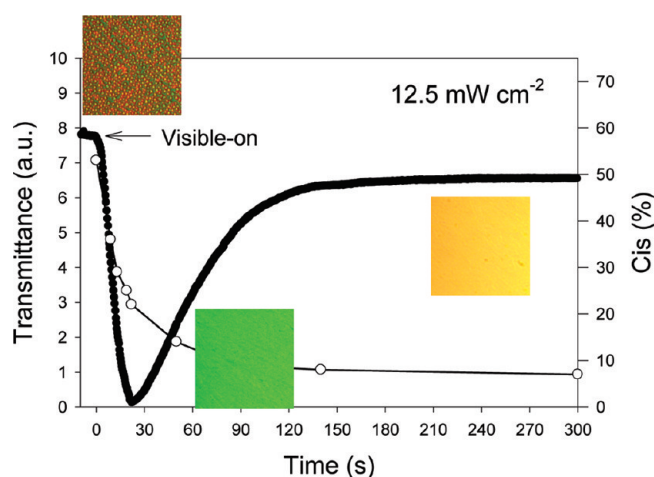
for the different transmittance recovery levels seen in Figure 5.

The transmittance recovery associated with the phase separation is mainly due to a realignment of LC molecules by rubbed surfaces as most cis azo molecules, which cause the disorder, are separated from the LC host. To illustrate the multiple photochemical processes involved, Figure 6 shows two series of polarizing photomicrographs taken at different UV exposure times with the two UV intensities in (b) and (c) of Figure 5. At the intensity of 20 mW/cm<sup>2</sup>, the apparent birefringence change (color change) after 8 s of irradiation corresponds to the minimum transmittance (Figure 5b) related to the disordering of LC molecules. The image taken 60 s after UV irradiation shows clearly the two-phase mixture with the appearance of dropletlike regions. The birefringence change indicates the realignment of LC molecules even though disordered regions (mostly with cis azo molecules) can still be noticed. At this point, the transmittance was already recovered to almost the initial level. After a long exposure time of 200 s, the two phases appeared to have evolved, resulting in, however, only a slight further increase in the transmittance. In this case, the phase separation followed the disordering process in a sequential way. By contrast, with the high UV intensity of 109 mW/cm<sup>2</sup>, the number of cis isomer increased rapidly and 6 s of exposure already gave rise to the phase separation. However, because of the short time available for the phase separation to develop, the large amount of cis azo molecules induced not only the disordering of LC molecules, but also the room-temperature nematic–isotropic phase transition, as revealed by the dark spots. In other words, the phase separation is coupled with the phase transition and evolves simultaneously. This situation became clearer after 60 s of UV exposure; the image shows the coexistence of a separated phase with realigned LC molecules (yellow spots), disordered nematic phase (green background), and a growing isotropic phase (dark spots). These photochemical processes appeared to compete against each other and, over a long exposure time, made the mixture evolve toward equilibrium of two separated LC phases—one highly ordered and one disordered (with cis azo molecules)—whereas the isotropic phase tended to disappear. The lower transmittance recovery in (c) of Figure 5 is caused by the presence of an isotropic phase.

Because the control factor for the photochemical processes leading to the two-phase mixture is the amount of cis isomer determined by the trans–cis isomerization upon UV absorption, the processes can be reversed by visible light inducing the reverse cis–trans isomerization. In other words, the phase-separated mixture can be rehomogenized by visible light irradiation. Figure 7 shows an example with the mixture of BL006 doped with 18% of the azo dye. When the two-phase mixture was exposed to visible light (12.5 mW/cm<sup>2</sup>), as the amount of cis isomer declined, the transmittance dropped first before being recovered. The inserted polarizing photomicrographs, taken before and after 25 and 220 s of visible light exposure, show the concomitant morphology and



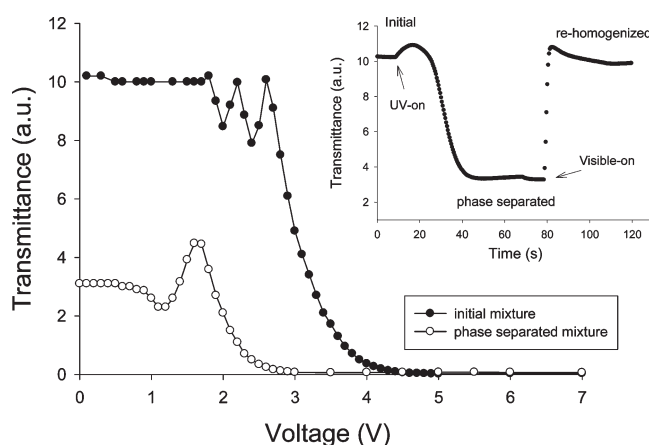
**Figure 6.** Polarizing photomicrographs of a mixture containing 18% of azo dye exposed to UV light of two different intensities (20 and 109 mW/cm<sup>2</sup>) at room temperature (picture area: 195  $\mu$ m  $\times$  195  $\mu$ m).



**Figure 7.** Change in transmittance and the amount of cis isomer vs visible light (12.5 mW/cm<sup>2</sup>) exposure time for a mixture containing 18% of azo dye previously exposed to UV light (20 mW/cm<sup>2</sup>, 60 s) for phase separation. The two-phase mixture and the photoinduced homogenization are visualized by the polarizing photomicrographs in the inset, taken before and after (25 and 220 s) the visible light exposure.

birefringence change of the mixture corresponding to the transition from the two-phase state to disordered single-phase and to ordered single-phase. The disordered LC phase (lowest transmittance) was observed with about 20% cis azo molecules, similar to the transitions from the homogeneous to phase separated mixture (Figure 5b). Of course, the rehomogenization can also be achieved at elevated temperatures that accelerate the thermal relaxation of cis isomers.

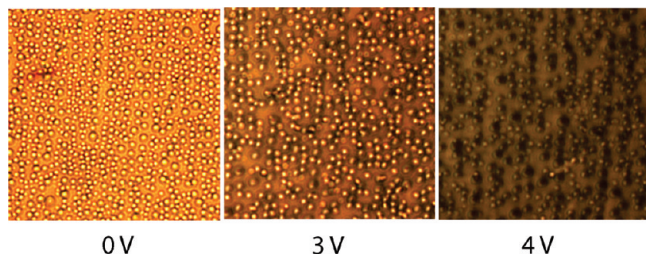
**3. Electro-optical Behaviors.** As mentioned above, the photochemical phase separation is driven by the increase in the amount of cis azo molecules that become immiscible with the LC host; therefore, one phase should be rich in the cis isomer, whereas the other phase should be rich in trans isomer. To get some insight into the difference



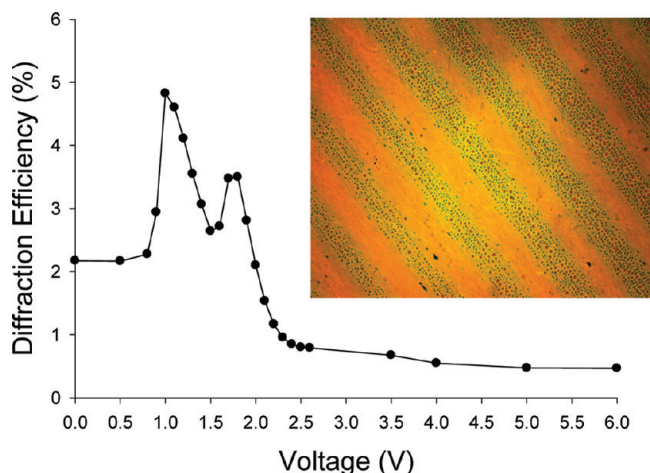
**Figure 8.** Change in transmittance vs applied voltage for a homogeneous mixture containing 18% of azo dye (before phase separation) and the two-phase mixture (after phase separation). The inset shows the change in transmittance vs time for the mixture upon UV (20 mW/cm<sup>2</sup>, 60 s) and subsequent visible light (15 mW/cm<sup>2</sup>) exposure, the mixture being filled in a perpendicularly rubbed cell with twist LC orientation.

between the two phases, we performed electro-optical measurements with the mixture of BL006 doped with 18% azo dye. To minimize the dynamic instability in the electro-optical response, we utilized perpendicularly rubbed LC cells, in which oriented LC molecules form helices (Figure 1b).<sup>8</sup> Figure 8 compares the changes in transmittance as a function of applied voltage for the homogeneous mixture (before phase separation) and the two-phase mixture (after phase separation), the difference is visible. The threshold voltage, at which LC molecules are reoriented along the electric field direction resulting in a drop of the transmittance, is lower for the two-phase mixture ( $\sim$ 2 V) than for the homogeneous mixture ( $\sim$ 3 V). This suggests that the disruption of the twist LC orientation by the phase separation process rendered the electric field-induced reorientation of LC molecules easier. The



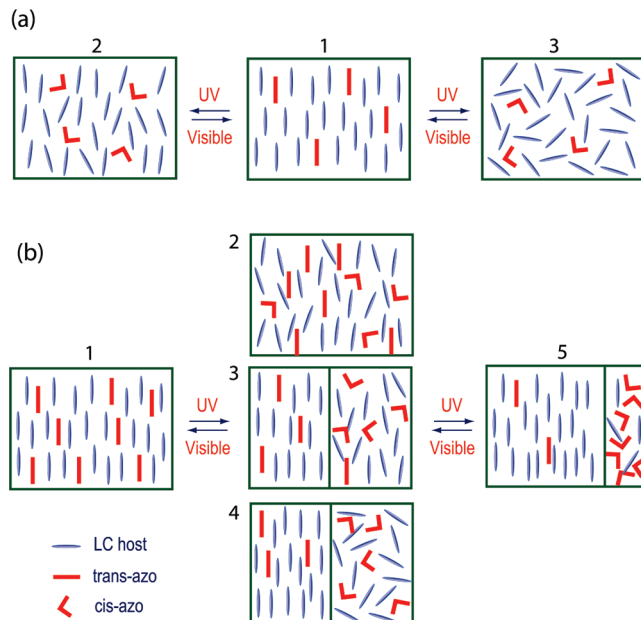


**Figure 9.** Polarizing photomicrographs of the two-phase mixture in Figure 8, showing the electric-field-induced orientation of LC molecules at 3 and 4 V (picture area:  $98\ \mu\text{m} \times 98\ \mu\text{m}$ ).



**Figure 10.** Change in the first order (+1) diffraction efficiency vs applied voltage for a grating recorded by exposing a mixture containing 18% of azo dye to UV light ( $20\ \text{mW}/\text{cm}^2$ , 60 s) through a grating photomask. The polarizing photomicrograph in the inset shows the regions ( $\sim 40\ \mu\text{m}$  fringe spacing) of the two-phase mixture (exposed to UV light) and the homogeneous mixture (not exposed).

different initial transmittances (at zero volts) of the two mixtures are explained by the inset of Figure 8 showing the photo-optical response of the mixture, which is different from that observed with the parallel rubbed cell (Figure 5). Upon UV irradiation ( $20\ \text{mW}/\text{cm}^2$ ), the isomerization induced perturbing effect on the twist LC molecular orientation resulted in a slight increase in the transmittance; the transmittance dropped only after about 20 s when the phase separation was developed (observable on polarizing microscope). After the UV light was turned off, the reverse photochemical processes could be obtained by applying visible light; the transmittance recovered first, followed by a slight decrease. The initial mixture and the mixture after 60 s UV exposure were used for the electro-optical measurements shown in Figure 8. Note that the initial LC orientations, determined by the surface rubbing of the cells, account for the apparently different photo-optical behaviors (Figure 1). Figure 9 shows the polarizing photomicrographs of the two-phase mixture without and upon application of an electric field (3 and 4 V). It is hard to tell which phase reacted at a lower voltage, even though the phase in the form of dispersed droplets seems to display a more complete reorientation of LC molecules (darker appearance) at 4 V. A thorough characterization was further complicated by the fact that the applied electric field could also induce the reverse cis–trans isomerization of



**Figure 11.** Schematic illustration of the reversible multiple photochemical processes in the LC azo dye-doped nematic liquid crystal: (a) disordering (from 1 to 2) or nematic–isotropic phase transition (from 1 to 3) with a low concentration of the azo dye; (b) phase separation through disordering (from 1 to 2 to 5) or phase separation involving disordering and/or nematic–isotropic phase transition (from 1 to 3 and/or 4 to 5).

azo molecules, similar to the action of heat and visible light. The phenomenon was previously reported.<sup>10</sup>

Finally, when the cell filled with the homogeneous mixture of BL006 doped with 18% LC azo dye was exposed to UV light through a grating photomask, a grating could easily be recorded because the photochemical processes took place only in the illuminated areas. The inset of Figure 10 shows such a grating (fringe spacing  $\approx 40\ \mu\text{m}$ ) viewed under crossed polarizers, with homogeneous and two-phase mixtures alternately separated. It is normal to expect a difference in the refractive index of the two regions. Indeed, the grating diffracted a probe light (633 nm). Figure 10 shows the first-order (+1) diffraction efficiency of the grating as a function of applied voltage. The different electro-optical responses of the homogeneous and two-phase mixture (Figure 8) gave rise to an apparently oscillating diffraction efficiency of the grating, reflecting a complicated fashion of the changing index modulation. The diffraction efficiency dropped at higher voltages ( $\geq 2.5\ \text{V}$ ) basically due to the reorientation of LC molecules in the two regions along the electric field direction. The grating could be erased either by heating the mixture or by visible light exposure or by keeping the mixture under a voltage. In all cases, the reverse cis–trans isomerization of azo dye molecules is responsible.

## Conclusions

The main findings of this study are recapitulated by the schematic illustration in Figure 11. On the one hand, in

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the regime of low azo dye concentrations (Figure 11a), where azo molecules in the cis form remain miscible in the LC host upon the complete trans–cis isomerization, the UV light-induced photochemical processes are the disordering of the nematic phase (from state 1 to state 2) or the isothermal nematic–isotropic phase transition (from state 1 to state 3). With the investigated LC azo dye, only the photochemical disordering process occurs at room temperature, with a precisely controllable disordering degree for the nematic phase. At elevated temperatures, but below  $T_{ni}$  of the LC, the photochemical nematic–isotropic phase transition can be observed. On the other hand, in the regime of high azo dye concentrations (Figure 11b), where azo molecules in the cis form are immiscible with the LC host when the amount of cis isomer passes a critical value, the photochemical processes are characterized by the phase separation in addition to the disordering of the LC phase and the nematic–isotropic phase transition, all of which can take place at room temperature. As depicted, upon UV exposure, the pathway from the homogeneous to the phase-separated mixture (from state 1 to state 5) can be different depending on the rate at which cis isomers are formed. If they are formed slowly, the disordering process develops and is followed by the phase separation when the amount of cis isomer passes a critical value (transitions from state 1 to state 2 and to

state 5). By contrast, if cis isomers are formed rapidly, the phase separation can occur simultaneously with the disordering and the nematic–isotropic phase transition before the mixture evolves over time and reaches two separated LC phases (transitions from state 1 to state 3 or/and state 4 and to state 5). It appears that at equilibrium, one LC phase is ordered and the other one, rich in cis isomer, is disordered. Because all these photochemical processes induced by UV light are controlled by the amount of cis azo molecules in the mixture, they can be reversed by visible light exposure that diminishes the amount of cis isomer. This study shows the richness of the photochemical processes by using an LC azo dye, which improves the solubility in the LC host. The various photo-optical and electro-optical behaviors associated with the multiple photochemical processes could offer new possibilities of exploitation of azo-dye-doped liquid crystals for applications.<sup>1–4</sup>

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