

Irreversible phase and anchoring transitions of chiral azodye-doped nematic liquid crystal triggered by photostimulation

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Reported herein are the simultaneous phase and anchoring transitions of the chiral azodye-doped liquid crystal (LC) mixture. The transitions are influenced by photostimulation and are stable against light and thermal treatments. The photochromic *trans* state of the azobenzene molecule used in the study is mesogenic with a chiral nature. The photoinstigated *cis* form of the molecule has a much-enhanced dipole moment with a broken chromophore symmetry. Due to the high dipole–dipole interaction, the *cis*-state molecules stack together and form nano-sized aggregates. Subsequently, the *cis* aggregates get phase-separated, resulting in the chiral- to achiral-phase transition of the host LC. The phase-separated *cis* aggregates diffuse to the interface between indium-tin-oxide and LC and modify the surface, causing planar to homeotropic anchoring transition of the host LC. The stability and irreversibility of the transition, and the fact that there is no need for pre-treatments for LC alignment, provide a fascinating opportunity for LC device applications.

Keywords: chiral; azodye; nematic liquid crystal; phase transition; alignment

1. Introduction

Liquid crystal (LC) is a fascinating phase of matter because of its orientational order with fluidity and optical anisotropy. By controlling its orientation, one can efficiently control its birefringence. Although one can manipulate its orientation by applying an electric field to it, its initial orientation without any field should also be kept under control. To enforce a specific orientation of the molecules without any external field, a predetermined modified surface is used. Thus, alignment control is one of the most crucial and essential processes for liquid crystal display (LCD) fabrication. The non-contact methods for the alignment of LCs have been a great topic of interest for the last two decades. The photoalignment [1–6] and doping of nanoparticles [7,8] have drawn much interest in line with the modification of the surface characteristics for the alignment of LC molecules. Gibbson *et al.* reported the azodye-doped anisotropic films formed by the polarized-light-stimulated rotation of the dye molecules for the LC alignment layer by irradiating intensive linearly polarized laser light [1]. In the pioneering works achieved by Ichimura *et al.*, the azobenzene derivatives were covalently attached to either the inorganic oxide surfaces or the polymer side chains, and were used as LC alignment layers [2]. In these cases, photochromic *trans* to *cis* isomerization was responsible for the anchoring transition of the LC molecules on the surface. The reversible

anchoring transition of azo-LC or azodye-doped LCs has also been reported and interpreted as the molecular adsorption of the *cis*-form isomer on the surface through the dipole–dipole and hydrogen bonding interactions between the dye molecules and the polar oxide surface [3,4]. Most of the above-mentioned methods require pretreatment of the surface for aligning the LC molecules. Recently, some photoresponsive or photoreactive additives doped to the nematic host were developed to instigate a vertical alignment of LCs upon UV light irradiation without a pre-treated alignment layer [9,10]. On the other hand, the transition from the nematic to the isotropic phase induced by photochromic isomerization has also been well documented for the azodye-doped LCs [11]. All the above-mentioned anchoring and phase transitions induced by *trans* to *cis* isomerization, however, are characterized by their reversibility.

In this report, the simultaneous phase and anchoring transitions of nematic LCs doped with a liquid crystalline chiral azodye and stimulated by UV light irradiation are described. The chiral-nematic- to nematic-phase transition and planar- to homeotropic-anchoring transition concurred under UV light irradiation. The resulting transitions were stable against the light and thermal treatments. The stability and irreversibility of the reported phenomenon, and the fact that there is no need for pretreatment for LC alignment, provide a great potential for practical device applications.

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2. Experiment

Nematic LCs with either positive (E7, Merck) or negative (MLC 6608, Merck) dielectric anisotropy were used as host LCs in the experiment in this study. The photochromic chiral azodye shown in Figure 1 was added to the LC host at different ratios ranging from 0.5 to 3.0 wt%. For homogeneous mixing, the mixture was melted by stirring it at a few degrees above the nematic- to isotropic-transition temperature (T_{NI}) of the host LCs. All the experiment data presented in this work had been taken from an LC with negative dielectric anisotropy (MLC 6608).

Electro-optic (EO) cells were fabricated using indium-tin oxide-(ITO)-coated glass, without any pretreatment for LC alignment. The cell thickness was maintained using 10- μm -thick tape spacers. The dye-doped LC mixture was loaded into the cells with a capillary action at 5 degrees above the T_{NI} , and was cooled to an ambient temperature. The cells were then exposed to UV light with 20 mW to 500 mWcm^{-2} intensity peaked at the 378 nm wavelength for 30 min to 6 h at room temperature. Spot Cure Model SP-9 (Ushio Inc.) was used as the UV source. The 378 nm wavelength was selected using a bandpass filter with 58 nm full width at half maximum.

Polarized optical microscope (POM) and conoscope images were taken using a Nikon Eclipse LV 100 POL equipped with a Nikon DS-R11 CCD camera and an Instec HCS 402 hot stage with an Instec STC 200 temperature controller. The UV-VIS absorption spectra of the dye solutions in chloroform were measured using a UV-VIS spectrophotometer (Jasco, ARSN-733). For particle size analysis, the count rate and particle size of the dye solutions in chloroform placed in a quartz cuvette were measured using a Brook Haven BioPlus particle size analyzer (Brook Haven Inc.). The surface morphology of the modified surface was studied via field emission scanning electron microscopy (FESEM, Hitachi, Japan).

3. Results and discussion

The EO cell was filled with an LC mixture doped with 3.0 wt% chiral azo component in the MLC 6608. Initially, it showed planar anchoring, as expected, on the bare ITO surface. The cell was exposed to UV light with 500 mW/cm^2 intensity for 30 min. A mask was used to observe the difference between the exposed and non-exposed areas.

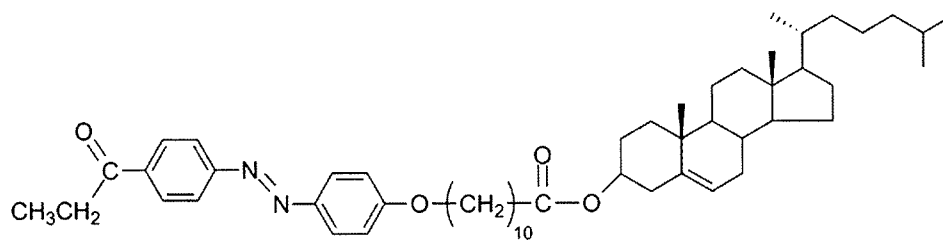


Figure 1. Molecular structure of the chiral azodye.

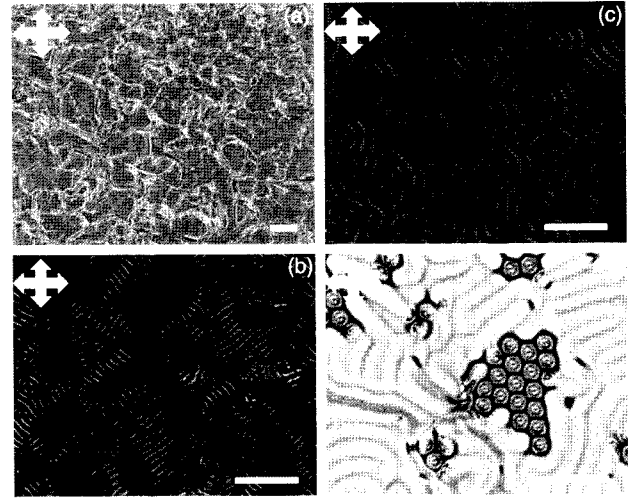


Figure 2. (a) The chiral nematic texture in the planar-anchored cell before UV exposure. (b)–(d) The POM images of the same cell after the UV exposure of the cell with 20 mW/cm^2 intensity. The POM images (b)–(d) correspond to the image after 2, 4, and 6 h of UV exposure, respectively. They clearly show the gradual increase in the helical pitch of the host LC (MLC 6608) with negative dielectric anisotropy.

After UV exposure, the exposed area exhibited a randomly oriented fingerprint texture, which is a crucial signature of the chiral nematic LCs with a homeotropic anchoring condition. This clearly indicated a modification of the surface anchoring state. To study this phenomenon further, a fresh cell was prepared with the same mixture, and was exposed to 20 mW/cm^2 UV light for 6 h while being examined under POM after every 2 h of UV exposure. Before UV exposure, a typical chiral nematic texture on a planar-anchored surface was observed. After the first 2 h of UV exposure, a highly dense fingerprint texture with a tight pitch was witnessed. As mentioned earlier, this clearly indicated the anchoring transition from the planar to the homeotropic state. After 2 more hours of UV exposure, the period of the fingerprint texture became wider. This behavior continued with the time of exposure. The widening of the fingerprint revealed a decrease in the chiral power of the mixture. As the only chiral component of the mixture was the azodye, the widening of the fingerprint directly proved that the azodye was getting phase-separated from the host LC and was losing its contribution to the helical

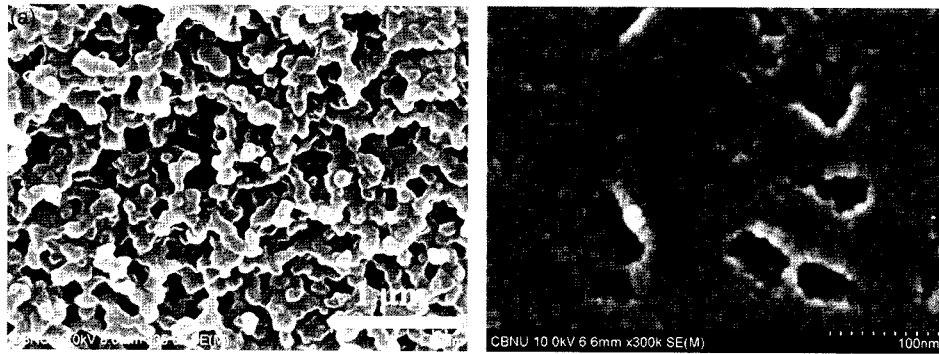


Figure 3. Figure 3(a) and 3(b) shows the FESEM images of the inner surfaces after LC removal. (a) Shows a relatively thicker deposition of larger aggregates, whereas (b) shows a thin layer consisting of 10–30 nm spherical particles with roughened surfaces. (a) Shows the inner surface of the top substrate, which was near the UV side, and thus, a relatively thicker deposition could be observed due to the stronger UV intensity. (b) Corresponds to the surface in the far UV side with a thinner layer.

twisting of the host LCs. Figure 2 shows (a) the initial planar state prior to UV irradiation, and (b)–(d) the phenomenon of anchoring transition upon exposure to UV light, and the gradual widening of the fingerprint with the continuation of UV exposure. On the other hand, to find the origin of the anchoring transition, the cell was immersed in pure hexane to selectively remove the LC, and the inner surfaces were visualized via FESEM.

Both the top and bottom substrates clearly showed the modification of the ITO surface with the numerous particles of aggregates evidenced in Figure 3(a) and 3(b). In addition to the uniformly thin layer composed of 20–30 nm particles, as seen in Figure 3(b), the relatively larger aggregates formed clusters, as shown in Figure 3(a). Comparatively, a larger amount of aggregate deposition was observed on the top surface (i.e. near-side surface from the UV source). In both cases, however, it was presumed that the aggregates had been formed from the *cis*-form isomer of the azodye due to the enhanced dipole moment [9]. Once the sample was exposed to UV light, the *trans* form of the azobenzene compounds transformed into the *cis* configuration. With continuous UV exposure, the population of *cis* isomer increased. The *cis* isomer exhibited a several-fold larger dipole moment due to the broken chromophore symmetry. On the other hand, the *cis* isomer also possessed lesser solubility in the LC host. As a result, a large population of *cis* isomers formed small aggregates due to the stronger dipole–dipole interaction and the phase separated from the LC host.

As was observed in the mixture with 3 wt% azodye molecules, even after 6 h of UV exposure, the mixture contained a significant amount of chiral component. To demonstrate the consumption of all dye additives with UV exposure for a shorter period of time, a new sample was prepared with 1.0 wt% dye molecules mixed in the host LC. The sample was then loaded into the EO cell and was observed under depolarized light. Figure 4(a) and 4(c) displays the respective macroscopic and microscopic images of the cell under crossed polarizers, confirming the state

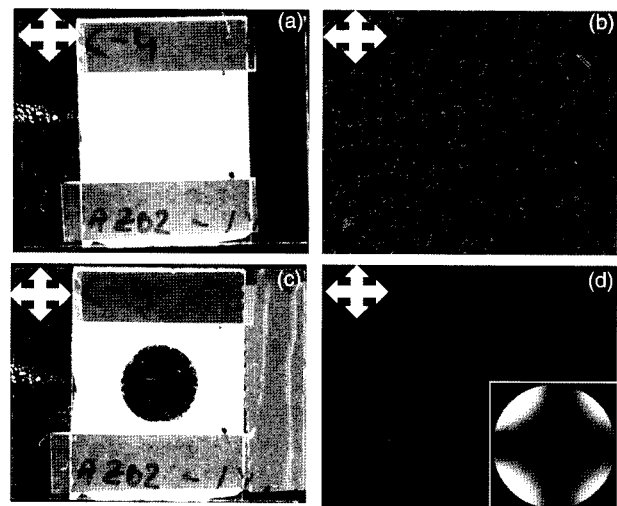


Figure 4. (a) and (c) shows the depolarized macroscopic images of the cell before and after UV irradiation with a circular mask, respectively. (b) and (d) corresponds to the POM images of the cell before and after UV exposure, respectively. The exposed area in (b) and (d) clearly demonstrates the simultaneous-phase transition from chiral nematic to nematic, and the anchoring transition from the planar to the homeotropic state. The MLC 6608 with negative dielectric anisotropy was used.

of planar-aligned cholesteric LCs. The cell was exposed to UV light with 500 mW/cm^2 intensity for 30 min, at room temperature. During the UV treatment, a circular mask was applied to clarify the difference between the exposed and unexposed areas in the same cell. After 30-minute UV exposure, the exposed area exhibited a homeotropically anchored state of the nematic LCs, as seen in Figure 4(b). The POM image for the exposed area shown in Figure 4(d) confirms that the optic axis (i.e. director) of the non-chiral nematic LC aligns normally to the surface. Although a planar-anchored chiral nematic state (i.e. cholesteric planar texture) was observed before the UV treatment, no chiral texture was noticed after UV irradiation. In the UV-illuminated area, the surface was completely modified

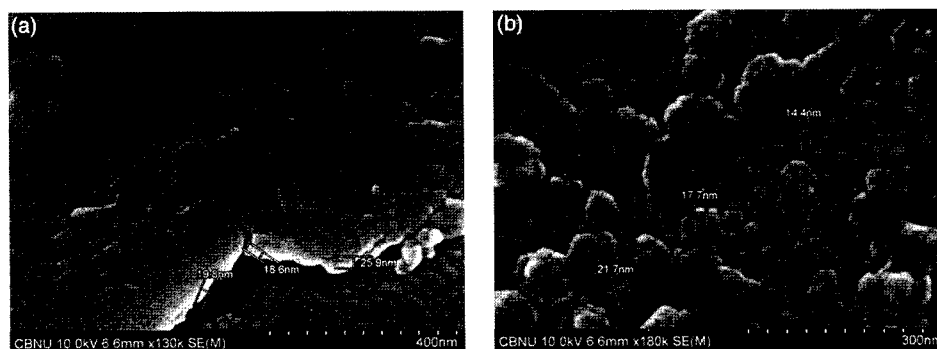


Figure 5. Figure 5(a) and 5(b) displays the FESEM images of the modified surface. (a) Shows a uniformly thin layer on the ITO surface, and (b) shows the fine structure of the layer at a higher magnification.

to give an anchoring transition from the planar to the homeotropic state.

To examine the stability of the surface anchoring condition, the cell was kept at 100°C for 3 h. No change in the anchoring condition was noticed. In addition, the cell was dipped in pure hexane for several hours to remove the LC. After the complete drying of the cell, it was refilled with a pristine nematic LC host without adding any chiral dopant. The exposed area maintained a homeotropic anchoring state, indicating that the surface modification was stable against heat and solvent treatments.

To examine the modified surface for homeotropic anchoring, the host LC was selectively removed again in the excess amount of hexane. The bare surfaces were explored via FESEM. A uniformly thin layer with an approximately 20 nm thickness was observed on the ITO surface throughout exposed area while the bare ITO surface was seen in the masked area. Figure 5(a) shows the thin layer on the ITO surface. The right bottom portion of the image corresponds to the ITO surface. The layer was found to be composed of fine beads a few tens of nanometers in size. These beads were closely packed, as shown in Figure 5(b). It is evident that the thin layer composed of fine particles was responsible for the anchoring transition observed during UV irradiation.

Based on the experiment results, it is obvious that the concurring phase and anchoring transitions are closely related to the thin layer observed on the FESEM images. To elucidate the source and process of forming a thin surface layer, UV–VIS absorption studies of the dye solution in chloroform were performed as a function of the UV irradiation time. Azobenzene compounds have two photochromic states of geometric isomers: the *trans* isomer, which is thermodynamically more stable, and the *cis* isomer. Once an azobenzene molecule in its more stable *trans* state is exposed to UV light, the molecule changes its configuration to the *cis* state. In general, the *cis* state is relaxed back to the thermodynamically more stable *trans* state through either the photochromic pathway under visible-light illumination or the thermal pathway in the ambient or elevated temperature. The relaxation time may vary from

microseconds to the order of minutes. In addition, another important fact is that the *cis* isomer has a significantly higher dipole moment than the *trans* isomer due to the broken chromophore asymmetry.

In the case of the chiral azobenzene molecule, it was dissolved in chloroform, and spectra were taken before and right after UV irradiation as a function of the irradiation time. Once the spectrum was taken from a freshly prepared solution, the solution was exposed to UV light for 5 min. Right after the UV exposure, the *trans* absorption peak decreased considerably, and an increase in the *cis* absorption peak was also observed, as shown in Figure 6(a). The solution was kept at ambient indoor light, and spectra were taken with regular time intervals. Complete recovery of the *trans* absorption peak was observed after around 180 min, as clearly seen in Figure 6(a). In the second solution, the fresh sample was exposed to UV light for 30 min. Similar spectral changes were observed before and right after UV irradiation, as seen in the first sample with 5-minute exposure. In the second sample, however, the *cis* absorption peak retained its magnitude for a longer period of time. Even after 15 h, no recovery of the *trans* absorption state was observed. In addition, the strong peak at 290 nm, which appeared after UV exposure, also maintained its absorption intensity. The peak at 290 nm indicates the formation of *cis*-form crystalline aggregates [9]. Figure 6(a) and 6(b) shows the clear difference in stability of the *cis*-form crystalline aggregates. It seems that the *cis*-form crystal was formed for both the 5- and 30-minute exposure time. Their stability at the ambient condition, however, is critically different. It is interesting to note that the prolonged stability of the *cis*-form crystal in the second sample may indicate the nucleation and growth process of the particle formation and the existence of a critical size (i.e. activation energy) for continued growth.

When a solution is exposed to UV light, it reaches a photostationary state with *trans*- and *cis*-form isomers. The increased population of *cis* isomers and their strong dipole–dipole interaction promote the formation of *cis*-form crystalline aggregates. Consequently, the insoluble aggregates are phase-separated from the LC host. Only

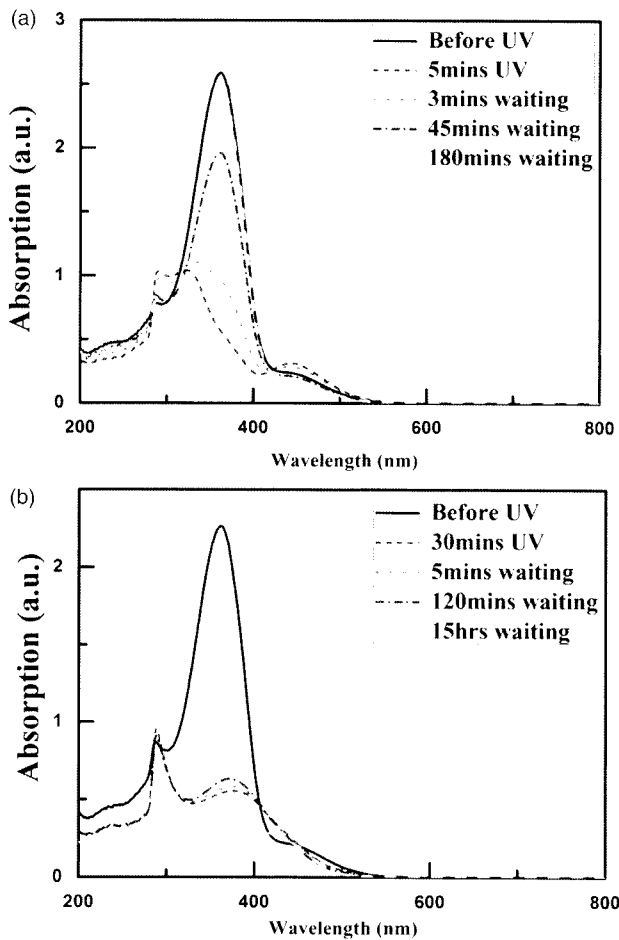


Figure 6. (a) Corresponds to the UV–VIS spectra of the azodye solution in chloroform before and after UV irradiation for 5 min, and its relaxation back to its initial *trans* state. (b) Shows the UV–VIS spectra of the same solution before and after UV irradiation for 30 min, and no recovery of its initial *trans* state even after 15 h of waiting. For both cases, the sharp peak at 290 nm indicates the formation of crystalline *cis*-form aggregates of the azodye.

aggregates larger than the critical value, however, continue to grow and become stable against *cis* to *trans* isomerization. Others below the critical size redissolve in solvent and stay in a photostationary state during UV irradiation. As a result, the particles grow to a size beyond the critical value for a prolonged UV exposure time, and become stable, while the smaller particles continuously vanish and relax back to the *trans* state for a short period of UV irradiation.

The stable particles phase-separated from the LC host diffuse toward the ITO–LC interface, are adsorbed by the interfacial tension, and continue to pack together at the interface. This is the origin of the formation of a thin azodye layer composed of spherical *cis*-form crystals and strongly adhered to the ITO surface. The adsorption of dye aggregates is analogous to the *Pickering effect* [12] on the interfacial adsorption of nanoparticles. The phase separation, interfacial adsorption, and interfacial packing

ultimately lead to surface modification, as shown in Figures 3 and 5, for the anchoring transition from a planar to a homeotropic alignment of LC molecules on the surface [9].

The phase transition from chiral to achiral nematic phase induced by the phase separation of the chiral azodye, and the anchoring transition from the planar to the homeotropic alignment of the LCs caused by the surface modification, simultaneously proceed due to the photo-stimulated *trans* to *cis* isomerization upon UV irradiation. The stability and irreversibility of the transitions depend on the undergoing process affected by the duration and intensity of UV irradiation.

4. Conclusions

Demonstrated herein were the simultaneous-phase and anchoring transitions of chiral azodye-doped nematic LC triggered by UV irradiation. Once the mixture is exposed to UV light, the azodye changes its configuration from *trans* to *cis* isomer. The *cis*-form isomers, due to their enhanced dipole moment, interact with the other *cis*-form molecules and form small insoluble aggregates. These *cis*-form aggregates gradually get phase-separated from the host LC and get deposited at the interface, ultimately leading to a surface modification on the ITO surface. The surface modification leads to anchoring transition from planar to homeotropic because of the roughened surface of the modifying layer created by the *in situ* condition. The surface modification is stable against temperature and solvent treatments. The stability and irreversibility of the reported transition, and the fact that there was no surface pretreatment for LC alignment, provide a great potential for practical applications.

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Notes on contributors



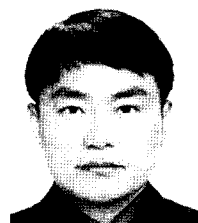
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