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# Photoinduced Phase Transitions in Chiral Binaphthyl-diol-doped Smectic Liquid Crystals by a Photochromic Azobenzene

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The liquid crystalline states of mixtures of smectic 4-octyl-4′-cyanobiphenyl, chiral binaphthyl-diol, and a photochromic azobenzene derivative, 4-*n*-hexyl-4′-(1-bromopropyloxy)azobenzene, are dependant on the chiral dopant and azobenzene concentrations. The trans-to-cis isomerization of azobenzene induces the phase transition from smectic to cholesteric and then to isotropic states.

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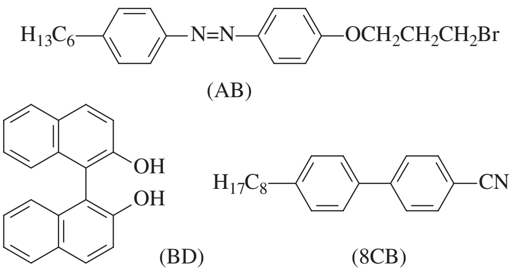
Photoinduced control of phase structures of liquid crystals (LCs) has received great attention for its extensive applications in optical memory, optical display, and optical switching.[1] Azobenzene chromophores are well-known photoresponsive molecules, which possess a unique photochromism between trans form with a rod-like shape and cis form with a bent shape. A small amount of azobenzene chromophores could be used as guest molecules to affect the structures and properties of host LCs, due to their trans-to-cis photoisomerization. The trans form stabilizes the phase structure of LCs, while the cis form tends to destabilize the phase structure of the mixture because of its bent shape.[2] The change in molecular shapes of azobenzene has been first studied to induce the nematic–isotropic transition in nematic LC systems by photoisomerization, where the change in the optical properties such as birefringence could be detected by the use of polarizers. Recently, much effort has been devoted to photoresponsive cholesteric liquid crystals (CLCs), which possess an inherent selective reflectivity, primarily for tunable reflectors and lasing elements. Three approaches have been examined for the azobenzene photochemical modulation of CLCs: 1) mixing azobenzene as a photoresponsive dopant with a CLC;[3] 2) mixing photoresponsive azobenzene nematic LCs with CLCs;[4] and 3) mixing photoresponsive chiral azobenzene derivatives with nematic LCs.[5] Here we report the effect of photoisomerization of azobenzene on the structures and properties of smectic LCs doped with a chiral molecule and an azobenzene derivative. The phase structures and transmittance (reflectivity) of the smectic LC mixtures could be controlled by photoirradiation.

The photoresponsive LC mixtures examined herein were formed by mixing a homemade azobenzene derivative and a chiral molecule with a smectic LC host. The corresponding chemical structures of the materials used are shown in Scheme 1. The photoresponsive 4-*n*-hexyl-4′-(1-bromopropyloxy)azobenzene (AB) was synthesized by Williamson ether synthesis of 4-(4-*n*-hexylphenylazo)phenol, which was obtained by azo coupling.[6] (*S*)-(−)-1,1′-Binaphthyl-2,2′-diol (BD) and 4-octyl-4′-cyanobiphenyl (8CB) are commercial compounds. 8CB is a smectic LC around room temperature (28 °C Sm 37 °C N 44 °C I). All the experiments were carried out at room temperature using a sandwich cell (thickness: ca. 5 µm) coated with rubbed poly(vinyl alcohol).



**Scheme 1.**

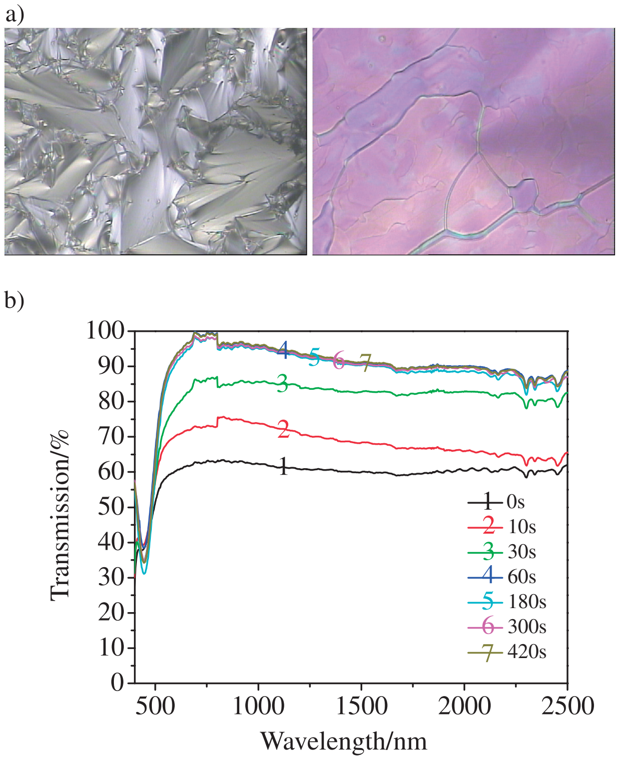


**Figure 1.** a) Polarized optical micrographs of the 8CB mixture containing 1% BD and 3% AB before (left image) and after UV irradiation for 60 s (right image). Magnification: 400. b) Transmission spectra of the 8CB mixture during UV irradiation of the cell.

The 8CB mixtures doped with photoresponsive AB and chiral BD exhibit a smectic A phase when the chiral BD concentration is as low as 1 wt %. Figure 1a shows the polarized optical micrographs (POMs) of the 8CB mixture containing 1% BD and 3% AB before and after UV irradiation (365 nm, 10 mW cm$^{-2}$). First, the smectic A phase could be observed before UV irradiation where the azobenzene was in trans form; after UV irradiation the azobenzene became cis form and the mixture was induced to exhibit a cholesteric phase. Although the azobenzene could be isomerized completely to its cis form, measured by its UV–vis absorbent spectra,[7] the isomerization could not proceed from cholesteric to isotropic, as could be ascribed to the low concentration of the azobenzene. To confirm this, the amount of AB was increased to 5% or more, and then the cholesteric to isotropic transition was observed during photoirradiation. The smectic A phase of the mixture could be recovered after the sample was kept in the dark for 12 h. The photoinduced phase transition from smectic to cholesteric and then to isotropic in the LC mixtures is brought out by the photoisomerization. It has been proven that the photoinduced phase instabilities in smectic A LCs were due to the photoisomerization, and a subsequent increase in the smectic layer spacing was observed.[8] The trans form of the azobenzene, which possesses a rod-like shape, stabilizes the smectic LC phase. After UV irradiation, the trans form is converted to cis form, which possesses a bent shape and decreases the order of the LC. The cis form induces the phase transition from smectic to nematic and then to isotropic when the amount of azobenzene is sufficient in the 8CB mixtures. The doped chiral BD converts the photoinduced nematic structure to cholesteric, as it is well-known that nematic LC mixing with chiral molecules can exhibit cholesteric structure. So the smectic 8CB LC doped with chiral BD and photoresponsive AB exhibited phase transition from smectic to cholesteric and then to isotropic after UV irradiation. The spectral properties during UV irradiation of the mixture of 1% BD and 3% AB in 8CB are shown in Figure 1b. The transmission increased with the increase of the irradiation time until it was saturated when all the trans isomers were converted to the cis. Combining the phase transition of the mixture revealed by POM, it can be concluded that the cholesteric phase exhibited higher transmittance than that of the smectic. Yet no selective reflectivity was found in this mixture doped with 1% chiral BD, as could be caused by the low helical twisting power at the low concentration of the chiral BD.

To investigate the effect of photoisomerization of AB on the smectic 8CB mixture doped with high concentration of the chiral BD, we prepared a sample of 8CB containing 3% BD and 5% AB. This mixture with high concentration of chiral molecules exhibited cholesteric phase at room temperature instead of the smectic shown at low concentration of chiral BD. After UV irradiation, the trans isomer of AB in this mixture was converted to the cis, and the cholesteric phase was induced to isotropic. Figure 2 shows the transmission spectra of the mixture during UV irradiation. The reflectivity of the mixture decreased, and the reflection notch was red-shifted a little from 1904 to 1906 and then to 1908 nm when UV irradiating for 0, 10, and 30 s. The reflection disappeared when irradiating for 60 s. After irradiating for 180 s where the cholesteric phase was completely induced to the isotropic revealed by POM, no reflection was found and the transmission was increased. White, Bunning, et al. reported that an azobenzene-based chiral molecule could phototune the reflection notch around 2000 nm.[5d] Thus the structure of photoresponsive azobenzene doped plays a great role in phototuning the properties of the cholesteric LCs.

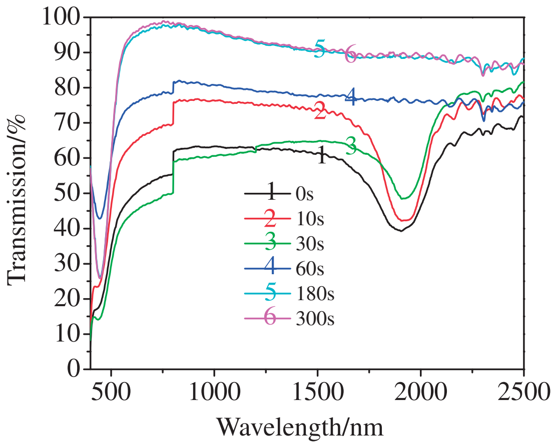


**Figure 2.** Transmission spectra of the 8CB mixture containing 3% BD and 5% AB during UV irradiation of the cell.

In summary, we have demonstrated that the structures and properties of smectic LCs could be phototuned by doping with photoresponsive azobenzene and chiral molecules. The photoinduced phase transition from smectic to cholesteric and then to isotropic is dependent on the concentration of the dopants. By adjusting the amount of the dopants in 8CB, a selective reflection could be controlled by photoirradiation.

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