

Preparation of Composites of Polymer Liquid Crystal/Cholesteric Liquid Crystal and Their Photochemical Switching and Memory Properties by Photoisomerization of a Chiral Azobenzene Molecule

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ABSTRACT: A chiral azobenzene compound was synthesized, and mixing the chiral azobenzene compound in a host nematic liquid crystal (LC) induced a cholesteric phase. The twisting power of the *trans*-form of the chiral azobenzene compound was larger than that of its *cis*-form produced by ultraviolet irradiation. A low molecular weight compensated nematic LC was then prepared by mixing of the chiral azobenzene and a nonphotochromic chiral compound, thus giving mutual opposite helical sense in the host LC. Reversible optical switching between transparent and opaque was

achieved by ultraviolet and visible light irradiation. However, the photochemically switched opaque state was not stable even in the dark. Stability of the opaque state was found to be improved by adding polymer LC to the low molecular weight compensated nematic LC. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2577–2580, 2004

Key words: azobenzene; chiral; composites; photoisomerization; cholesteric liquid crystal (LC)

Cholesteric liquid crystals (Ch LCs) have a helical structure and show a selective reflection of light with wavelength proportional to the helical pitch. By photochemically modulating the helical pitch, Ch LCs would make promising materials for various optical devices such as photoaddressable display, photocontrollable light reflector, memory, and so on. Thus, there are many studies on the photochemical control of the helical structure of Ch LCs by means of photoisomerization of azobenzenes,^{1–4} menthone,^{5,6} spiropyrans,⁷ flugides,⁸ and others.⁹ We also reported the photochemical control of the helical structure of LC mixtures that were prepared by adding a chiral azobenzene compound and a nonphotochromic compound with an opposite twisting ability in a host low molecular weight LC, and demonstrated (1) photochemical control of helical pitch in any direction to longer or shorter, (2) photochemical phase transition between a compensated nematic phase and a Ch phase, and (3) photochemical inversion of the helical structure by means of a *trans*–*cis* photoisomerization of the chiral azobenzene compound.¹⁰ In this study, we achieved a photochemical switching between

transparent and opaque, which is based on the photochemical phase transition between the compensated nematic and the Ch phases. However, the opaque state was not stable in the dark because of a *cis*–*trans* thermal back isomerization of the chiral azobenzene compound.

On the other hand, a glassy state of polymers and glass-forming materials, or higher viscosity of polymers, is known to hold an anisotropic molecular orientation of LC systems.^{5,11} Therefore, to improve the stability of photochemically switched opaque state, composites consisting of low molecular weight compensated nematic LC and polymer LC were prepared, and their photochemical switching behaviors were investigated.

It is well known that a Ch structure can be induced by adding a nonmesogenic chiral compound to a nonchiral LC. In this study, a chiral azobenzene, **Azo** (Fig. 1), was used to give the Ch structure by addition to a low molecular weight LC, **E44** (purchased from Merck Co., Darmstadt, Germany). In such a binary system, consisting of a nonchiral host nematic LC and a chiral compound, the reciprocal of helical pitch ($1/p$) is increased linearly with concentration (c) of the chiral compound at lower c , and the slope of the $1/p$ versus c is the twisting power of the chiral compound. The twisting power of **Azo** for **E44** was $23 \times 10^2 \mu\text{m}^{-1} \text{mol}^{-1} \text{g}$ **E44** at 40°C. The helical pitch induced with **Azo** was increased and decreased by ultraviolet (UV,

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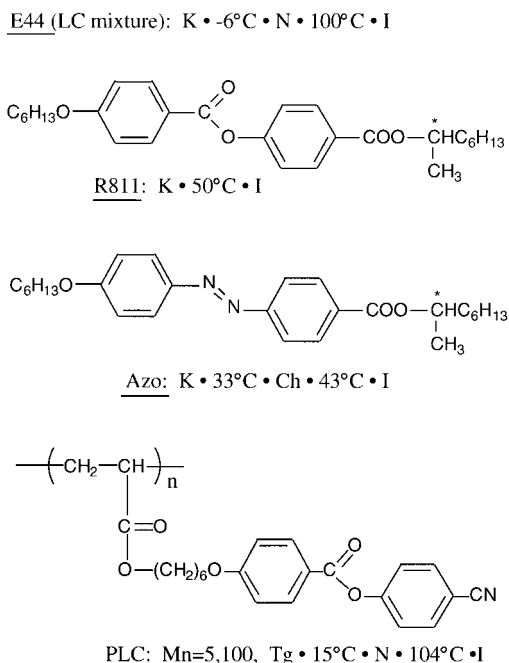


Figure 1 Materials used in this study.

366 nm) and visible (vis, 433 nm) light irradiation, respectively, as shown in Figure 2. A *trans*-Azo isomerizes to a *cis*-Azo by UV irradiation, and the *cis*-Azo can return to the *trans*-Azo by vis irradiation photochemically, or thermally even in the dark. That is, the result given in Figure 2 means that the twisting power of the *trans*-Azo is greater than that of the *cis*-Azo.

The helical structure induced by doping Azo in E44 was a left-handed helix.¹⁰ Thus, a compensated nematic phase can be obtained by adding R811 (Merck) to the induced Ch LC, consisting of Azo and

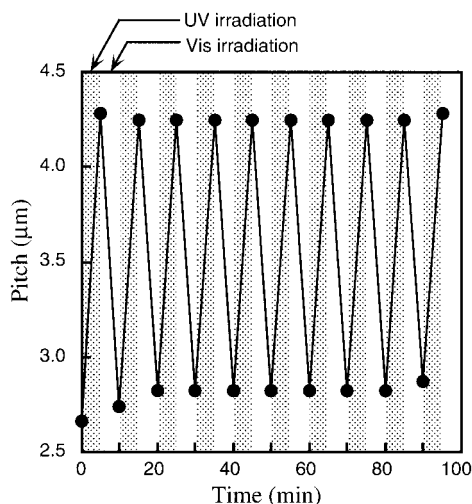


Figure 2 Reversible change in the helical pitch of E44/Azo (95 : 5 wt %) mixture by UV and vis light irradiation at 30°C.

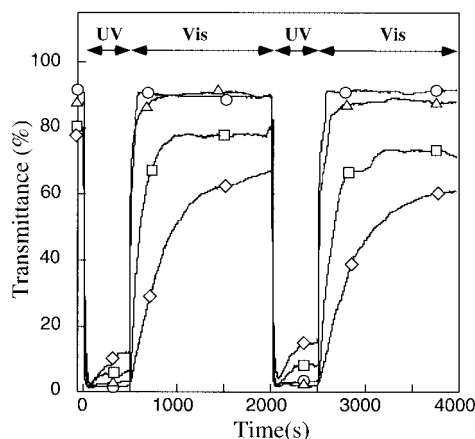


Figure 3 Changes in the transmittance of the (E44/PLC)/(R811/Azo) mixtures in a 15- μ m homogeneous glass cell by UV and vis irradiation at 30°C. The content of (E44/PLC)/(R811/Azo) was 80 : 20 wt %, where the ratio of R811:Azo was kept at 43 : 57 wt %, and that of E44:PLC was varied as 100 : 0 (—○—), 90 : 10 (—△—), 80 : 20 (—□—), and 70 : 30 (—◇—) wt %.

E44 at a ratio of R811 : Azo = 43 : 57 wt %, because R811 gives a right-handed helical structure.¹⁰ A low molecular weight compensated nematic LC, E44/(R811/Azo), having the ratio of E44 to (R811/Azo) of 80 : 20 wt %, was prepared and charged to a 15- μ m homogeneous glass cell. The compensated nematic LC mixture in the cell was found to show photochemical switching between transparent and opaque by UV and vis irradiation, as shown in Figure 3. The transmitted light intensity from a diode laser (670 nm) was measured under UV and vis irradiation. The LC sample was transparent before UV irradiation, attributed to a uniaxial molecular orientation [Fig. 4(a)], then was transformed to a focal conic structure under UV irradiation [Fig. 4(b)]. The twisting power of the *trans*-Azo was higher than that of its *cis*-Azo produced by UV irradiation, as can be seen in Figure 2. Consequently, the lower twisting power of the *cis*-Azo caused the breaking of the compensated state, and resulted in the appearance of the Ch phase that robustly scattered light. However, the opaque state was not stable, even in the dark, because of the *cis*-*trans* thermal back isomerization.

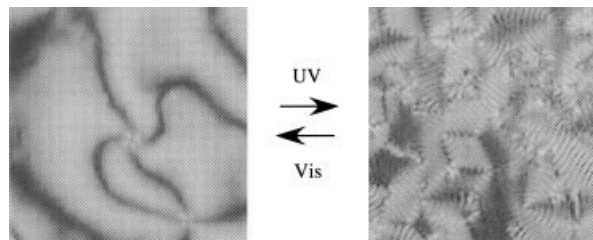


Figure 4 Micrographs of the compensated nematic phase (left) and the cholesteric phase (right).

Next, three composites of the low molecular weight compensated nematic LC and polymer LC (PLC) were prepared: (E44/PLC)/(R811/Azo). A ratio of (E44/PLC) to (R811/Azo) was maintained at 80 : 20 wt % for all composites, where R811 : Azo was 43 : 57 wt %, as described above, and the ratio of E44 to PLC was varied at 90 : 10, 80 : 20, and 70 : 30 wt %. Figure 3 shows the photochemical switching behavior of the composites in a 15- μm homogeneous cell by UV and vis irradiation at 30°C. All composites exhibited an almost similar decrease in the transmittance to the E44/(R811/Azo) compensated nematic LC without PLC. Contrary to the decrease in the transmittance, a recovery of transparency by vis irradiation became slow with increasing content of PLC. The glass-transition temperature (T_g) of PLC was found to be 15°C, measured by means of differential scanning calorimetry (DSC), whereas the T_g value of the prepared composites could not be determined by DSC. It has been reported that the melting point of E44 is -6°C, and E44 exists in the nematic phase up to 100°C.¹² It can be assumed, therefore, that E44 acts as a plasticizer for PLC in the composites, and the T_g of composites consequently becomes <15°C. On the other hand, the viscosity of the composites increased with the increase of PLC content of the composites. The slow switching rate from opaque to transparent under vis irradiation may be brought about by the increase in the viscosity of the composites, rather than by the freezing effect in the molecular orientation below T_g .

Stability of the switched opaque state of the composites is shown in Figure 5 at 30 and 0°C. Thermal recovery of the transmittance of the composites was examined as a function of time in the dark after UV irradiation. At 30°C, the E44/(R811/Azo) compensated nematic LC without PLC returned to the transparent state after 10 h in the dark, whereas the time required for the composite (E44 : PLC = 70 : 30 wt %) was >15 h, as can be seen in Figure 5(a); that is, the stability of the opaque state can be improved by an increase in the PLC content in the composites, but was not sufficient. The result given in Figure 5(b) indicates a notable temperature influence on the stability of the opaque state produced photochemically. The time required for the thermal recovery of the transparency was substantially prolonged by decreasing temperature, and consequently little change was observed for the composite (E44 : PLC = 70 : 30 wt %), even after >70 h at 0°C. The improvement in the stability may be closely related to the motion and fluidity of the mesogenic molecules in the composites. Because the T_g values of the composites could not be determined, we cannot discuss the improvement in terms of T_g of the composites. However, it is likely that the increase in the viscosity of the composites contributes to improvement of the stability of the switched opaque state.

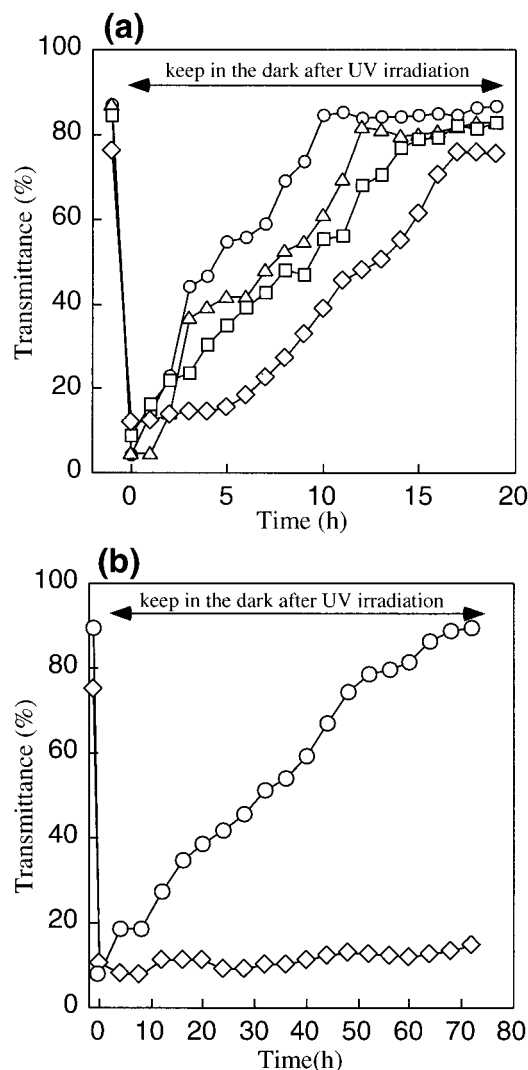


Figure 5 Changes in the transmittance of the (E44/PLC)/(R811/Azo) mixtures in a 15-mm homogeneous glass cell after UV irradiation as a function of time in the dark at 30°C (a) and 0°C (b). The components and symbols are identical to those in Figure 3.

In this study, we were able to achieve a memory property on the photochemical switching between transparent and opaque states. However, the composites required cooling for the stable opaque state in the dark because the T_g of PLC is lower than the ambient temperature. It may be expected that the use of polymer LCs with higher T_g will provide more stable memory property of the switched opaque state at a higher temperature. Further studies are now in progress.

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