Photo-Controllable and Fixative Optical Properties of Non-polymeric Liquid Crystals with Azobenzene Chromophore

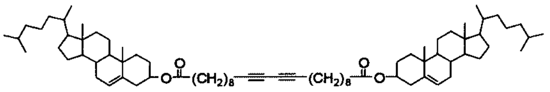
Masaya Moriyama[†,††] and Nobuyuki Tamaoki*[†]
[†]National Institute of Advanced Industrial Science and Technology (AIST), Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565
[††]Japan Science and Technology Corporation (JST), 4-1-8 Honmachi, Kawaguchi, Saitama 332-0012

(Received July 19, 2001; CL-010677)

A new series of non-polymer photochromic liquid crystalline compounds which form glassy solids maintaining the liquid crystalline molecular alignment has been synthesized; their optical properties such as cholesteric reflections, controlled by the intramolecular photoreaction and temperature, can be utilized for the construction of information-storing materials.

The photochromic reaction in liquid crystals (LCs) is one of the effective stimuli inducing modification of the LC optical properties. For example, photochromic reactions in cholesteric liquid crystals (CLCs) can induce changes in the cholesteric iridescent reflections (reflected colors) due to the helical molecular alignment.[1,2] Since the molecular alignment of the CLC is dependent on the molecular composition, the photochromic reactions transforming the molecular structure can change the cholesteric reflection. This photo-induced modification can be utilized for color optical information recordings. Meanwhile, compounds showing the glassy solid state in LC phases have advantages of stable information-storage compared to those with just a normal LC phase having fluidity. In general, polymeric LC materials can easily form glassy solids that maintain the LC molecular alignment, though they are inferior to low molecular weight materials in their response time to stimuli.

Recently, it was reported that dicholesteryl compounds with ca. 1000 molecular weight such as **1** have properties showing a CLC phase with good response to stimuli and forming a stable glassy solid that maintains the cholesteric helical alignment of the molecules.[3] The mixtures of these kinds of CLC compounds and photochromic compounds can be effective materials for color information recordings.[2]



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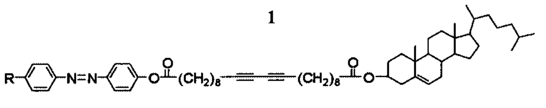
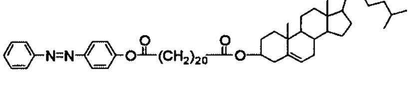


2 (R = H), **3** (R = C_7H_{15})



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In this study, photochromic, non-polymeric and glass-forming LC compounds, **2**, **3** and **4**, consisting of a cholesteryl group and an azobenzene moiety connected with a long flexible aliphatic spacer, were prepared and their properties were studied. Although analogous compounds, whose central parts are shorter, have been extensively investigated from the viewpoint of sol–gel formations,[4] nonlinear optics[5] and photoswitching dopants,[1i] the study on the glass-forming LC analogues has never been reported. Additionally, the repetitive photo-control and storage of cholesteric iridescent reflections of single-component materials (not mixtures) have been first achieved in this study.

These materials were obtained by esterification of the corresponding dicarboxylic acids with cholesterol and the corresponding hydroxyazobenzenes. Compounds **2** and **4** showed CLC phases with iridescent reflection in themselves, and **3** showed only a smectic phase with no iridescent reflection. All the materials formed glassy solids which maintained the LC structure by rapid cooling from the LC phase. Their phase transition temperature observed by DSC measurements (±2 °C min^{-1} rate of temperature) and λ_{max} of the cholesteric reflection band are summarized in Table 1. For cholesterics **2** and **4**, the λ_{max} shifted to a small value with an increase in the temperature ($d\lambda_{max}/dT<0$). The reflection region of **2** having a diyne unit was wider than that of **4** having a long *n*-alkyl chain. Azobenzenes substituted at the 4,4' positions with appropriate alkyl chains show a smectic phase,[6] accordingly, it is reasonable that **3** shows a smectic phase. The glass transition temperature of all compounds is 30–45 °C.

Table 1. Phase transition temperatures and λ_{max} of cholesteric reflection of the photochromic LC compounds

Compound	Phase transition Temperature/°C[a]	λ_{max}/nm (Temperature/°C)
2	Cr 70 Sm 76 Ch 82 I	696(50), 595(60)
	I 80 Ch and Sm 36[b] Cr	514(70), 463(80)
3	Cr 90 Sm 114 I	-
	I 111 Sm 31 Cr	
4	Cr 97 Ch 104 I	533(88), 515(90)
	I 101 Ch 81 Cr	485(95), 457(100)

[a]I: isotropic phase, Ch: cholesteric phase, Sm: smectic phase, Cr: crystal. [b]A broad signal was observed. Ch–Sm and Sm–Cr transitions could not be separated.

Upon irradiation at 366 nm, which induced *E/Z* isomerization of the azobenzene units, the λ_{max} of the cholesteric reflections of **2** and **4** shifted to a shorter wavelength as shown in Figure 1.[7] The *Z* isomer would cause disorder in the cholesteric molecular arrangement, with the result that the λ_{max} shifted to a disorder sense which is the same as the thermally disordered sense of the CLC compounds.[1g] In this case, because the thermal behavior of **2** and **4** shows $d\lambda_{max}/dT<0$, λ_{max} shifts to a small value. The cholesteric reflections including the changed ones due to the photoisomerization were fixed in the glassy solid obtained by the rapid cooling from the CLC phase. The fixed reflection did not change upon irradiation of the glassy solid state. Due to the rigidity of the glassy solid matrix, the molecular alignment would not be disturbed by the isomeriza-

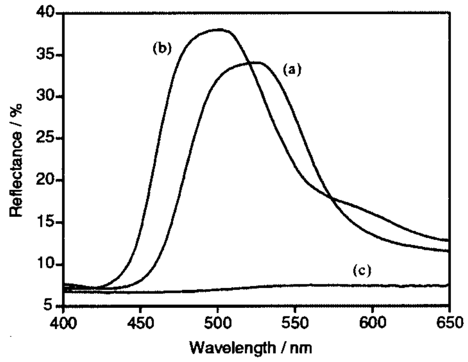
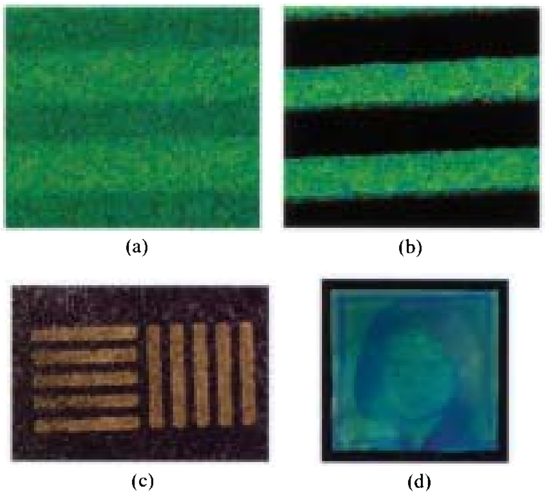


Figure 1. Reflection spectra of the films of **2** obtained by dipping the samples in ice water before and after irradiation at 70 °C. (a) Before irradiation. (b) After irradiation with 366-nm light for 10 s. (c) After irradiation for 30 s.

tion of the azobenzenes. However, raising the temperature above the isotropic one induced *Z/E* thermal back isomerization and the CLC alignment returned to its initial state. Meanwhile, prolonged irradiation induced a phase transition from the cholesteric to isotropic phase. The cooling from the isotropic phase produced crystals which showed no reflection but optical light scattering (Figure 1(c) and Figure 2(b)). For the smectic LC compound **3**, although the difference in the reflection could not be produced, switching of light transmission was possible. As compound **3** spontaneously aligned homeotropically, the transparent and colorless films could be prepared. In the films, the *E/Z* photoisomerization induced a phase transition from the homeotropic smectic to the isotropic phase and a contrast formed and was fixed after rapid cooling (Figure 2(c)).


(a) (b)

(c) (d)

Figure 2. (a) Microscopic image (reflection mode) of the solid film of **2** obtained after irradiation for 10 s at 70 °C through a photomask. Green area is not irradiated. (b) Microscopic image (reflection mode) of the solid film of **2** obtained after irradiation for 30 s at 70 °C through a photomask. The non-irradiated green area maintained the cholesteric structure. As the black area irradiated is a crystal, no reflection is observed (c) Microscopic image (transmission mode and cross polarized) of the solid films of **3** obtained after irradiation for 30 s at 90 °C through a photomask. The black area is not-irradiated and has a homeotropic molecular alignment. Irradiated orange area is crystalline. (d) Displayed image prepared by annealing the cholesteric films of **2** to 73 °C after irradiation in glassy solid state (r.t.) through a photomask.

On the other hand, although the series of **1** show a monotropic CLC phase only during the cooling process, **2**, **3** and **4** show an enantiotropic LC phase. Hence, we demonstrated the latent image recording based on the *E/Z* isomerization of the azobenzenes in the glassy solid states. Temperature is regarded as a “gate” for transmission of the information written by the photoisomerization. When the gate is opened by heating, the photochromic dopants direct the surrounding liquid crystalline molecules to realign. Upon irradiation (λ = 366 nm) of the glassy solid films through a photomask at room temperature, no change occurs in the reflected color because *E/Z* isomerization of the azobenzene in the rigid glass cannot affect the molecular alignment. However, the latent image is certainly drawn in the glassy solid by the *E/Z* isomerization of the azobenzene. When the films are then put on the hot stage controlled at the cholesteric temperature, the latent image is quickly displayed (within a few seconds). Furthermore, the displayed image is fixed in the glassy solid by subsequent rapid cooling. Figure 2(d) shows a photograph prepared actually. A similar method can be used for polymer CLCs, but the display speed is slower after annealing, because the realignment rate of the polymer molecules is slow.[1d] For the image recording application, this method using **2**, **3**, and **4** would have an advantage in saving energy at drawing and display of the image.

In summary, we prepared a new series of photochromic LC compounds which formed the glassy solids maintaining the LC molecular alignment although they were non-polymeric materials. Their macroscopic optical properties based on molecular alignment were changed and fixed by the control of photochromic reaction and temperature. The controllable optical properties can be utilized for energy-saving information recordings.

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7 Upon UV irradiation even at 254 nm, diyne compounds **2** and **3** did not topochemically polymerize in the crystalline state. Therefore, the photo-controllable and fixative optical properties of **2** and **3** are not attributed to the topochmical polymerization.