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Color Tunable Novel Amphotropic Liquid Crystalline Acrylate End-capped with a Cholesteryl Group

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We report a novel, monomeric, lyotropic, cholesteric liquid crystal revealing selective reflection in the visible light region and having photochromic properties in the lyotropic liquid crystal phase. Monomer (+)-cholesteryl (6-acryloyloxyhexyloxy)-4-cinnamate was synthesized. Liquid crystal phases of M1 were identified using polarized optical microscopic and X-ray diffraction methods. Reflection light spectra were analyzed using an optical fiber system.

Liquid crystals are partially ordered, anisotropic fluids that are thermodynamically located between solid-state crystals with three-dimensional order and isotropic liquids. Liquid crystalline materials are generally divided into thermotropic and lyotropic categories. The former mesophases, originating from their own inherent molecular skeletons, are formed in response to a change in temperature, while the latter mesophases form in the presence of a suitable (isotropic) solvent. Some mesogens exhibiting both thermotropic and lyotropic phases are called amphotropic.[1]

Lyotropic liquid crystals can be classified into three subgroups on the basis of the nature of component molecules: amphiphilic, chromonic, and polymeric lyotropic liquid crystals.[2] Unlike amphiphilic compounds such as ionic and nonionic surfactants, which consist of a hydrophilic head and a lipophilic tail, chromonic lyotropic liquid crystals are formed in highly concentrated aqueous solutions of water-soluble, disk-shaped, polyaromatic molecules with hydrophilic substituents. Polymers with a relatively rigid backbone in a planar or helical conformation and with relatively flexible side groups attached to the main chains show the greatest potential to develop lyotropic liquid crystal phases.[3]

In recent years, interest in cholesteric liquid crystals has increased considerably as a result of their unique optical properties, namely, large optical rotation and selective light reflection, which are caused by the helical structure of the cholesteric mesophase. The selective reflection wavelength (λ), based on the pitch length of the helical structure for normal incident light, is given by $\lambda = np$, where n indicates the average refractive index, and p is the helical pitch length. The selective reflection wavelength can be altered by adjusting the helical pitch length under the action of various external factors such as temperature, electrical fields, or mechanical stress. Hence, cholesteric liquid crystalline materials have found many applications in twisted nematic displays, thermography, linear and nonlinear optics, sensors, and in novel electro- and magnetooptic devices and detectors.[4]

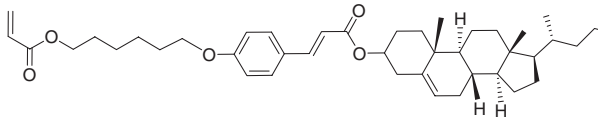
The cholesteric mesophase is usually exhibited by chiral calamitic molecules, mixtures of calamitic compounds with chiral dopants, and cholesteryl derivatives that also form thermotropic liquid crystals. However, lyotropic cholesteric systems are less common and are based on cellulose derivatives, polyamides, polyisocyanates, polycarbodiimides, or polyglutamates. Thus far, only a few attempts have been made to produce lyotropic cholesteric liquid crystals with selective reflection in the visible light region.[5] To our knowledge, this work is the first report of a small molecular system of lyotropic cholesteric liquid crystals revealing selective reflection in the visible light region and of photochromic properties in lyotropic liquid crystals in general.

In this paper, a novel monomeric (+)-cholesteryl (6-acryloyloxyhexyloxy)-4-cinnamate (M1) with a photochromic cinnamoyl functional group was synthesized, and the amphotropic properties of the monomer were investigated. The pure monomer M1 exhibited a thermotropic cholesteric liquid crystal phase, with a phase transition temperature of K 74 Ch 84 I. Dissolving this monomeric liquid crystal in the isotropic solvent dichloromethane (CH_2Cl_2) led to the formation of a lyotropic liquid crystal phase. Interestingly, the lyotropic liquid crystal cell revealed significant selective light reflection in the visible region.

The molecular structure of the synthesized novel monomer (M1) is shown in Scheme 1, where compound **1** was synthesized by following procedures described in our previous report.[6] Compound **1** (8 g, 0.025 mol), cholesterol (10.7 g, 0.028 mol), and DMAP (0.61 g, 0.005 mol) were dissolved in 50 mL of CH_2Cl_2. DCC (6.23 g, 0.03 mol) dissolved in 25 mL of CH_2Cl_2 was added to the mixture then was stirred for 48 h at 30 °C. The resulting solution was filtered and the precipitated urea was removed, washed twice with 0.5 M HCl and then with saturated aqueous $NaHCO_3$ solution, evaporated, and dried in vacuum. The crude product was purified using column chromatography (silica gel, ethyl acetate/hexane = 1/2) and then recrystallized from the mixture of ethyl acetate/hexane (1/2). White crystals of M1 were obtained. Yield: 72.3%. FT-IR (KBr, ν_{max}/cm^{-1}): 2943, 2865 (CH_2, CH_3), 1716 (C=O in Ar–COO–), 1600, 1510 (C–C in Ar), 1253, 1167 (COC), 1634 (C=C), 981 (=C–H).

^{1}H NMR: ($CDCl_3$, δ): 0.69 (m, 3H, CH_3), 0.85–1.04 (m, 12H, CH_3), 1.10–2.40 (m, 36H, CH_2), 3.97–4.19 (t, 4H, OCH_2), 4.74–4.75 (m, 1H, $OCHCH_2$ in Chol.), 5.40 (t, 1H, $CHCH_2$ in Chol.), 5.80–5.83 (dd, 1H, CH_2=CH), 6.08–6.15 (dd, 1H, CH_2=CH), 6.26–6.30 (dd, 1H, CH=CH), 6.37–6.38 (dd, 1H, CH_2=CH), 6.86–6.89 (d, 2H, Ar–H), 7.26–7.44 (d, 2H, Ar–H), 7.60–7.64 (dd, 1H, CH=CH). Anal. Calcd for $C_{45}H_{66}O_5$: C, 78.67; H, 9.68%. Found: C, 78.62; H, 9.66%.

Phase transition temperature and liquid crystal phases of chiral monomer M1 were identified using differential scanning



Scheme 1. Synthesis of chiral monomer M1.

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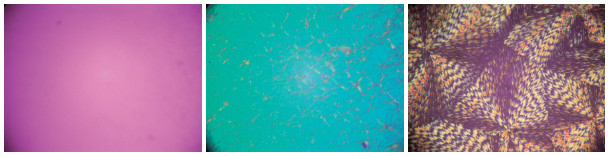

Figure 1. (a) Isotropic phase ($M1/CH_2Cl_2 = 30/70$), (b) plannar texture ($M1/CH_2Cl_2 = 60/40$), and (c) crystal phase of pure M1; POM textures were measured at room temperature.

calorimetry (DSC) and polarized optical microscopy (POM), respectively. Results of POM analysis show the M1 film displays a Grandjean texture under POM at 80 °C. This result suggests that M1 is a cholesteric liquid crystal. The colorful appearance of the M1 film at 80 °C is due to the selective reflection of the incident light. Furthermore, M1 was found to dissolve in both dichloromethane (CH_2Cl_2) and chloroform ($CHCl_3$). The optical properties of selective light reflection caused by the variation of solvent content were studied. Lyotropic liquid crystal phases of the mixtures of M1 and dichloromethane with various weight ratios were confirmed by POM. As seen in Figure 1, isotropic, lyotropic, and crystalline phases of the $M1/CH_2Cl_2$ mixture were confirmed. Figures 1a, 1b, and 1c show isotropic phase, typical planar texture of cholesteric liquid crystals, and spherulites of crystals, respectively. These results suggest self-assembly of M1 when dissolved in dichloromethane solvents at the proper weight ratio. A lyotropic phase was found to exist for $M1/CH_2Cl_2$ weight ratios between 55/45 and 70/30. Similar phenomena could be seen in the case of $M1/CHCl_3$ mixtures, although the exact weight ratios of $M1/CHCl_3$ were not investigated. In the case of the lyotropic liquid crystal phase formed with CH_2Cl_2, the characteristic reflection color revealed a blue shift from green to purple as the ratio of solvent to monomer was gradually decreased. These results suggest that reducing solvent ratios may change the arrangement of lyotropic liquid crystals and shorten the helical pitch, resulting in the observed blue shift. High ratios of CH_2Cl_2 to M1 may lead to the formation of an isotropic liquid phase.

From the calculated molar ratio of the lyotropic system, one M1 molecule is arranged in an ordered unit with 3–6 CH_2Cl_2 molecules. X-ray diffraction analysis (XRD) was used to investigate the molecular arrangement of these lyotropic liquid crystals. Figure 2a shows the representative XRD pattern for a lyotropic liquid crystal state with a weak board amorphous peak centered at about $2\theta = 17.5°$, corresponding to a lateral packing distance between mesogenic groups of approximately 5 Å. These results suggest the presence of two CH_2Cl_2 molecules between two Ml molecules, if we assume that the size of CH_2Cl_2 corresponds to the calculated value of 2.5 Å. As compared with the calculated lyotropic molar ratio, some solvent molecules may exist around the highly ordered $M1/CH_2Cl_2$ cluster, helping to preserve the helical structure of the cholesteric liquid crystal phase. In contrast, for pure M1 in a crystalline state, the appearance of sharp peaks in the low angle region corresponding to spherulites was observed from XRD patterns as shown in Figure 2b.

As seen in Scheme 1, the carbonyl groups and oxygen atoms in M1 may exhibit polarity and display a certain level of molecular interaction. In addition, π–π interaction between

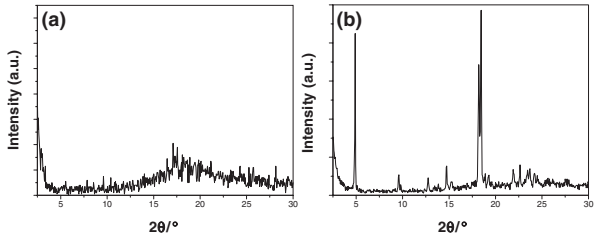

Figure 2. XRD patterns for (a) typical lyotropic liquid crystal state ($M1/CH_2Cl_2 = 60/40$) and (b) spherulites state (pure M1).

benzene rings and C=C bonds is expected as well. Finally, chiral effects from cholesteryl groups may exhibit some steric interaction. The effect of these intermolecular forces acting in concert is the formation of a thermotropic, cholesteric liquid crystal phase. It has been observed that, for small molecular systems, hydrogen bonding, hydrophilic–hydrophobic interactions, and ionic interactions could play important roles in the molecular assembly process required to form lyotropic liquid crystals.[2] In this study, the solvent effect on the development of a lyotropic liquid crystal phase may have been due to interactions of solvent molecules around the arranged $M1/CH_2Cl_2$ cluster through van der Waals or dipole–dipole interactions, forces that are partially analogous to the molecular interactions of thermotropic liquid crystals. The arrangement of suitable solvent molecules surrounding the M1 molecules might supply fluidity and maintain the necessary birefringence to obtain a lyotropic liquid crystal phase.

Temperature variation and UV irradiation of the lyotropic liquid crystal cell were also performed in order to investigate the effects of temperature and light on the helical pitches within the liquid crystal. Figure 3a shows the temperature dependence of selective light reflection for a sealed lyotropic liquid crystal cell containing a 60/40 (w/w) mixture of $M1/CH_2Cl_2$. As the temperature increased from 30 to 55 °C, the reflected light displayed a blue shift from a peak wavelength of approximately 575 to 470 nm. It was noteworthy that the temperature-induced variation was in the visible region and was completely reversible. These results suggest that temperature variations could change the arrangement of assembled molecules, thereby tuning the pitch of the helical structure. Theoretically, the central wavelength and reflection band of the reflection light could be calculated using following equations:

$$\lambda_0 = np \quad (1)$$

$$\Delta\lambda = \Delta np \quad (2)$$

where n indicates the average refractive index, λ_0 is the central wavelength of the reflected light, Δn is the birefringence of the liquid crystal, and p is the helical pitch length. The pitch of the helical structure and molecular order within the liquid crystal may also impact the optical properties of reflected light.

The synthesized compound M1 contains a cinnamoyl group and reveals E–Z photoisomerization during UV irradiation, resulting in conformational changes from the linear E form to the bent Z form. The effects of UV exposure on selective light reflection from lyotropic cholesteric liquid crystals containing M1 were also investigated. As shown in Figure 3b, an irreversible blue shift of selective reflection bands was observed for UV irradiation of a sealed cell containing a 60/40 (w/w)

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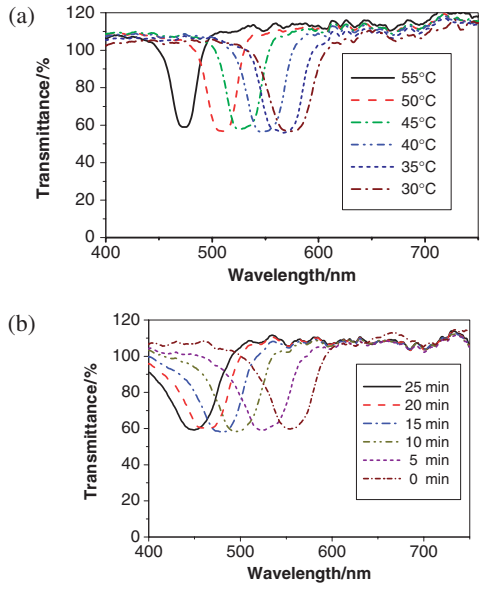

Figure 3. Dependence of (a) temperature and (b) UV irradiation on selective light reflection for a sealed lyotropic liquid crystal cell containing a 60/40 (w/w) mixture of M1/CH_2Cl_2. Reflection light of the cells is located in visible reason.

mixture of M1/CH_2Cl_2 at 40 °C. According to ^{1}H NMR analysis, the blue shift of selective reflection bands of the lyotropic cholesteric liquid crystal following UV irradiation is attributed to the irreversible photoisomerization of the C=C bond in the M1 monomer's cinnamoyl functional group. It is noteworthy that more than 1 h of UV exposure may destroy the helical structure entirely, resulting in decreased transmittance of wavelengths in the selective reflection band (results not shown). Overall, these results suggest that brief (<1 h) UV exposure may produce irreversible E–Z isomerization. However, longer periods of UV irradiation may cause serious degradation of the M1 molecule.

Nevertheless, it is interesting to observe that many other studies of chiral photochromic compounds in liquid crystal matrices have reported changes in the configuration of the chiral molecular fragments in the course of the isomerization process. These changes are often accompanied by a decrease in the anisometry of chiral constituents and, as a consequence, their helical twisting power, resulting in unwinding of the helical structure and a red shift of the selective reflection band.[7]

As seen in Figure 3b, the unusual phenomenon of blue shifts in this study is ascribed to the molecular structure of M1, and in particular to the linkage of a photoisomerizable cinnamoyl group to a cholesteryl group, resulting in mesogenic and chiral properties that affect not only the helical twisting power of the chiral group but also the configuration of mesogenic fragments in the lyotropic liquid crystal phase. Photo-induced E–Z isomerization should also affect the polarity of M1. In addition, the solvent molecules surrounding M1 may also stabilize the molecular orientation of M1 to maintain helical structure during UV irradiation. Due to the Bragg reflection, a significant reflected color could be seen.

In conclusion, we have synthesized a novel functional monomer, M1, end-capped with a cholesteryl group. The monomer reveals amphotropic properties. Thermochromic properties of M1 and photochromic properties of a lyotropic liquid crystal of M1/CH_2Cl_2 with a 60/40 weight ratio were investigated. Increasing cell temperature caused a reversible blue shift, while brief UV exposure caused an irreversible E–Z configurational isomerization. However, longer periods of UV irradiation caused photodegradation.

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