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Photochemically Driven Smectic−Cholesteric Phase Transition in an Inherently Photoactive Dimesogen

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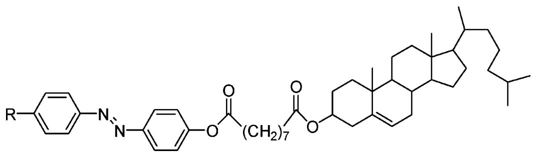
Photostimulated reversible phase transition in liquid crystals (LCs) has received considerable attention in recent years due to their potential importance in molecular devices and optical image recording systems.[1−4] So far, various kinds of photoinduced phase transitions including nematic−isotropic and smectic−isotropic have been reported.[5−7] Other well-studied LC systems are nematic LC doped with photoactive chiral chromophores. It is well-known that small amounts of optically active guest molecules added to a nematic host induce a cholesteric phase and that the helical pitch in twisted nematic phase is sensitive to the chemical modifications of guest molecules. Reversible photoswitching of LC phase between nematic and cholesteric in doped systems using circularly polarized light have also been described.[8−12] Ogura et al. reported the smectic to cholesteric phase transition in a mixture containing 4-*n*-octyl-4′-cyanobiphenyl, cholesteryl nonanoate, and azobenzene at smectic−cholesteric phase transition temperature.[13] Surprisingly, there are no reports on the photoswitching of smectic−cholesteric modulation in a single compound.

Chart 1



n7, R = H
7n7, R = C_7H_{15}

We describe herein the first successful demonstration of the photochemical modulation between smectic A and cholesteric phases using an inherently photoactive cholesterol−azobenzene-containing dimesogenic compound. Dimesogenic compounds (Chart 1) investigated in this study were prepared as described in the synthesis of related compounds.[6,14] LC behavior of these compounds were studied using polarizing optical microscopy (POM) as well as small-angled X-ray diffractometry (SAXRD) and the sharp phase transitions observed in heating and cooling cycles were further confirmed by differential scanning calorimetry (DSC). Table 1 summarizes the phase transition temperatures

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Table 1. Phase Transition Temperatures and Enthalpies of the Dimesogens

	phase transition temperature/°C^{a,b}(ΔH/kJ mol^{-1})	
	heating	cooling
n7	Cr 110.6(23.4) Sm 114.9(0.13) I	I 112.6(0.6) Sm 95.5(31.5) Cr
7n7	Cr 122.7^c Sm 125.4 Ch 145.7(1.3) I	I 141.6(1.3) Ch 106.3 Sm 58.5(26.6) Cr

^{a} Transition temperatures are obtained from DSC analysis at a rate of 5 °C min^{-1} in the first heating and cooling cycles. ^{b} Cr = crystalline, Ch = cholesteric, Sm = smectic A, and I = isotropic. ^{c} Obtained from polarizing optical microscopic analysis.

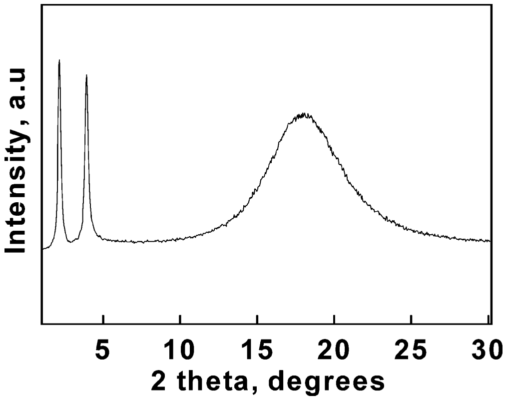

Figure 1. Intensity profile of an X-ray diffraction pattern obtained for **7n7** at 100 °C (cooling cycle).

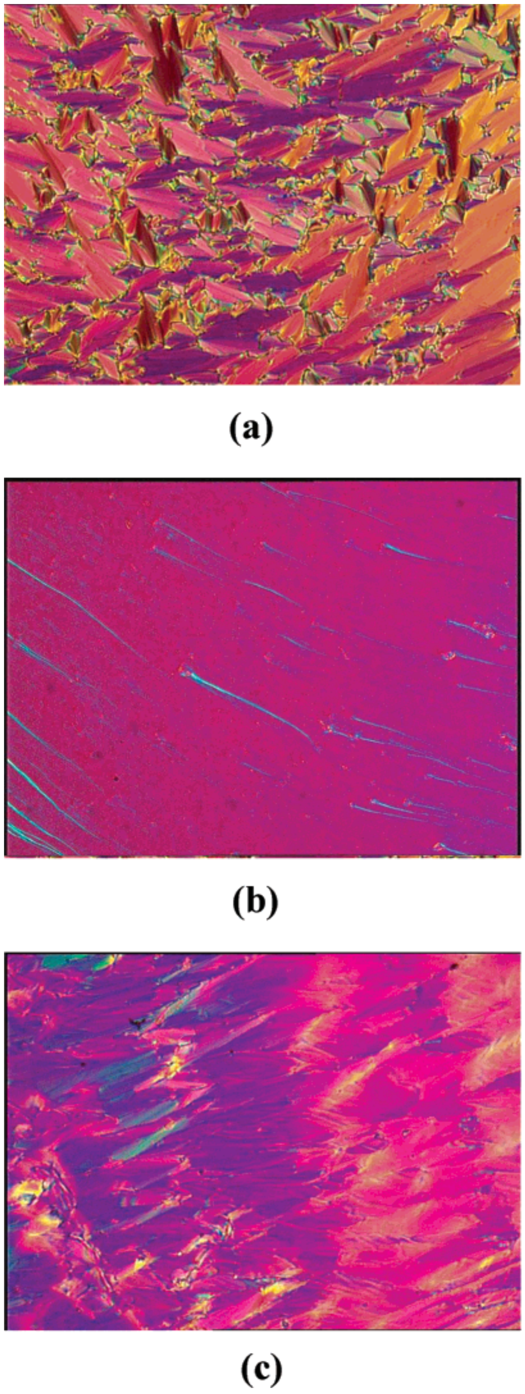

Figure 2. Optical photographs of **7n7** at 100 °C, in the cooling cycle (a) before photolysis SmA phase, (b) after photolysis for 30 s using 366-nm light, Ch phase, and (c) SmA phase regenerated after thermal cis−trans reversal.

of the derivatives with their thermodynamic parameters.

Compound **n7** melts to a focal conic texture at 110.6 °C, which isotropizes at 114.9 °C. Absence of single wavelength reflection in **n7** suggests the formation of smectic A (SmA) phase. Smectic layer spacing, d obtained from X-ray diffraction analysis, has been found to be 46.1 Å, which is significantly larger than the calculated dimension of the molecule, L (L = 39.1 Å, d/L = 1.2). This could not be explained with the known SmA structure. For further investigation on layer spacing of SmA arrangement, we have synthesized **7n7**. Dimesogenic compound **7n7** shows a cholesteric phase from 141.6 to 106.3 °C and a smectic phase from 106.3 to 58.5 °C in the cooling cycle. In the heating cycle SmA phase was observed only for a small temperature range (Table 1). SmA phase observed in this mesogen was also verified by X-ray diffraction studies, which exhibit two sharp low-angle reflections (Figure 1). Coexistence of multiple periodicities has been observed for other nonsymmetric dimesogens in two-dimensional modulated or incommensurate phases.[6,15] Interlayer distances (d) calculated from SAXRD for **7n7** are 22.4 (d/L = 0.49, where L is the length of the molecule) and 40.5 Å (d/L = 0.9) (Figure 1). This could be due to the formation of intercalated and monolayer-type arrangements.[16,17] The relation between SmA arrangement and length of the molecule in these dimesogens is under investigation.

Photoinduced phase changes were studied for **7n7**. Thin layers of the dimesogen **7n7** were sandwiched between cover slips containing 10-μm glass spacers and the film was heated to its isotropic state and slowly cooled to 100 °C. At this temperature the film showed focal conic fan-shaped texture characteristic of a SmA phase (Figure 1 and Figure 2a). The film turned cholesteric on irradiation with light from a 500-W medium-pressure mercury lamp, for 30 s filtered through a 366-nm filter, which was confirmed by the presence

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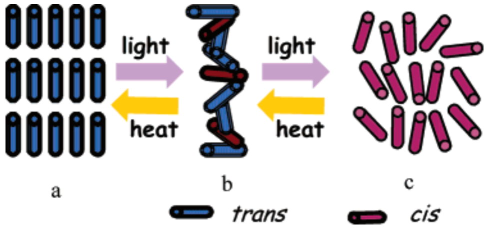

Figure 3. Schematic illustration of the photochemical switching process in **7n7**: (a) SmA, (b) cholesteric, and (c) isotropic.

of selective violet reflection and the cholesteric texture as shown in Figure 2b. Photolysis of trans-**7n7** would lead to partial isomerization to its cis form. Trans to cis ratio present in the 30-s irradiated sample (cholesteric state) was found to be 95:5 by HPLC analysis. For the HPLC experiment the trans-**7n7** was irradiated in its SmA state (100 °C) for 30 s using 366-nm wavelength and it was suddenly cooled to 25 °C.

Cholesteric to isotropic phase transition was observed upon continuous photolysis for 60 s of the thin film of **7n7** using a 366-nm filter because conversion from trans to cis isomer leads to the destabilization of LC phase due to its bent structure. When the irradiated isotropic film of **7n7** was kept at the same temperature (100 °C), cis to trans reversal occurred, which changes the phase to cholesteric and further to SmA. The entire photochemical switching process in **7n7** can be schematically represented as shown in Figure 3.

Figure 4 shows the reflection spectra obtained for **7n7** at 100 °C before and after irradiation studies. After irradiation for 30 s, a reflection band of 394 nm was observed, which was red-shifted to 415 nm, suggesting partial thermal reversal of cis-**7n7** back to its trans form. When the film was kept at the same temperature for 60 s after irradiation, SmA phase was completely regenerated. Microscopic molecular realignment caused by cis to trans isomerization has a similar impact (bathochromic shift in the reflection wavelength) to lowering of the temperature of dimesogen. At 140 °C **7n7** exhibits a reflection band at 390 nm, which was red-shifted to 457 nm (at 114 °C) before changing to the SmA phase. Recently, we have demonstrated that the change in reflection wavelength in cholesteric LCs can be explained considering the formation of smectic cybotactic groups, which restricts helical twisting and increases the wavelength.[14] To explore the mechanism of shift in reflection wavelength in the case of **7n7**, small-angled X-ray diffractometric studies were carried out at different temperatures. X-ray diffraction studies of **7n7** in the cholesteric phase show low-intensity reflections (smectic fluctuations or smectic cybotactic groups) at small angles. As the cholesteric phase is cooled, the smectic fluctuations become more pronounced, leading to sharpening of the small-angled peak.[14] These studies suggest that the mechanism of change in reflection wavelength in the dimesogen **7n7** could be due to the variation in smectic cybotactic groups.

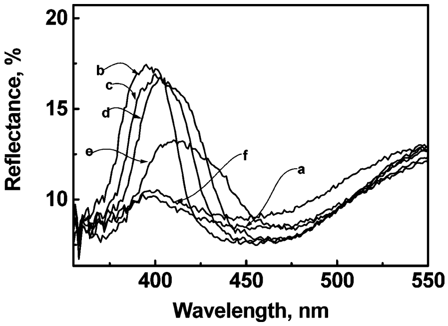

Figure 4. Reflection spectra of **7n7** at 100 °C (cooling cycle) (a) before irradiation (SmA phase) and (b) irradiated for 30 s using 366-nm light. Thermal cis−trans reversal: (c) 15 s after irradiation; (d) 30 s after irradiation; (e) 45 s after irradiation; (f) 60 s after irradiation (SmA) phase.

In summary, we have demonstrated the photochemical phase transition from smectic to cholesteric LC state in an inherently photoactive azobenzene−cholesterol-containing dimesogenic compound. Compounds that show smectic to cholesteric photochemical phase transition can be potential candidates in color information technology; we are now in a process of exploring such materials. Also, a detailed mechanism of smectic−cholesteric photochemical phase transitions is currently in progress.

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