Photochemical Phase Transition in Hydrogen-Bonded Liquid Crystals

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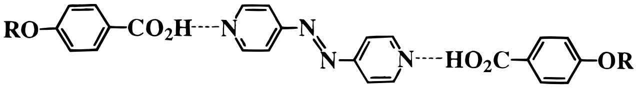
Photochemically driven phase transitions in liquid crystalline hosts containing photoresponsive additives have attracted a lot of attention in view of their importance in erasable direct read after write (EDRAW) memory devices.[1−6] Recent studies have shown that photoresponsive molecules which are inherently liquid crystalline possess much faster switching times compared to host−guest systems.[7,8] In most of the reported systems, however, the change in phase transition temperatures brought about by irradiation is very small (<1 °C). It has recently been recognized that liquid crystalline materials can be obtained through noncovalent interactions between molecules possessing the desired complimentary structural elements. Thus hydrogen-bond, ionic, charge transfer, and ion-dipolar interactions between donor−acceptor moieties have been utilized to generate new liquid crystalline materials.[9−17] In this paper we describe the liquid crystalline behavior and photoswitching characteristics of liquid crystalline materials formed via hydrogen bonding between 4,4′-azabipyridine and 4-alkyloxybenzoic acids.

Chart 1



1a-e

a, R = C_4H_9 **d**, R = $C_{10}H_{21}$

b, R = C_6H_{13} **e**, R = $C_{12}H_{25}$

c, R = C_8H_{17}

Table 1. Phase Transition Behavior of Hydrogen Bonded Assemblies

	phase transition behavior[a]	
compd	heating	cooling
1a	K 140 S 161 I	I 159 N 154 S 119 K
1b	K 95 S 148 I	I 146 N 135 S 78 K
1c	K 104 S 156 I	I 156 S 85 K
1d	K 90 S 144 I	I 141 S 74 K
1e	K 86 S 143 I	I 142 N 141 S 79 K
1e[b]	K 133 S 140 I	I 137 S 90 K

[a] K, crystallline; S, smectic; N, nematic; I, isotropic. [b] After irradiation.

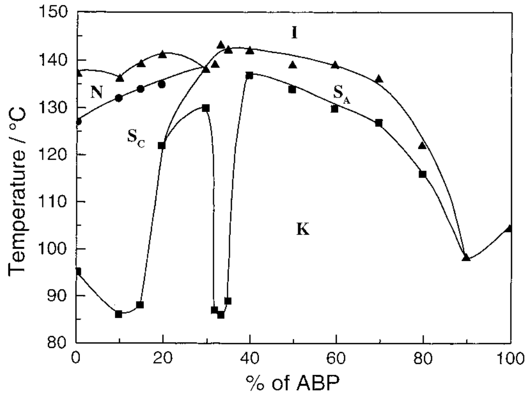


Figure 1. Binary phase diagram of ABP and 4-dodecyloxybenzoic acid (heating).

4,4′-Azabipyridine (ABP) was synthesized from 4-aminopyridine using a reported procedure.[18] The hydrogen-bonded mesogens (Chart 1) were prepared by melting the corresponding acid and ABP in a 2:1 molar ratio.[17] The thermal behavior of these complexes, studied using a polarizing optical microscope (POM) equipped with a hot stage, indicated sharp phase transitions and formation of homogeneous mesophases. The thermal properties of the complexes were distinctly different from those of the individual components. A homogeneous phase with a fan-shaped texture characteristic of a smectic A (S_A) phase was observed for the complexes (Table 1).[19] Neither of the individual components possessed a smectic A phase. In the cooling cycle **1a** and **1e** showed an additional nematic phase within a narrow temperature range. The phase diagram for the mixtures of ABP and 4-dodecyloxybenzoic acid is shown in Figure 1. The smectic A (S_A) phase has a maximum temperature range for the composition containing 33.3 mol % of ABP, confirming that the formation of a 2:1 hydrogen-bonded assembly shown in Chart 1 is mainly responsible for the liquid crystalline properties of the material. The involvement of hydrogen bonds in the formation of these materials was confirmed from their infrared spectra. The O−H stretching frequency of **1e** for example, at 2437 and 1941 cm^{-1} is indicative of strong hydrogen bonding.[12]

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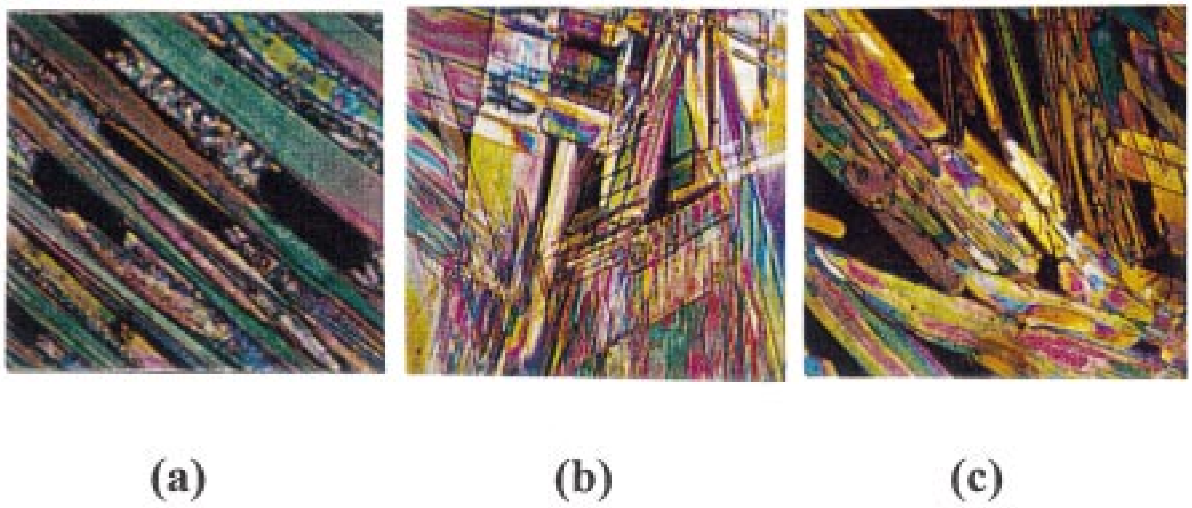

Figure 2. (a) Smectic A texture of unirradiated **1e** at 110 °C (cooling cycle). (b) Crystalline texture of irradiated **1e** (110 °C). (c) Smectic B texture of irradiated **1e** at 134 °C (heating cycle).

Photoinduced phase changes were studied for **1e**. Thin films of **1e** were prepared by slow cooling of the isotropic liquid to 110 °C. At this temperature the film showed the fan-shaped texture with the narrow and elongated ellipsoid texture characterstic of smectic A[19] and flow properties of liquid crystals (Figure 2a). The film turned crystalline and immobile on irradiation for 5 min with light from a 500 W medium-pressure mercury lamp, filtered through a 325-nm band-pass filter (Figure 2b). Further irradiation does not bring about additional changes to the films. After irradiation, the film was cooled to 79 °C and subsequently subjected to a heating and cooling cycle, and the associated phase changes observed are shown in Table 1. In the heating cycle the crystalline to smectic phase transition for the irradiated film occurs at a much higher temperature (133 °C) than for the unirradiated sample. In the cooling cycle the irradiated film shows a stable liquid crystalline phase up to 90° C. Besides the change in the phase transition temperatures, irradiation of these films also brings about a clear change in the nature of the liquid crystalline phase. For the irradiated films, rodlike and rounded grains typical of smectic B (S_B)[19] liquid crystals were observed in the 133−90 °C temperature range (Figure 2c). On subsequent heating and cooling cycles, additional phase transitions were observed, suggesting partial thermal reversal of *cis*-ABP back to its trans form. The photoinduced effects were thermally fully reversible within 3 h of irradiation and could be repeated over several cycles.

The observed changes in the films can be attributed to the trans to cis photoisomerization of the azo moiety in the supramolecular assembly. Irradiation of *trans*-ABP would lead to its photostationary state consisting of the cis and trans forms. The quantum yield (Φ_f) of trans to cis photoisomerization of ABP in benzene was estimated as 0.025, using azobenzene as actinometer. This was only slightly lower in trifluoroethanol ($\Phi_f = 0.016$) suggesting that hydrogen bonding could only lead to a slight reduction in the photoisomerization efficiency of ABP. The thermal stability of the *cis*-ABP in toluene solutions was investigated by UV−vis spectroscopy. The activation energy for the thermal cis to trans isomerization process was estimated as 4 kcal/mol. Due to the poor optical quality of the films, the kinetics of cis−trans isomerization of ABP in the liquid crystaline assemblies could not be studied spectroscopically. However the time required for the full reversal of the photoinduced effects in the irradiated films stored at room temperature are very similar to the time required for the completion of cis−trans isomerization at room temperature in solutions. This suggests that the rates for cis−trans isomerization are not very different in the films. HPLC analyses of the irradiated films indicated only the presence of ABP and the dicarboxylic acid. This confirms that the photoinduced phase changes of the films are due to the trans−cis photoisomerization of ABP and not due to any other photochemical transformation.

The cis form of the ABP moiety could be expected to have a destabilizing effect on the liquid crystalline properties of the material. Apart from the increase in the phase transition temperature of the materials, there is also a drastic reduction in the temperature range of the smectic mesophase range from 57 to 7 °C (Table 1) in the irradiated films. These studies clearly show that liquid crystalline materials generated via intermolecular hydrogen bonding would be highly suited for the design of novel photoactive liquid crystals. With the proper choice of the molecular components in the hydrogen-bonded liquid crystal assemblies, it would be possible to obtain photoactive liquid crystals wherein the liquid crystalline properties could be turned on and off by irradiation. We are currently exploring such systems for the design of photoactive liquid crystals with a much wider phase transition temperature.

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Supporting Information Available: Binary phase diagram of ABP and 4-dodecyloxybenzoic acid (cooling) and textures of **1a**−**1e** on heating and cooling (6 pages). See any current masthead page for ordering information and Internet access instructions.

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