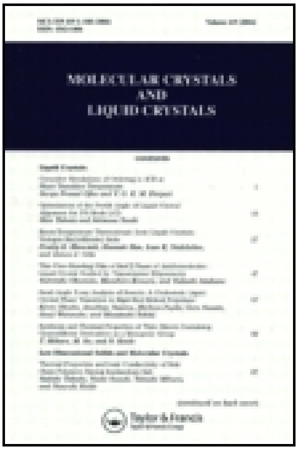

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First Observation of a Photo-Induced Transition to a More Ordered Phase in a System Exhibiting Reentrant Nematic - Smectic A Phase Sequence

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First Observation of a Photo-Induced Transition to a More Ordered Phase in a System Exhibiting Reentrant Nematic - Smectic A Phase Sequence

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Materials composed of photoactive molecules like azobenzenes are known to show photo-induced isothermal phase transitions. However, in all the cases investigated so far, the trans-cis conversion brought about by photoisomerization always leads to an order to disorder transition, i.e., the ordering decreases in the process. In this paper we report observation of the reverse behavior, namely, a photo-induced disorder to order transition. Experiments have been done on a binary liquid crystalline system doped with a photoactive azo molecule, showing a reentrant nematic-smectic A phase transition. In the reentrant nematic phase UV illumination of the sample and the consequent photoisomerization leads to the transformation to the smectic A phase. A possible explanation for this behavior is suggested on the basis of the recently proposed photo controlled nanophase segregation mechanism.

Keywords: photo-induced transition; reentrant nematic; nanophase segregation

INTRODUCTION

Investigations of the photo-induced effects on different liquid crystalline phase transitions have been attracting a lot of attention [1–8]. A part of the reason for this interest is due to their proposed application in optical storage device [9]. The phenomenon is observed in materials comprised of molecules with photoresponsive groups, which when exposed to radiation of suitable wavelength exhibit photoisomerization. A well known photoresponsive group is azobenzene which shows a *trans-cis* photoisomerization when irradiated with UV light of ~365 nm wavelength. As the *trans* form is more stable, the reverse *cis-trans* isomerization

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will occur due to a thermal back relaxation process. It can also be brought about by illuminating the sample with a radiation of wavelength ~ 450 nm.

The liquid crystalline phase is stabilized by the *trans* form of the azo group as it is rod-like, but is destabilized by the cis form, which has a bent shape. Therefore, the *trans-cis*transformation is generally found to decrease the phase transition temperature. For example, if the material exhibits a nematic-isotropic (N-I) transition and is UV irradiated in the nematic phase, the lowering of the transition temperature, T_{NI}, could induce an isothermal N-I transition. In fact, a number of studies [1–7] have been done near the N-I and the chiral smectic C-smectic A (Sm C^*-Sm A) transitions. Very recently, photo-induced TGB-cholesteric, Sm A -TGB and Sm C^*-cholesteric transitions have also been observed [8]. A common feature in all the reported cases is that the *trans-cis* conversion brought about by photoisomerization always leads to an order to disorder transition, i.e., the ordering gets reduced in the process. Hence it should be interesting to study the phenomenon in a material that exhibits a reentrant nematic phase. In this paper we report measurements on such a system having the N-Sm A-N_{re} phase sequence, where N_{re} is the reentrant nematic phase. The results demonstrate that the *trans-cis* isomerization can lead to a more ordered phase, as UV radiation is shown to induce an isothermal N_{re} -Sm A transition. Finally, we discuss, briefly, the X-ray data obtained in the Sm A phase, which support the recently proposed [10] idea of photo-induced nano-phase separation in such materials.

EXPERIMENTAL

The host mixture used for the measurements was a 24 wt% 4-cyanophenyl 4′-octyloxybenzoate in 4-octyloxy 4′-cyanobiphenyl exhibiting the phase sequence N-Sm A-Nre on cooling from the isotropic (I) phase. The photoactive guest compound was p-(p-Ethoxyphenylazo)phenyl hexanoate which was doped at a low concentration of 2.9 wt% to the host mixture. The transition temperatures of the resultant guest-host mixture are I 80.7 °C N 48.7 °C Sm A 32.4 °C N_{re}.

A schematic diagram of the experimental set up is shown in figure 1. The probe beam, used for monitoring the phase transitions was obtained from a 5 mW laser diode (Thorlabs, USA) at 670 nm wavelength. The light transmitted through the sample was collected using a photodiode with built-in current-voltage converter/ amplifier (Thorlabs). The UV irradiation was done using an intensity stabilized UV source with a fiber-optic guide (Hamamatsu L7212–01, Japan). A narrow bandwidth (10nm FWHM) UV-pass filter was employed to select the desired radiation of 365 nm. An additional IR-block filter was inserted just before the sample to prevent any effects of heat radiation from the UV source. The actual power of the radiation passing through the filter combination and falling on the sample was measured with a UV power meter (Hamamatsu, C6080–03) kept in the sample position.

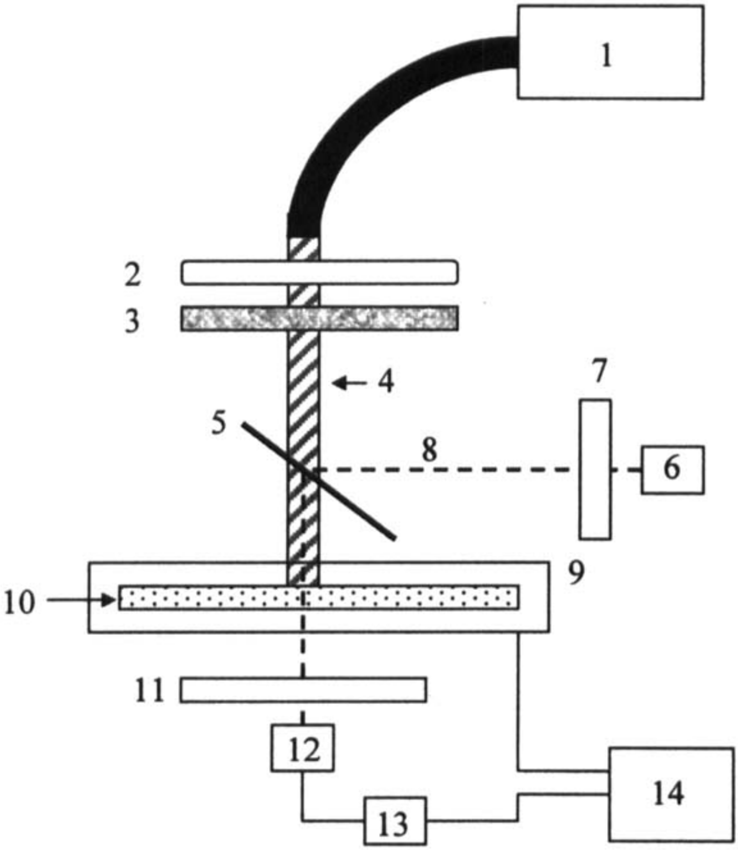

FIGURE 1 Schematic diagram of the set up used for laser transmission experiments. 1) UV source, 2) 365 nm filter, 3) IR blocking filter, 4) UV beam, 5) Beam splitter, 6) Laser diode, 7) Polariser, 8) Laser beam, 9) Hot stage, 10) Sample, 11) Analyser, 12) Photodetector, 13) Multimeter, 14) PC

A sandwich cell was formed with two glass plates, one coated with silane to promote homeotropic alignment and the other, with a polyimide solution and unidirectionally rubbed, to get planar alignment of the molecules. Two mylar spacers of 9.4 μm thickness defined the cell gap. This particular geometry, usually referred to as hybrid geometry, was chosen as it resulted in a large change in the transmitted intensity, between crossed polarizers, for the Sm A-N and Nre-Sm A transitions. The sample cell was mounted in a temperature controlled hot stage (INSTEC HS250). The data acquisition and control was handled by a PC. Microscopic observations were made with a LEICA DMRXP polarizing microscope. Photo-absorbance measurements were carried out at room temperature in the Nre phase as a function of wavelength in the range of 250nm to 800nm, using a UV-VIS spectrophotometer (Lambda 20, Perkin Elmer) using samples sandwiched between two optically flat quartz plates separated by mylar spacers.

RESULTS AND DISCUSSION

Plots of absorbance as a function of wavelength for the guest-host mixture before UV irradiation and after exposing to 0.1 and 0.5 mW/cm^2 are given in figure 2. At wavelengths greater than 350 nm, the non-irradiated sample shows two absorption maxima, similar to the spectra obtained for the pure azo dopant material, confirming that the origin of these peaks is the azo-linkage of the dopant molecule. Therefore, one can identify one maximum at ~ 365 nm to be corresponding to the π-π^*transition of the *trans* form and the second at ~ 450nm with the n-π^*transition in *cis* isomers of the azo moiety. As is to be expected, illumination of the UV radiation leads to a decrease in the peak at ~ 365 nm, owing to a decrease in the number of *trans* isomers, the effect being greater for a higher radiation level.

The first experiment that we carried out was to keep the sample in the three different mesophases just below (~1 °C) their transitions to respective high temperature phases and illuminate with 0.1 mW/cm^2 UV radiation. When irradiated in the Sm A and high temperature N phases, the material transforms into N and I phases respectively. This is not surprising and in agreement with the results in the literature [1–8] that the UV irradiation can lead to a "melting" of the phase, or in other words, that it leads to a transition to a less ordered state. But when the experiment is done in the Nre phase, we observe a novel feature: The Nre phase transforms into the Sm A phase, i.e., to a more ordered state. Figure 3 shows a microphotograph obtained by irradiating the sample in the Nre phase through a mask. The darker regions on the left and right hand sides are from the Nre phase, while the middle portion is from the photo-induced Sm A phase exhibiting the focal conic texture. In fact, the interface region, which arises because of the light leakage from the edge of the mask, shows the chevron texture usually observed at the transition between Sm A and N phases.

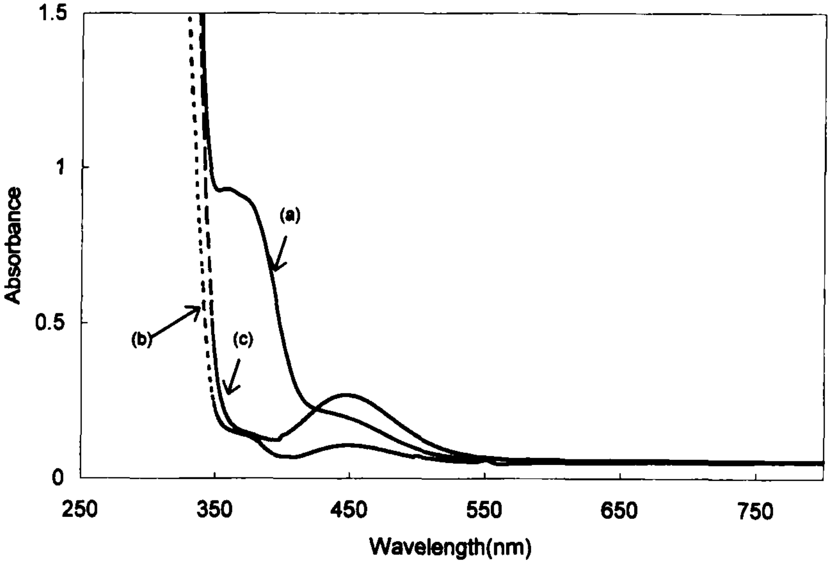

FIGURE 2 Absorbance spectra obtained in the reentrant nematic phase, at room temperature before (a) and after (b,c) exposing to a 365nm UV radiation. The intensity of UV radiation used is 0.1 mW/cm^2 in (b) and 0.5 mW/cm^2 in (c). The absorption maximum at ~ 360nm corresponds to the π-π^* transition of the *trans* isomer and the higher wavelength (~450nm) peak is due to the n-π^* transition of the *cis* isomer. After irradiation the decrease in the absorbance value at ~ 360nm is due to the *trans-cis* photo-isomerization

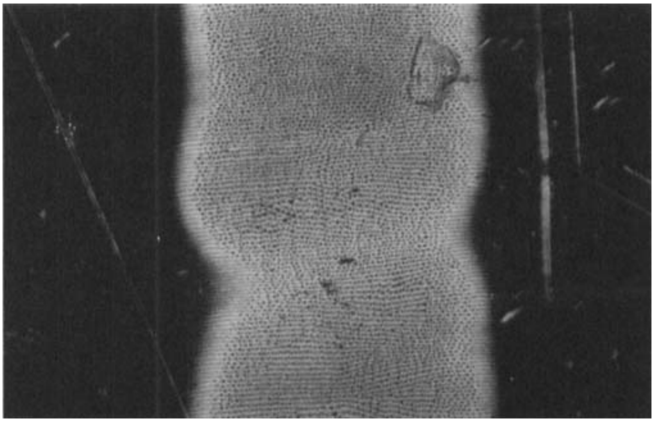

FIGURE 3 Photomicrograph obtained by irradiating the sample in the reentrant nematic phase through a mask. The middle portion shows the photo-induced focal conic texture characteristic of the smectic A phase, while the darker regions on the left and right hand sides are in the reentrant nematic phase (See Color Plate V at the back of this issue)

In order to get the amount of shift in the transition temperatures for the different transitions, we did the laser transmission experiments. To prevent any influence of the thermal back relaxation process, the UV radiation was on throughout the temperature scans. Figures 4a-d show the plots of transmitted intensity as a function of temperature before irradiation and after exposure to 0.1, 0.5 and 3.5 mW/cm^2 radiation. Abrupt intensity changes are observed at all the three transitions, helping in calculating the transition temperatures accurately. Upon UV irradiation, clear shifts in the transition temperature are observed, with the shift increasing as the power of the radiation increases. The shift is small for the Sm A -N transition, being about 3 °C for 3.5 mW/cm^2 power, as against a shift of ~ 9°C for the N-I transition. But it is for the N$_{re}$-Sm A transition, that the effect is spectacular. In fact, the Nre phase is not seen at all as the sample remains in the Sm A phase till crystallization at ~13 °C, from which we may infer that even at a very low radiation level of 0.1 mW/cm^2, the shift is more than 20 °C. We ascertained this feature by microscopic observations. Notice that there is a drastic difference in the behavior at the high and low temperature Sm A-N transitions. Before attempting to give an explanation for the observed features, we present preliminary X-ray layer spacing (d) measurements done in the Sm A phase with and without exposing the sample to the UV radiation. Experiments were done using Lindemann capillaries and an Image Plate set up (MAC Science, Japan). The d value obtained at 40 °C changed from 28.6 Å to 29 Å upon irradiation, i.e., the photo-effect increases the d value by ~ 0.4 Å. The change can be reversed either by illuminating with white light or allowing the system to relax by the thermal back relaxation process, proving thereby that the effect is caused by the *trans-cis* photoisomerization. These features agree with the results recently reported [11] on a similar system, except that it showed a smaller change of only ~ 0.15 Å. Lansac et al [10] have tried to explain this behavior using a mechanism referred to as "photo controlled nanophase segregation". According to these authors, when the UV radiation is absent the azo molecules are in their *trans*-form which have a rod-like shape and are therefore easily accommodated into the smectic layers. But the photo-induced *cis*-form molecules have a bent shape and therefore get expelled from within the layers and occupy the region between the layers. This shows up as an increase in the overall layer spacing value.

The frustrated spin-gas model developed by Berker and collaborators [12] has been found to describe the reentrant transitions quite successfully. The model is essentially designed for molecules that have a strong polar group at one end like the ones in the host mixture used in the current study; as it turns out, the reentrant nematic is generally observed in strongly polar materials. In the Sm A phase of such systems, the model considers a two-body dipolar potential with ferroelectric

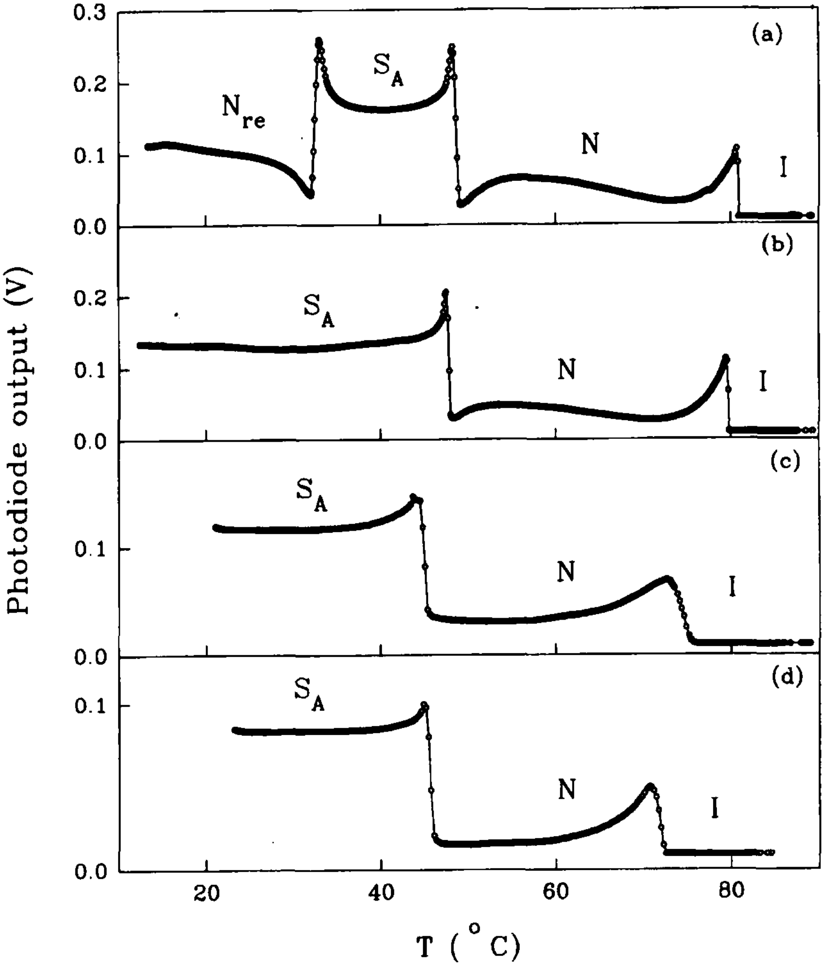

FIGURE 4 Temperature dependence of the intensity of laser transmission through the sample (a) before and (b, c and d) after exposure to UV radiation. The intensity of UV radiation used is 0.1 mW/cm^2 in (b) 0.5 mW/cm^2 in (c) and 3.5 mW/cm^2 in (d). The Sm A-N and N-I transitions show gradual shifts in the transition temperatures, with increasing level of the UV radiation. But the N_{re}-Sm A transition temperature gets depressed to such an extent (~ 20°C) that it is preempted by crystallization at about 13°C, even for the lowest power (0.1 mW/cm^2) of the UV radiation used in these experiments

and antiferroelectric interactions, and then looks for the effect on a third dipole, with the dipoles oriented parallel to the layer normal. When the dipolar forces between two particles cancel, the third dipole experiences no force and is therefore free to *permeate or diffuse* from one smectic layer to the next one, thus "frustrating" the smectic order. Consequently, the nematic phase reenters. On the other hand, if the cancellation is not complete, the presence of the triplet is supposed to stabilize the smectic order through short-range dipolar interactions.

Now, consider the nanophase segregated Sm A phase. The guest azo-rich regions (in *cis*-form) and the Sm A layers of the host molecules are not favored to mix with each other. The permeation of the molecules from one layer to another is now less preferred. Consequently, the situation becomes less conducive for the formation of a reentrant nematic phase. This argument should also apply for the transition to the high temperature nematic phase. However, increase in thermal fluctuations can help overcome the problem (albeit at temperatures not far from the transition temperature for the non-irradiated case) and the system can transform to a nematic phase. Perhaps for this reason the shift in the Sm A-N transition temperature is quite small compared to that for the N-I transition.

In conclusion, we have observed a photo-induced reentrant nematic to smectic A transition in a binary mixture doped with a photoactive azo compound. The results show for the first time that *trans-cis* photoisomerization can cause the appearance of a more ordered phase. The phenomenon has been explained on the basis of the recently reported photo controlled nanophase segregation.

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