Photoinduced phase transitions in liquid crystalline systems[†]

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In recent years, a field of research that is growing steadily is the photoinduced phenomenon in which the incident light itself brings about molecular ordering/disordering of the liquid crystalline system. This particular aspect of photonics, in which light can be controlled by light as a stimulus, is being proposed as the future technology for high-speed information processing and photochromic materials. The azo compounds in particular, have been found to be promising candidates for optical data storage. An illustration of nature utilizing photoinduced effects is that of the biological photochrome bacteriorhodopsin found in the eye. Apart from their biological and technological importance, these systems exhibit photo-driven phase transitions, thus providing a new tool to study phase transitions and the associated critical phenomena. In this article we review some of our recent contributions to this field of photoinduced isothermal phase transitions in various liquid crystalline systems. In particular, we discuss the application of the random-field Ising model to describe the photoinduced nematic–isotropic transition, the influence of nanophase segregation to bring about a unique photo-driven disorder to order transition, local racemization phenomenon in bent-core banana B_2 phase and the effect of high pressure.

OVER the past two decades, liquid crystals[1] have attracted ever-increasing interest because of their ability, due to their self-assembling nature, to dramatically alter the properties of light reflected from or transmitted through them. Traditionally, low-magnitude electric fields have been used to control/alter the molecular ordering of these systems resulting in the highly successful electro-optic display applications. In such devices an applied electric field induces a change in the material properties, which in turn affects the birefringence of the sample. More recently, a field of research that is growing steadily is the photoinduced phenomenon in which the incident light itself brings about molecular ordering/disordering of the liquid crystalline system. This particular aspect of photonics, in which light can be controlled by light as a stimulus, is being proposed as the future technology for high-speed information processing[2]. It has been shown[3] that even in non-photo absorbing liquid crystals, optical fields, albeit large, can be used to cause a reorientation of the molecules. However, addition of chromophores, such as azo groups, has been found to significantly lower the required optical field[4]. Furthermore, the photoinduced birefringence has extremely high long-term stability, and holograms recorded show hardly any degradation[5]. This feature has made the photochromic materials, in particular the azo compounds, promising candidates for optical data storage. An illustration of nature utilizing photoinduced effects is that of the biological photochrome bacteriorhodopsin found in the eye. In fact, the photosensitive nature of this material has found uses in the construction of spatial light modulators and optical storage devices[6]. Apart from their biological and technological importance, these systems exhibit photo-driven phase transitions, thus providing a new tool to study phase transitions and the associated critical phenomena[7–11]. In this article we describe some of our contributions[11–20] to this field of photoinduced isothermal phase transitions in various liquid crystalline systems.

We concentrate here on the photoinduced effects observed in systems having the photochromic azo (–N=N–) group. The azo group is either chemically attached to the molecule or is used as a dopant in a liquid crystal host material. The heart of the phenomenon in such systems is the reversible photoinduced shape transformation of the molecules containing the photochromic azo groups. Upon UV irradiation (around 360 nm, corresponding to the $\pi - \pi^*$ band of the azo group), the energetically more stable trans configuration, with an elongated rod-like molecular form, changes into a bent cis configuration. The reverse transformation can be brought about by illuminating with visible light (in the range 400–500 nm, corresponding to the $n - \pi^*$ band). This latter change can also occur spontaneously in the 'dark' by a process known as thermal back relaxation. In the case of the photoactive guest–non-photoactive host systems, the trans form of the azo dopant, as it is rod-like, is favourable for the stabilization of the liquid crystalline phase. On the other hand, the bent cis form acts like an 'impurity' and therefore destabilizes the liquid crystalline phase. Hence, photoisomerization from the trans to the cis form causes, in general, a lowering of the transition temperature. If, for instance, the material exhibits a nematic–isotropic (N–I) transition and the UV irradiation is done in the nematic phase, the lowering of the transition temperature, T_{NI}, could induce

an isothermal *N–I* transition. It is this photochemically induced transition that is promising for the optical image-storing systems.

Experimental

The UV radiation to bring about the photoinduced effects was obtained using one of the following conventional sources: (i) a low-power UV source from Edmund Scientific, and (ii) a variable high power source from Hamamatsu. In all the cases, a 365 nm filter in conjunction with an IR filter was used before the light fell on the sample. The latter was used to remove any heating effects due to the radiation falling on the sample.

One of the requirements for technological applications is that the lowering of T_{NI} be appreciable[10,11]. Although large shifts in T_{NI} can be obtained if the host material itself is photoactive, from the operational point of view it is obviously better to dope small quantities of guest photoactive material into a host liquid crystalline system that has been optimized for temperature range, viscosity, etc. For this purpose, in the studies mentioned here, we have employed guest–host systems in which the host non-photoactive material is chosen with the kind of phase transition that is to be studied and the guest compound (hereafter referred to as EPH and obtained from Eastman Kodak), is a photoactive molecule with the molecular structure and phase transitions given below.

$$C_5H_{11}\text{-COO}-\underset{}{\bigcirc}-N=N-\underset{}{\bigcirc}-OC_2H_5$$

EPH
Isotropic 129.3°C Nematic 74.4°C Crystal
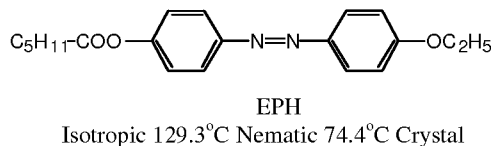
The fact that the photoactive compound is also liquid crystalline helps in obtaining a homogeneous mixing of the guest and the host materials.

Results and discussion

N–I phase transition

As mentioned earlier, due to the shape difference, while the *trans* isomer of the photoactive molecule stabilizes the liquid crystalline phase, say the nematic phase, the *cis* isomer destabilizes it. Thus the photo-controlled conversion of one isomer to another can lead to a transition from the nematic to the isotropic phase. Owing to its technological importance, extensive studies have been done on the photoinduced *N–I* transition, a few of which we mention here.

Absorption spectra: Measurement of the UV–VIS spectra of the sample provides a simple method to judge the occur-

rence and extent of photoisomerization. The absorption spectra obtained in the nematic phase of the guest–host mixture before and after UV irradiation are shown in Figure 1. In the absence of the UV radiation (curve (a)) two absorption maxima, one corresponding to the π–π^* transition of the *trans* form at ~365 nm and the second at ~450 nm usually associated with the n–π^* transition of *cis* isomers of the photoactive molecule are seen. Upon radiation-induced *trans–cis* photoisomerization, there is a drastic decrease in the absorbance level at 365 nm (curve (b)). The apparent extent of photoisomerization (or the disappearance of the *trans* isomer) can be determined[15] by $P = (A_0 - A_1)/A_0$, where A_0 and A_1 correspond to absorbance at 365 nm before and after irradiation. For example, using the values from Figure 1, we estimate P to be 0.8, i.e. 80% of the *trans* isomers have been converted to *cis* isomers.

Visual observation: Due to the finite birefringence of the nematic phase, polarizing microscopy can be used to visually observe the photoinduced *N–I* isothermal transition. Figure 2 shows a photomicrograph taken when the sample in the nematic phase is exposed to UV radiation through a mask. The areas adjoining the central region, which are exposed to the radiation, have undergone photoinduced isothermal transition and therefore appear dark between crossed polarizers, indicating that they are in the isotropic phase, while the central un-irradiated strip stays in the birefringent nematic state.

Opto-dielectric effect: Being a measure of its anisotropy, the order parameter in the nematic phase manifests itself in the anisotropy of the dielectric constant. In the uniaxial
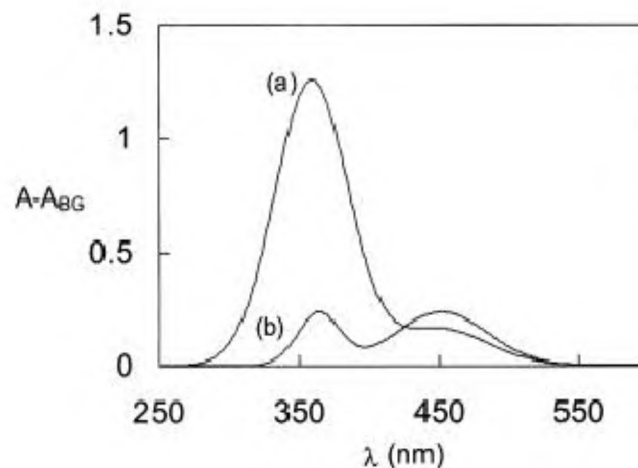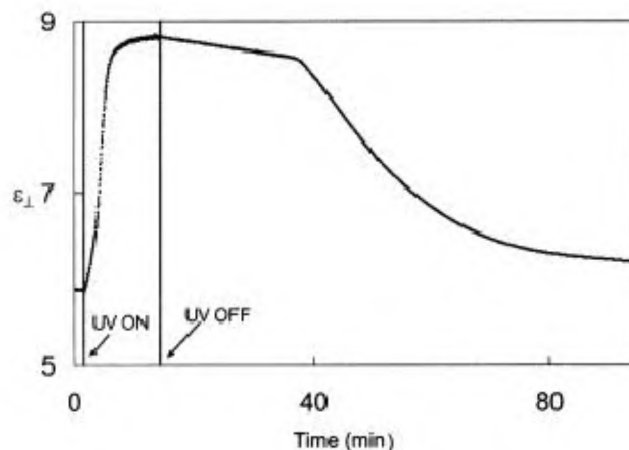

Figure 1. Absorbance spectra obtained in the nematic phase of mixture 1 (4.5 mol% mixture of EPH in E7, a room-temperature nematic liquid crystal from E-Merck) before (curve (a)) and after (curve (b)) exposing to a 365 nm UV radiation of 0.1 mW/cm². Decrease in the absorbance value at 365 nm after irradiation is due to the *trans–cis* photoisomerization and indicates conversion of 80% of the *trans* isomers.
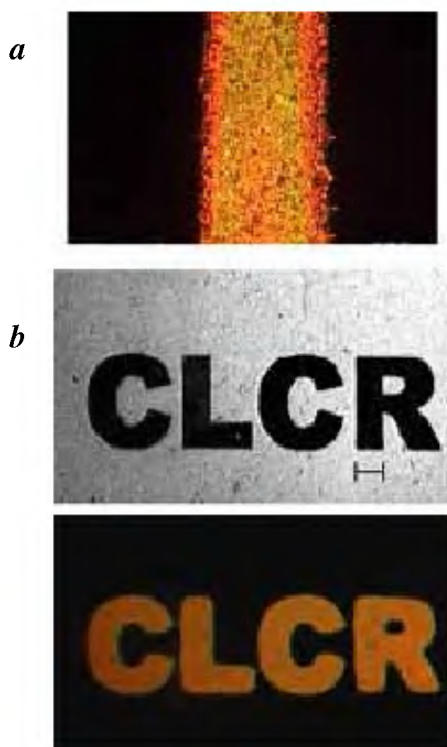
Figure 2. *a*, Polarizing microscope photograph (crossed polarizers, magnification × 100) of the sample in the nematic phase, exposed to UV radiation through a mask. After UV illumination, the central region that is covered by the mask continues to have a bright birefringent appearance characteristic of a nematic phase, whereas the adjoining UV-exposed regions appear dark as the sample in those regions is in the isotropic phase caused by the photoinduced *N–I* transition. The bright droplets seen near the periphery of the central bright area are regions which are undergoing reverse transition induced by the ~ 450 nm radiation contained in the illumination used with the microscope. *b*, Illustration to show that the phenomenon of photoinduced *N–I* transition can be used for image storage applications. (Top panel; mask used and bottom panel; image stored.) Horizontal bar (top panel) corresponds to a linear distance of 1 mm.

Figure 3. Time-resolved variation of $\varepsilon_\perp$ measured at a fixed temperature in the nematic phase of mixture 1 after the UV radiation is turned ON and switched OFF after ~ 12 min. The *trans–cis* isomerization due to the 365 nm radiation leads to an isothermal nematic to isotropic transition, causing the $\varepsilon_\perp$ values to increase. After the UV radiation is switched OFF, reverse isomerization takes place through a thermal back-relaxation process and changes the isotropic phase back to the nematic phase, also isothermally.
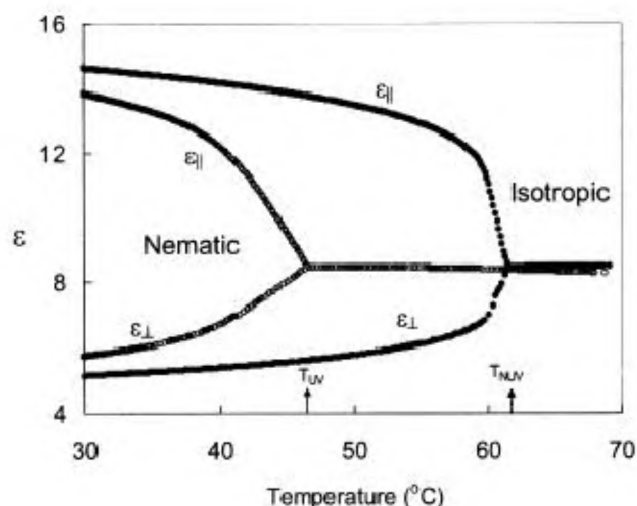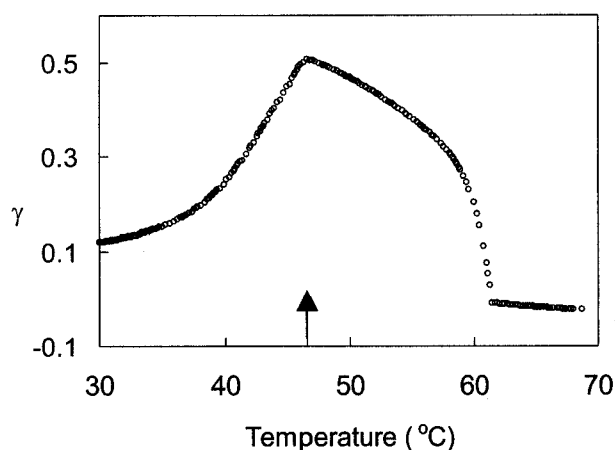

Figure 4. Temperature dependence of two principal dielectric constants $\varepsilon_\parallel$ and $\varepsilon_\perp$ with (O) and without (●) UV radiation. Two arrows marked T_{NUV} and T_{UV} indicate the transition temperature obtained without and with UV radiation respectively, showing a shift of ~ 15°C in T_{NI} upon irradiation (sample used was mixture 1).

nematic phase there are two principal dielectric constants, $\varepsilon_\parallel$ and $\varepsilon_\perp$, parallel and perpendicular to the director, with the difference between the two referred to as the dielectric anisotropy, $\Delta\varepsilon$. It is clear then that a decrease in the nematic order parameter, say by *trans–cis* isomerization, should decrease the dielectric anisotropy to become zero in the isotropic phase. The material used for this study has a positive dielectric anisotropy and hence across the nematic–isotropic transition $\varepsilon_\perp$ should increase, while $\varepsilon_\parallel$ should decrease.

The time-resolved variation of $\varepsilon_\perp$ measured at a fixed temperature in the nematic phase is given in Figure 3. Before irradiation, the sample is in the nematic phase. On turning the UV radiation ON, the value of $\varepsilon_\perp$ starts increasing rapidly and saturates after 4 min of exposure. When the radiation is turned OFF and the sample is left in the dark, reverse isomerization takes place, the sample transforms back to the nematic phase and consequently $\varepsilon_\perp$ decreases. The switching kinetics for this thermal back-relaxation is, however, very slow (recovery is not com-

plete even after ~ 70 min) compared to the *trans–cis* isomerization.

The temperature dependence of the two dielectric constants $\varepsilon_\parallel$ and $\varepsilon_\perp$ in both the un-irradiated and the irradiated states is shown in Figure 4. In the latter experiments, to ensure that there is no effect of thermal back-relaxation during the measurements, the radiation was kept ON throughout. One salient feature observed is the drastic decrease by 15°C in the value of T_{NI} on UV exposure. Of course, comparable values for the diminution in the tran-

sition temperature have been reported[10,21], but what is significant in our case is that the power of the UV irradiation is only 0.1 mW/cm^2, which is much smaller than those used in earlier studies[7–10]. The second feature to be noticed is that upon irradiation, the magnitude of change in both $\varepsilon_\parallel$ and $\varepsilon_\perp$ decreases as $T_{NI} - T$ increases, i.e. on moving deeper into the nematic phase. This is to be expected for, with increasing nematic order parameter the efficiency of the *trans–cis* conversion by a given intensity of the radiation should decrease. By taking the difference in $\varepsilon_\perp$ values in the two cases, i.e. before and after UV irradiation, one can get the 'efficiency of the opto-dielectric effect'. Figure 5 shows this parameter $\gamma[= (\varepsilon_{\perp UV} - \varepsilon_{\perp no UV})/\varepsilon_{\perp noUV}]$ as a function of temperature. It is seen that the efficiency is quite high over a large temperature range with the maximum occurring in the vicinity of the T_{NI} for the irradiated case. In fact, the efficiency remains within 20% of the maximum over a range of 10°C. This is more than a factor of three compared to any of the previously reported cases[22]. In the nematic phase, the variation of the dielectric constant can be directly related to the change in the birefringence of the sample. Hence, it should be of interest for image-storing applications that near-maximum birefringence changes can be maintained over an extended temperature range. These systems can, in principle, be used for the fabrication of light-dependent capacitors and resistors.

Random field model: In the case of polyisocyanate co-polymer materials, it was observed[23] that in the presence of a low concentration of chiral moieties (sergeants), the system with a majority of achiral moieties (soldiers) exhibits a large chiral amplification resulting in substantial chiral ordering. Comparing the phenomenon of photoinduced shift in the transition temperature to this induction


Figure 5. Plot showing temperature dependence of the 'opto-dielectric effect'. Here $\gamma = (\varepsilon_{\perp UV} - \varepsilon_{\perp no UV})/\varepsilon_{\perp no UV}$. Maximum effect is seen around 46°C, corresponding to the transition temperature T_{NI} of the irradiated sample (indicated by the arrow) of mixture 1. The value becomes zero above the transition temperature of the un-irradiated sample.

of cooperative chiral order in 'sergeant–soldier' copolymer systems[23], we have shown[14] that the magnitude of the shift in the transition temperature as a function of the magnitude of the radiation can be described in terms of a random-field model[24]. The contribution to the free energy of the liquid crystalline system comes from the orientational ordering of the host molecules and the local orientational entropy due to the guest photoactive molecules. When the UV radiation is present, the photoactive molecules are bent and therefore introduce a local region of higher orientational entropy compared to the regions of the host molecules. This is similar to the regions of higher chiral bias where the chiral units are present on the polymer chain. The amplified chiral cooperative response of the polymer system can be compared with the amplification of the local disorder due to the bent photoactive molecules, leading to an isothermal transition from the nematic to the isotropic phase. Thus, perhaps one can consider ΔT, the shift in the $N–I$ transition temperature to be analogous to the chiral order parameter of the polymer. There exist two important differences between the two systems, though. First, while in the case of the polymer, the effect of the sergeant chiral units is to enhance the ordering of the whole system, the sergeant-bent photoactive molecules lead to a higher disordering of the entire medium. The main implication of the reverse role of the sergeants is that whereas the cooperative effect increases with decreasing temperature for the polymer, it decreases with decreasing temperature for the $N–I$ case. Secondly, in the polymer system, the chiral and achiral units are covalently bonded together by the polymerization process, and they cannot redistribute themselves. In contrast, in the liquid crystalline system, the photoactive dopants are free to redistribute themselves in the host 'solution'. Thus it may appear that this is a case of annealed randomness as opposed to quenched randomness. But based on observations described below, we feel that it is a case of quenched randomness. As was discussed for Figure 2, by illuminating the sample through a patterned mask it is found that the isotropic regions are highly localized without getting diffused into the non-illuminated regions. From the fact that the concentration of photoactive molecules is quite small, along with the observation that the region of illumination gets transformed to the isotropic phase and remains localized, we can infer that the effect of UV on the photoactive molecules gets amplified substantially. Within the timescales of measurement, which are much shorter than the thermal back-relaxation time, the photoinduced disorder can be considered quenched.

Effect of pressure: Application of pressure reduces the shift in the transition temperature induced by photoisomerization (see Figure 6), even leading to complete absence of such a shift above a certain pressure. As has been stated earlier, the photoinduced isothermal $N–I$ transition occurs because of the fact that the *cis* isomer of the

azo molecule has a bent shape and therefore acts like an impurity in the midst of rod-like host molecules. Measurements at constant temperature have established that there is a decrease in the specific as well as transition volumes as one moves up to higher transition pressures and temperatures[25]. Such a reduction in volume would mean that the intermolecular space available for the azo molecule to take a bent shape decreases as the pressure is increased. In other words, the system opposes the formation of the *cis* isomers. Consequently, the photoinduced shift in the transition temperature caused by the *cis* isomer also becomes smaller as the pressure is increased and finally vanishes. This opposition due to reduction in the intermolecular space can be countered, at least to a certain extent, by increasing the energy of the UV radiation pumped into the system. If this argument is true, then a higher intensity level of the radiation will force the *trans* isomer of the azo to transform to the *cis* isomer. This will then lead to at least a partial restoration of the photoinduced shift in the transition temperature, as has indeed been seen in the experiments[16]. The balance between these two opposing forces decides the pressure at which the shift becomes zero for a given intensity of the UV radiation.

Dynamics: The dynamics of the *N–I* transition was studied using a pulsed Nd–YAG laser source (energy ~ 10 mJ/cm²) for bringing about photoisomerization and a He–Ne laser as a probe. Typical time-dependence of I_{probe}, the transmitted intensity of the He–Ne beam, obtained by keeping the sample in the *N*-phase and irradiating with a single pulse of the YAG laser is shown in Figure 7. The
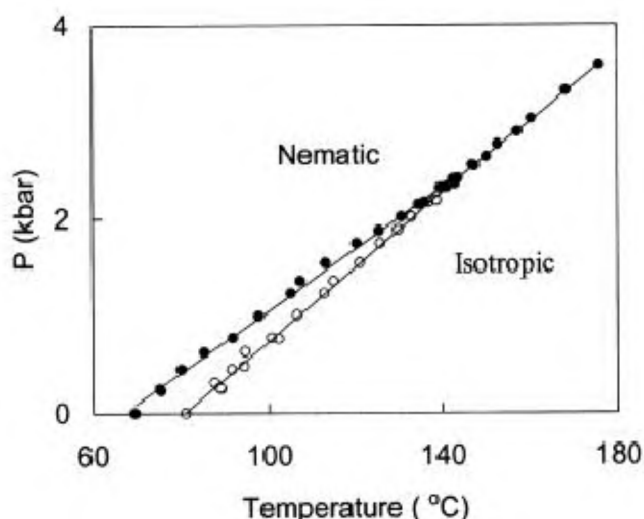

Figure 6. Pressure–temperature phase diagram showing the nematic–isotropic boundary obtained when there is no UV radiation (O) as well as in the presence of 16 mW/cm² UV radiation (●). The UV-induced shift in the transition temperature decreases as the pressure is increased. Beyond a pressure, P_0 ~ 2.5 kbar, the UV radiation does not cause any change in the transition temperature. The lines are meant as a guide to the eye.

response time τ_r, defined as the time required for the intensity to change from 90 to 10% of the initial value, was determined from these data and was found[13] to be extremely small (485 ns), making it the fastest observed for any photochemical transition involving a liquid crystalline phase. Further, this number is only 40 times more compared to the value reported for the *trans*-to-*cis* conformational change to take place. This is interesting because it demonstrates that a phase transition involving a cooperative action between the molecules of the system takes place approximately on the same timescale as that for conformational changes of individual molecules.

Disorder-to-order transition

As a rule, the *trans–cis* conversion brought about by photoisomerization always leads to an order-to-disorder transition, i.e. the ordering of the medium decreases in the process. Recently, we found[12,13] a system in which photoisomerization leads to an ordering in the medium. The system used exhibits a nematic–smectic A–reentrant nematic phase sequence when the sample is cooled from the isotropic phase. Here smectic A (Sm A) refers to a phase in which a one-dimensional mass density wave is superposed over the orientational ordering of the nematic phase resulting in a layered arrangement of the molecules. The notable feature of this system is the existence of the *N*-phase both above and below the Sm A phase; the lower temperature *N*-phase is termed reentrant (N_{re}) because of its re-appearance on the temperature scale[26]. When irradiated in the Sm A and high temperature *N*-phases, the material transforms into *N* and isotropic phases respectively. This is not surprising and, in fact, is in agreement with the results mentioned above that the UV irradiation can lead to a 'melting' of the phase, or in
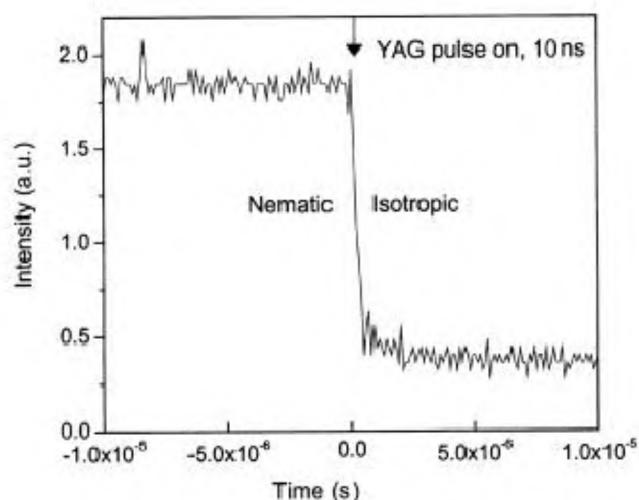
Figure 7. Time-resolved probe beam intensity measurements of the photoinduced *N–I* transition. The transition takes place extremely fast, with about 485 ns as the response time.
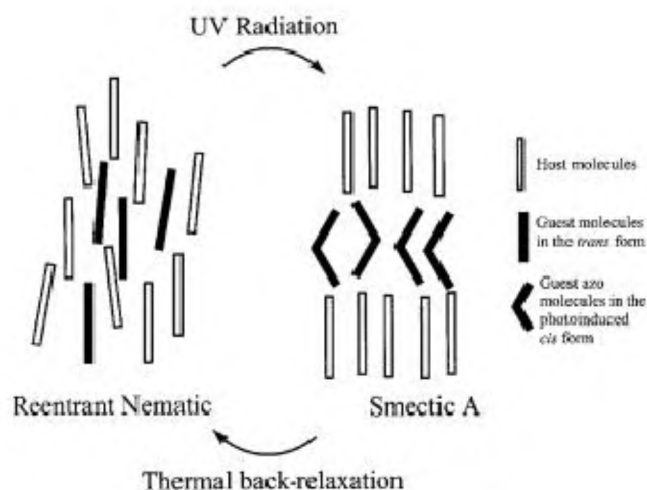
Figure 8. Schematic diagram illustrating the photoinduced nanophase segregation and the resulting N_{re}–Sm A transition. The azo molecules in their *trans* form having a rod shape can permeate freely, just like the host molecules, thereby allowing the formation of the reentrant phase. However, in the photo-driven *cis* form, the azo molecules with their bent shape are nanophase-segregated, a situation less conducive for the formation of the N_{re} phase, leading to the appearance and stabilization of the Sm A phase.

other words, that it leads to a transition to a less-ordered state. But when the experiment is done in the N_{re} phase, we observe a novel feature: The N_{re} phase transforms into the Sm A phase i.e., to a more ordered state. To explain this feature, we make use of the photo-controlled nanophase segregation mechanism[27]. The principle behind this nanophase segregation (see Figure 8) is that when the UV radiation is absent the azo molecules are in their *trans* form with a rod-like shape and are therefore easily accommodated into the smectic layers. But in the photoinduced *cis* form, the molecules assume a bent shape and therefore get expelled from within the layers and occupy the region between the layers.

The frustrated spin-gas model developed by Berker and collaborators[28] 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 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 favoured 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. In the case of photoinduced N–I transition, a mere reorientation of the host molecules followed by the shape change of the guest molecules is sufficient to bring about the transition. In contrast, the creation of the UV radiation-driven, nanophase-segregated regions or the recovery of the uniform structure of Sm A/N_{re} phase requires physical movement of the azo molecules, obviously taking a longer period. For the Sm A–N transition, the nematic phase occurs at a higher temperature than the Sm A phase. Also, as the photoinduced shift in the Sm A–N transition temperature is small compared to that for the other two transitions, one can presume that the tendency to form nanophase segregation decreases as the transition is approached. The N_{re} phase occurs at a lower temperature than the Sm A phase and thus thermal fluctuations, which will always try to mimic a higher-temperature situation, cannot lead to the appearance of the N_{re} phase. Perhaps the only way for recovery is for azo molecules in the segregated region to slip back physically into the smectic layers of host molecules and create frustration in packing, which will result in the appearance of the N_{re} phase.

A system with bent-core molecules

In 1975, Meyer *et al.*[29] showed that tilted, smectic liquid crystalline phases in materials composed of chiral molecules exhibit a spontaneous polarization. Since then, considerable theoretical and experimental efforts have been put forth on such ferroelectric liquid crystals[30]. Till recently, a prerequisite to observe ferroelectricity in liquid crystals was the presence of chiral molecules. But a few years ago ferroelectricity was reported in a mesophase referred to as B_2 phase, exhibited by an achiral system with bent-core or banana-shaped molecules[31,32]. The origin of spontaneous polarization in these systems is believed to be a combination of the following factors. These molecules have a highly polar character, are arranged in smectic layers in such a way that the dipoles point along a common direction within the layer and are tilted with respect to the layer normal. These factors can give rise to chiral layer symmetry, although the molecules themselves are achiral. Recent investigations have clearly established that the B_2 phase is antiferroelectric[33]. Representative

current response traces obtained at a constant reduced temperature of $T_c - 4°C$ (T_c is the B_2–Iso transition temperature), before (trace a), during the process of illumination with UV radiation (trace (b) as well as after switching the radiation OFF (trace (c)), are given in Figure 9. (The last mentioned measurements were done keeping the sample in the dark.) Evidently, UV radiation causes both the peaks to decrease in height as well as in area (traces (a) and (b)), thus decreasing the P_s value. If the radiation is switched OFF, the process is reversed and the original P_s value is recovered (see trace (c)). The decrease and recovery in P_s are highly reproducible and can be repeatedly observed by turning the radiation ON and OFF. The temporal variation of P_s and the response time τ obtained at a reduced temperature of $T_c - 4°C$ (where T_c is the B_2–isotropic transition temperature) are shown in Figure 10. Now, we will explore the possible causes for the observed behaviour of P_s. Changes in the magnitude of different properties due to photoisomerization of azobenzene molecules have been attributed to one of the following phenomena. The first of these is the most commonly observed[10,11,21] shift (generally lowering) in the transition temperature, which we have discussed earlier. However, it should be mentioned that the UV-induced shift in the transition temperature in this case is extremely small, being about 0.2°C. The reason for such a small shift, unlike for the N–I transition, could be the strong first-order character of the B_2–isotropic transition. From the temperature dependence of P_s it is noted that at $T_c - 4°C$, a shift of 0.2°C would lower the P_s value by about 70 $\mu C/m^2$. However, the decrease seen at this reduced temperature due to photoisomerization is much larger (see Figure 10), a feature which is true at all temperatures for which measure-

ments have been done. Hence, the magnitude of the opto-polarization effect observed here is too large to be explained by the shift in the transition temperature of the B_2–isotropic transition.

The second phenomenon in photoisomerization processes, particularly applicable to layered smectic phases is the 'nanophase segregation' mechanism discussed previously. This mechanism has also been invoked to explain results obtained on classical ferroelectric chiral smectic C* liquid crystals, in which one of the chiral constituents is a photoactive azobenzene derivative. The chiral photoactive molecules in the $trans$ configuration are incorporated into the smectic C layers and contribute to the overall ferroelectric polarization of the material. On $trans$–cis photoisomerization, the cis isomers are expelled from the layers (nanophase segregation) and their contribution to the ferroelectric polarization decreases, thereby lowering
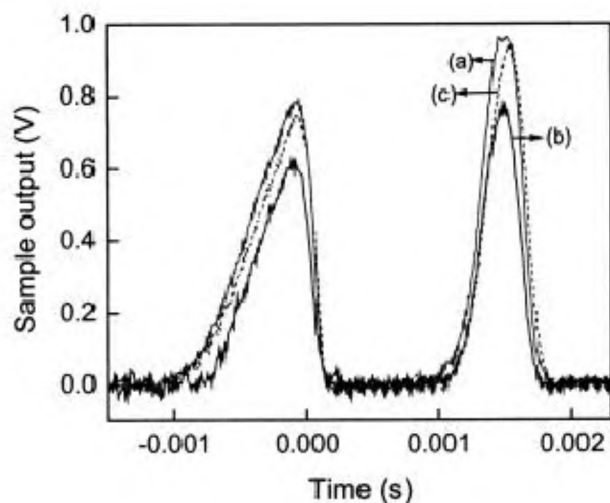

Figure 9. Current response traces when a triangular wave field is applied to the sample at a fixed temperature and exhibiting a B_2 phase, obtained before (a), during the process of illumination with UV radiation (b) and after switching the radiation OFF (c). Notice that on UV illumination, the height of the response (trace (b)) decreases, but recovers after the radiation is switched OFF (trace (c)).
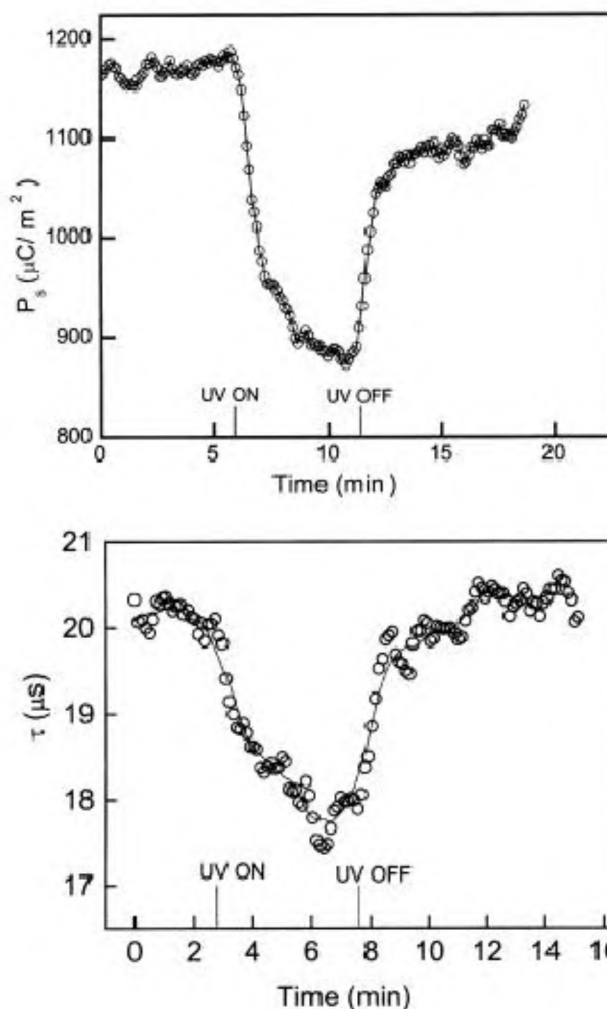
Figure 10. Temporal variation of P_s and the response time τ upon UV illumination and subsequent switch OFF. The sample is kept at 4°C below the B_2–Iso transition temperature. The time required for substantial change in the value seems to be comparable for both illumination and switch OFF processes.
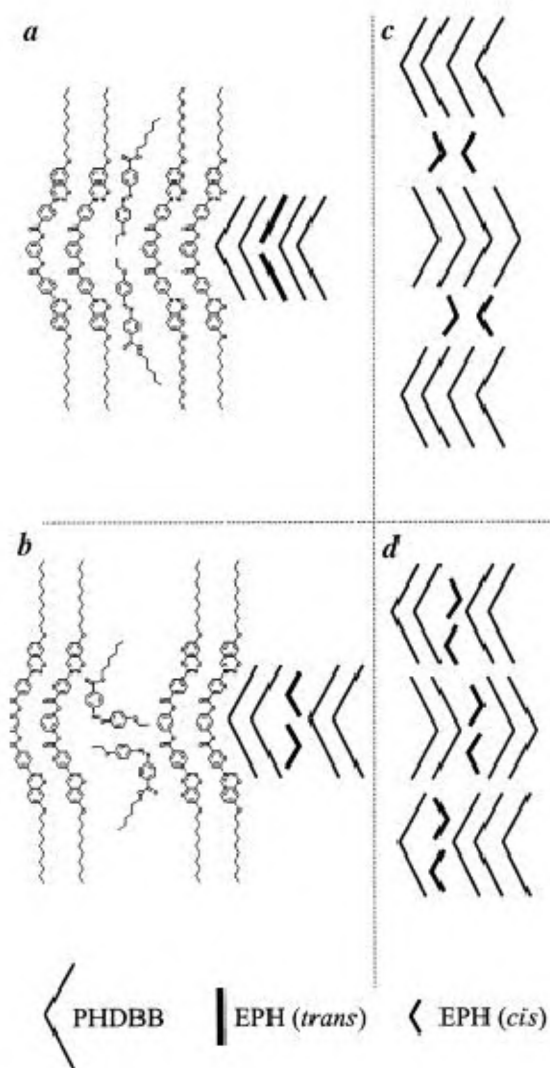
Figure 11. Schematic diagram illustrating (*a*) disposition of the PHDBB (bent structure with thin lines) and EPH (linear thick lines) molecules before UV illumination. A pair of EPH molecules that are in the *trans* confirmation can stack in the fashion shown, as they have a much shorter length compared to the PHDBB molecule and (*b*) bent conformation of the EPH molecules in the *cis* form induced by the UV radiation. (*c*) and (*d*), Two possible mechanisms for the observed decrease in P_s values upon UV illumination. All the illustrations show the view in the polar plane, i.e. the plane containing the two-fold symmetry axis and the layer normal.

the overall value of polarization. Now, to apply this mechanism to the results of the present study, let us consider the arrangement of the non-photoactive, bent-core molecules (hereafter referred to as PHDBB) and the photoactive EPH molecules in a layer of the B_2 phase. Schematic representations of such arrangements when the EPH molecule is in the *trans* as well as in the *cis* configurations are shown in Figure 11 *a* and *b* respectively. The configurations of the molecules have been obtained by running an energy-minimization process (MM2 package, Cambridge Software) on the chemical structure of the individual molecule. This procedure yields the following

values for the lengths of the molecules: PHDBB – 5.43 nm, EPH (*trans*) – 2.41 nm and EPH (*cis*) – 1.5 nm. Notice that the length of PHDBB is more than double that of even the *trans* form of EPH. Also to be noted is that the *cis* form of EPH, due to its bent nature, is about 30% smaller than the *trans* form. Keeping these features in mind, we can imagine the following scenario. In the absence of UV radiation, the azobenzene EPH molecules are in the *trans* form, with rod-like shape. Being about half the length of PHDBB, two EPH molecules can stack as shown in Figure 11 *a*, occupying the space between two neighbouring PHDBB molecules within the same layer. When a pair of *trans* EPH molecules is arranged in this fashion, it also supports the polar character of the smectic layer. On photoisomerization, the EPH molecules also assume a bent shape (*cis* form). If nanophase segregation occurs like in the case of chiral smectic C* phase mentioned above, the *cis* EPH molecules are expelled from within the smectic layer and occupy the region between two smectic layers (Figure 11 *c*). This would result in an apparent increase in the volume of the system and therefore a reduction in the dipole moment/volume. As a consequence, the measured P_s would be lower than before UV illumination. This qualitatively accounts for the observed reduction in the P_s values. However, from X-ray measurements in systems having EPH or similar azobenzene molecules, upon UV illumination the maximum observed increase in layer spacing is about 0.05 nm[34]. Thus the volume change due to this increase in layer spacing caused by the nanophase segregation would be only 1% of the actual volume. Consequently, the decrease in dipole moment/unit volume and therefore P_s should be of the same order. Evidently, the measured P_s change is much larger, perhaps making the nanophase segregation mechanism the less probable cause for the results seen here.

An alternative mechanism that is possible is shown in Figure 11 *d*. In this scenario, the EPH molecules will remain in the smectic layer, even in the presence of the UV radiation. As it does not cost additional volume, unlike for the host bent core PHDBB molecules, the polar axis of the bent EPH molecules within one layer could point in either direction compared to the polar axis of the smectic layer. Due to the antiferroelectric character of such an arrangement, this would reduce the polar character of the layer and therefore decrease the P_s values. In the tilt plane, i.e. the plane normal to two-fold symmetry axis, the two *cis* molecules within one smectic layer can adopt a synclinic geometry. The disposition of the EPH molecules in this manner can perhaps be thought of as a 'local racemization'. Studies on the dynamics of the system also support this idea.

In summary, we have discussed some examples where illumination of the sample with light of certain wavelength leads to interesting results. These studies indicate that light can mimic the role played by a thermodynamic parameter like temperature, thus providing a new tool to in-

vestigate phase transitions and the associated critical phenomena. Ongoing experiments both at our lab and elsewhere are expected to provide a better insight into the quantitative aspects of photoinduced phase transitions.

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