Chapter 3

Electric-field-dictated phase diagram and accelerated dynamics of a reentrant nematic liquid crystal under photostimulation

Overview

In a system consisting of photoactive molecules that exhibit light-driven isomerization transformations, actinic light can diminish or enhance ordering to the extent that transitions from the equilibrium to a more disordered phase can be brought about isothermally. This feature enables light to be used as a thermodynamic-like parameter to investigate phase behavior and adds another dimension to the studies owing to the nonequilibrium character of the isothermal transitions. Experiments which exploit the combination of two recent findings, viz., an electric field can accelerate the return to the nematic liquid crystalline phase from a photodriven isotropic phase; and in a reentrant mesogen, the photoinduced phase can be more ordered, have been carried out. Unique temperature-electric-field phase diagrams of a liquid crystal exhibiting isotropic-nematic-smectic $A$-reentrant nematic sequence have been mapped out using light transmission as a probe.

The results are published in Phys. Rev. E., 80, 021703 (2009).
3.1 Introduction

A system is said to undergo a reentrant phase transition, if a monotonic variation in any thermodynamic field such as temperature or pressure results in two or more phase changes and finally attains a state which is macroscopically similar to the initial state. This phenomenon is exhibited by diverse condensed-matter systems [1-8]. When a typical liquid crystal (LC) material is cooled from the isotropic (I) phase, the usual sequence of transitions is I-N-Sm-Cr, where N, Sm and Cr represent nematic, smectic and crystal phases respectively. In other words the ordering of the system increases or symmetry decreases as the sample is cooled. The first exception to this behavior was discovered in 1975 by Cladis with the observation of a N-SmA-Nre sequence, where Nre represents the reentrant nematic phase, in the temperature-concentration plane of a binary system [9], and subsequently in the temperature-pressure plane for a pure compound [10]. Soon such a feature was reported for single component systems at room pressure [11, 12]. LC systems especially have proved to be very rich in exhibiting the phenomenon of reentrance involving a diverse number of phase transitions, namely, nematic-smectic A (including double [12] and triple [13, 14] reentrant sequences), ferroelectric-ferrielectric, ferrielectric-antiferroelectric smectics [15], twist grain boundary-smectic A [16, 17], synclinic-anticlinic smectic C [18], uniaxial-biaxial nematic [19], and uniaxial-biaxial smectic A [20] transformations. Recently, it was demonstrated that a third, albeit nonthermodynamic parameter, viz., actinic light can be employed to induce the reentrant nematic sequence in a system that does not exhibit it in the normal thermal process [21, 22]. The principle behind this light-induced phase transition is the phenomenon of reversible photoinduced shape transformation of chromophoric molecules, such as azobenzenes, a topic that has been extensively studied [23, 24] and outlined in the following.

The azobenzene molecule has been particularly attractive for photoinduced phase transitions due to its easily accomplished geometric isomerization about the azo bond, converting the molecule from the E to the Z isomer. For this reason it has been employed for
altering molecular, macroscopic, and even biological properties [25]. Upon UV irradiation, wavelength of \(~360\) nm, corresponding to the \(\pi - \pi^*\) band of the azo group, the energetically more stable E configuration with an elongated rodlike molecular form changes into the bent Z configuration. The reverse transformation can be brought about by illuminating with visible light of \(~450\) 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 (TBR). A schematic representation of the photoisomerization process is shown in Figure 3.1. The liquid crystalline phase is stabilized by the rodlike E form, but is destabilized by

![Figure 3.1: Schematic representation of the phenomenon of photoisomerization showing that while the isomerization from the E to the Z form is driven by the UV radiation, the reverse process can either be stimulated by the blue (436 nm) light, or occur spontaneously by a process referred to as thermal back relaxation.](image)

the bent Z form. Therefore, the E-Z change generally leads to a diminution of the transition temperature, which if substantial causes an isothermal photoinduced transition from a liquid crystalline phase, say, the nematic phase to the isotropic phase. Such light-driven transitions have been observed for a variety of systems exhibiting different phases [26-28]. A general feature of such transformations is that the photoinduced phase would be more disordered than the equilibrium one. An exception to such an established principle was
reported in a system where the photoisomerization drives the system to the layered SmA phase from the disordered reentrant nematic present under equilibrium conditions [21, 29]. The time taken for the phase transition to take place following the isomerization of the photoreactive molecules is of significant interest not only from a basic point of view, but it also has paramount significance especially for applications such as storage devices [30, 31]. For the photoinduced nematic-isotropic (N-I) transition the time $\tau_{ON}$ required for the change following the E-Z isomerization to occur, the typical duration required is of the order of a few minutes with a conventional type of UV source [29]. In contrast, $\tau_{OFF}$, the thermal back relaxation time restoring the N phase, takes much longer, at least an order of magnitude more. In fact, it is this longer $\tau_{OFF}$ that puts a limitation on the time response of dynamic optical devices. Although illuminating the sample with longer wavelength (around 420 nm) light hastens the reverse isomerization, the process however increases the complexity of the system by the requirement of a second light source and the associated problems of having the aligning optics. In this context the recent development [32] that an applied electric field can accelerate the relaxation to the equilibrium from the photodriven state, is important. It was found that the acceleration is as fast as that could be achieved by the longer wavelength light and the actual response time can be fine tuned by controlling the magnitude of the electric field. This feature further provides a new dimension to map the phase diagrams of the photo induced transitions as a function of electric field. It should be emphasized that the Z isomers are non-equilibrium structures and therefore the isothermal photodriven transformations occurring due to their presence also have nonequilibrium nature. In contrast to equilibrium cases, nonequilibrium phase transitions are yet to be understood, owing to the sheer diversity of systems which exhibit such transformations involving physical, chemical, biological, and even sociological situations [33-36].
3.2 Experimental

3.2.1 Materials

The host liquid crystalline material is a binary mixture of the eighth (C₈) and the tenth (C₁₀) homologues of the series 4-(2-cyanoethyl) phenyl-4-(alkoxy)benzoate. While C₁₀ exhibits the I-SmA-SmC sequence, C₈ shows only the I-N transition [37]. The UV active dopant 4-(4-ethoxy phenylazo) phenyl hexanoate (EPH) from Kodak Organics, also liquid crystalline exhibiting the N phase, acts as the guest compound. The chemical structures and transition temperatures of the host as well as the guest materials are given in Table 3.1.

The binary phase diagram of the C₈/C₁₀ host system exhibiting the reentrant phenomenon, first reported by Pelzl and Demus [37], is reproduced in Figure 3.2. As seen from this diagram the Nₑ phase occurs over a reasonably large concentration range of 50-80 % of C₁₀. As the primary interest in the current investigations was the effect of the electric field on the photodriven transition involving the Nₑ and SmA phases we chose a particular concentration of C₈:C₁₀ = 30:70 host mixture which as seen from Figure 3.3 has a stabilized thermal range of the Nₑ as well. Addition of EPH at low concentrations to this host system hardly affects the phase behavior, as has been previously demonstrated (see Figure 3.3),

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structures</th>
<th>Transition temperatures</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₈</td>
<td>C₈H₁₇OCOOC-CH₂CH₂CN</td>
<td>I 66°C N 55.5°C Cr</td>
</tr>
<tr>
<td>C₁₀</td>
<td>C₁₀H₂₁OCOOC-CH₂CH₂CN</td>
<td>I 66°C SmA 60°C (SmC 33°C) Cr</td>
</tr>
<tr>
<td>EPH</td>
<td>C₉H₁₁COO-N=N-OC₂H₅</td>
<td>I 129.3°C N 74.4°C Cr</td>
</tr>
</tbody>
</table>

Table 3.1: The chemical structures and transition temperatures of the host and guest materials.
with the temperature ranges of all the three mesophases of interest, viz., N, SmA and N$_{re}$ being large enough for the present experiments. It may be mentioned here that the host system is very stable even under long duration of UV illumination. Also, in combination with EPH, this system has earlier been used to realize a rich variety of photodriven features, including the first observation of dynamic self assembly of the SmA phase. All the results described in this Chapter have been obtained with a guest (EPH) concentration of 3 % (by weight) in the above mentioned host material. The transition temperature exhibited by this guest-host ternary mixture is shown in Figure 3.3

Figure 3.2: The binary phase diagram of the C$_8$/C$_{10}$ host system reported by Pelzl and Demus [37]. Here is, N, S$_A$, N$_{re}$, and S$_C$ refer to the isotropic, nematic, smectic A, reentrant nematic, and smectic C phases, respectively.
3.2.2 Absorption measurements

The absorption spectrum for pure EPH was obtained using 0.01 % concentration solution, prepared using 1,4 dioxane, taken in a 1 cm path length quartz cell. The background-subtracted data is shown in Figure 3.4. While the peak at 365 nm is associated with the \( \pi - \pi^* \) transition of the E form, the weaker one at 450 nm is due to the \( n-\pi^* \) transition of the Z isomer of the EPH molecule. These peaks get retained in the ternary mixture of EPH with the host material.

3.2.3 Cell fabrication

The liquid crystal cell consisted of a pair of optically flat glass plates, separated by Mylar spacers of known thickness, and glued together. The cell gap, typically in the range of 10-12 \( \mu \)m, was determined using an interferometric technique by employing a UV-vis spectrom-
Figure 3.4: Diagram showing two clear absorption maxima at 365 and 450 nm corresponding to the $\pi - \pi^*$ transition of the E form and the $n-\pi^*$ transition of Z isomers, respectively of the guest photoactive EPH compound.

In order to obtain good transmitted intensity change at the transitions involving the smectic and the two nematic phases, the cell yielding a hybrid geometry was used. This was realized by having planar alignment of the molecules at one surface of the cell, and homeotropic alignment at the other. To obtain planar alignment the glass plate was spin coated (coating unit: Single Wafer Spin Processor, Laurell Technologies Corporation, Model WS-400A-6NPP/LITE) with a pre-polymer (PI-Kit, E-Merck) and cured at 300 °C for 3 hours yielding in situ polymerization of the pre-polymer; the polymer surface was then rubbed unidirectionally. To obtain the homeotropic alignment, the other glass plate was coated with a thin film of octadecyl trimethoxy silane (ODSE) by dip-coating the cleaned glass plate with a very dilute solution of ODSE in distilled water and cured at 150 °C for 3 hours.
3.2.4 Methods

The schematic diagram of the pump-probe beam setup used for the static and dynamic measurements both in the presence and in the absence of UV light are presented in Figure 3.5. A He-Ne laser (Spectra-Physics) beam served as the probe. The laser light transmitted through the sample was detected using a photodiode (OSI-5) in conjunction with a trans-impedance amplifier. The output of the amplifier was measured with the help of digital multimeter (Keithley DMM 2000). The UV radiation was obtained from an intensity-stabilized UV source equipped with a fiber-optic guide (Hamamatsu L7212-01). A narrow bandwidth UV-pass visible-cut filter (UG-11) was employed to select the desired radiation of 365 nm. An additional IR block filter (Mettler-Toledo) was inserted just before the

Figure 3.5: Schematic diagram of the pump-probe setup for light transmission and photoisomerization experiments, also showing the possibility of measuring simultaneously the dielectric properties.
sample to prevent/minimize any heat radiation arising from the UV source. $I_{uv}$, the actual power of the radiation after 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. The hot stage in which the sample was mounted, and the multimeter were interfaced to a PC for data acquisition through a user-written code in Visual Basic. The setup also permitted the simultaneous acquisition of the dielectric properties of the medium using an impedance analyzer (HP 4194A) connected to the electrical leads of the sample cell.

### 3.3 Results and Discussion

#### 3.3.1 Temperature-dependent measurements and phase diagram

The intensity of the probe laser beam ($I_{\text{laser}}$) transmitted through the sample kept between crossed polarizers provides a convenient method to locate the phase transitions in liquid crystalline systems. The birefringence and/or textural changes across the phases result in abrupt changes in $I_{\text{laser}}$ indicating phase transformations and can therefore be used to map the phase diagrams. Temperature dependent $I_{\text{laser}}$ scans under different conditions of no UV, with UV, and simultaneous presence of UV light and an applied DC voltage are employed for the purpose. Figure 3.6 shows such raw intensity scans obtained under these different conditions. The magnitude of the UV light used was very low, being $I_{UV} = 100 \mu\text{W/cm}^2$. Therefore, in addition to the precautions taken - mentioned in §3.2.4 - this low magnitude UV beam ensured that the local heating effects could be neglected. The first feature to be noted in these diagrams is that all the three transitions, I-N, N-SmA, and SmA-N$_{re}$, exhibit a lowering of the transition temperature upon photoisomerization driven by the UV illumination. Such a diminution in transition temperature has been well documented in literature primarily for the I-N transition [28]. Figure 3.6 shows, however, that the magnitude of this shift in the transition temperature $\Delta T$ is least for the N-SmA transition, intermediate for I-N and maximum for the SmA-N$_{re}$ transformation. Such an
enhanced destabilization of the $N_{re}$ phase has been observed earlier [29]. It should be noted that when UV-illuminated, the SmA and N phases get photodriven to the N and I phases respectively, i.e., become more disordered. In contrast, photoisomerization in the $N_{re}$ phase results in the system becoming more ordered, transforming to the SmA phase. This feature has been argued [29] to be due to a combination of the photodriven nanophase segregation [38] and the frustrated spin-gas situation [39]. Owing to the fact that the concentration of
the Z isomers can affect the magnitude of $\Delta T$, the intensity of the UV radiation, $I_{UV}$, is a control parameter. Since a longer wavelength ($\sim 450$ nm) facilitates a stimulated recovery of the E isomers, its intensity can be the second control parameter. Very recently [32], a new control parameter, viz., the magnitude of the electric field, has been discovered to strongly influence the extent of the photostimulated shift in the I-N transition temperature. This study also found that the effect is the strongest for dc field and drastically diminishes as the frequency of the applied field is increased. Hence, the present measurements were performed employing only dc voltages.

The scans presented in the upper three panels of Figure 3.6 were obtained by applying the mentioned voltages while simultaneously illuminating the sample with UV radiation. Not only I-N, but the other two transitions also show that application of the electric field reduces the diminution in the transition temperature effect imparted by the UV radiation through photoisomerization demonstrating that the electric field influence is universal, and not particular to the type of transition. In addition to obtaining the signatures of the transition through transmitted intensity changes, we performed (to get a further confirmation on the transition temperatures) dielectric measurements under no UV, no electric field condition, as a representative case. These measurements were carried out simultaneously with the light transmission measurements. Before we discuss this data, certain points need to be mentioned. The employed material has a positive dielectric anisotropy, i.e., $\Delta \varepsilon = \varepsilon_\parallel - \varepsilon_\perp > 0$, where $\varepsilon_\parallel$ and $\varepsilon_\perp$ represent the dielectric constants parallel and perpendicular to the director, respectively. For such a material the nematic director couples to the electric field and if the voltage is large enough it gets oriented along the field direction. Owing to the hybrid geometry employed, when no voltage is applied the molecules are parallel to the substrate at one surface and perpendicular to it at the other. Therefore, at least in the two nematic phases, the configuration would be that of a uniform bend deformation in the absence (and also at values below a threshold) of the electric field. In the SmA phase, the bend deformation would be restricted to small regions close to the substrate/s and the bulk.
would have some resultant orientation. Such a geometry was primarily employed since it is known to yield large changes in the transmitted light intensity across the N (or N$_{re}$)- SmA transition. As shown in Figure 3.7, the transitions can be clearly followed with dielectric data (obtained with a low probing voltage) as well, which not only confirm the identification of the transformations made using the light transmission data, but that the transition temperatures from the latter measurements are reliable. When the field is high enough a large majority of the molecules would be aligned along the field direction resulting in a near-uniform homeotropic alignment, and therefore the signatures of the transitions involving the SmA phase become much weaker, especially in the dielectric measurements, as shown in Figure 3.8. Perhaps, the formation of the chevrons results in sufficient intensity

Figure 3.7: Clear signatures of the transitions observed in the (a) capacitance as well as (b) transmitted intensity measurements, at matching temperature values.
Figure 3.8: Plot of $\varepsilon$ vs. temperature with an applied voltage of 15 V. It is seen that the signatures of the transitions involving are weak.

changes that helps in keeping track of the transitions. These features explain a smaller and more rounded variation in intensity for the 20 V case depicted in Figure 3.6.

Figure 3.9 shows the unique temperature-electric field phase diagram realized from measurements without and with UV illumination. It should be emphasized that the electric field data (solid lines joining the data points) represent the influence of the field in a dynamic equilibrium state, since the UV light is kept on and therefore the system driven away from the equilibrium situations due to the presence of the Z isomers. The large influence of photoisomerization on the N$_{re}$-SmA transition and the varied influences of the electric field on the different transitions are clearly seen. The interesting features are that (i) when the voltage is 20 V (field of $\sim$2 V/µm) the photodriven reduction in the transition temperatures is nearly annulled; (ii) the rate at which such an annulment takes place is not the same for the different transitions; and (iii) whereas the phase lines obtained without UV (dashed lines in Figure 3.9) represent the equilibrium transitions, the boundaries realized with UV illumination - with or without voltage (solid lines through the data sets) - are
nonequilibrium situations. This is due to the fact that the Z isomers responsible for such a feature revert eventually to the E form spontaneously. Therefore, the actual coordinates of the “with UV” phase lines are dependent on various extrinsic parameters such as the amplitude of the UV intensity, the E-Z conversion efficiency of the photoactive guest molecule, etc. Thus the diagram given in Figure 3.9 is specific to an $I_{UV}$ value of 100 $\mu$W/cm$^2$ and the EPH molecule being used as a dopant. Figure 3.10 presents the UV-induced shift in the transition temperature as a function of the voltage for the different transitions. Assuming that the effect of the electric field is linear, the data were fit to a straight line (shown in Figure 3.10) and the slope values are I-N: 0.27 ±0.06, N-SmA: 0.12 ±0.01, SmA-N$_{re}$: 0.6 ±0.11, clearly the effect is the highest for the reentrant transition. We shall discuss
in a later section the possible reasons for the effect of the electric field in diminishing the influence of the photo-driven phenomenon.

Figure 3.10: *UV-induced shift in the transition temperature as a function of the applied voltage for the different transitions. The line drawn is the fit of the data to a straight line.*
3.3.2 Dynamics

ON process

Figure 3.11: The time-resolved variation in the transmitted intensity when the UV light is turned on at time=0 instant, keeping the sample temperature 2 °C below the respective equilibrium transition temperature. The notations used to define the delay (τ_{d1}) and the response (τ_{ON}) times are shown. It can be seen from the plot that the N_re-SmA transition has the sharpest response.

The photochemical transition, also referred to as the ON process here, triggered by the transformation of the equilibrium E to the photodriven Z conformer, is fast, occurring on the time scales of minutes in the case of the N-I transformation when a conventional UV source is used. To analyze the ON process quantitatively, in the present system, the transmitted intensity of the probe laser beam, I_{laser}, was monitored as a function of time. The temporal variations of I_{laser} when the photodriven N-I, SmA-N and N_re-SmA transitions take place from the equilibrium N, SmA, and N_re phases, respectively, are shown in Figure 3.11. During these measurements the sample temperature was maintained 2 °C below the respective equilibrium transitions. The signatures of these isothermal temporal transitions
Table 3.2: The delay and response times for the photostimulated change across the different transitions.

<table>
<thead>
<tr>
<th>Transition</th>
<th>$\tau_{d1}$ (s)</th>
<th>$\tau_{ON}$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-I</td>
<td>163</td>
<td>431</td>
</tr>
<tr>
<td>SmA-N&lt;sub&gt;re&lt;/sub&gt;</td>
<td>490</td>
<td>899</td>
</tr>
<tr>
<td>N&lt;sub&gt;re&lt;/sub&gt;-SmA</td>
<td>128</td>
<td>194</td>
</tr>
</tbody>
</table>

are quite similar to their thermal counterparts shown in Figure 3.6. However, the features appear as if on an expanded scale, perhaps owing to the fact, the temporal resolution is better than the thermal one in these experiments. The fact that such temporal scans help in better resolving the features associated with the transition, than the thermal scans has been earlier seen in the dielectric measurements across a photoinduced transformation of an aerosil-nematic system [40]. Notice that, for all the temporal transitions, the sample response starts only after an initial delay from the instant at which the UV radiation is switched on. This is quantified in terms of a delay time $\tau_{d1}$. A second characteristic time is the actual response itself, which sets in after the delay, and quantified by $\tau_{ON}$ given by the time difference between the instant at which the response gets completed and the end of the delay. $\tau_{d1}$ and $\tau_{ON}$ values determined for the different transitions are given in Table 3.2. It is seen that both $\tau_{d1}$ and $\tau_{ON}$ are smallest (fastest dynamics) for the N<sub>re</sub>-SmA transition, largest for the SmA-N, and intermediate for the N-I transition. Such a feature was indeed noticed earlier by our group [29]. Specifically the delay and response times are about four times faster for the N<sub>re</sub>-SmA transition, than for the SmA-N transition.

The advantage of the higher temporal resolution, mentioned above, is especially seen in the case of the profile for the SmA-N (Figure 3.11 (b)). The photo-driven transformation from the SmA to the N phase appears to occur in two steps. As we shall see later this feature is seen in the back relaxation process also. If this is indeed the transmitted intensity characteristic of the SmA-N transition, it should have been observed for the N<sub>re</sub>-SmA transition also. The fact that Figure 3.11 (c) does not show such a feature could be owing to the fact that the time scales for the latter transformation are much smaller than
for the SmA-N transition, a point that will be revisited while discussing the back relaxation process. We shall defer the discussion on the possible causes for the faster dynamics of the $N_{re}$-SmA transition (quicker disappearance of the $N_{re}$ phase to the SmA phase) to a later section, except to comment that even a small perturbation is enough to drive the $N_{re}$ phase to a layered structure, thus achieving a faster dynamics.

**Thermal back relaxation (off) process**

Figure 3.12: The time-resolved variation in the transmitted intensity after the UV illumination is turned off, while the sample temperature is maintained 2 °C below the respective equilibrium transition temperature. The notations used to define the delay ($\tau_{el}$) and the response ($\tau_{off}$) times are shown. The thermal back relaxation process for the recovery of the $N_{re}$ phase (SmA-$N_{re}$ transition) takes much longer than in the case of the other two phases.

The spontaneous thermal back relaxation (TBR) of the Z isomer to the equilibrium E isomer is generally a slow process. This is especially true for the azobenzene molecule (In solution, for a linear alkoxy-substituted azobenzene molecule the TBR could be a few days [See e.g., Ref [41]]). Consequently the relaxation from the photo-driven phase to the
equilibrium one is also slow. It is also known that the time scale of this process depends on many factors. For example, in the case of the photo-driven N-I transition it has been shown that the timescale is non-monotonic with the reduced temperature (with respect to the equilibrium $T_{IN}$), at which the UV-illumination is done in the N phase [42]. The confining environment of the sample is also known to influence the TBR process [43]. The parity and length of the spacer of a dimeric azobenzene molecule [44] and applied pressure [45] are other factors studied. In the previous section, we have already seen that the electric field can significantly diminish the response time of the photochemical transition. Now we look at the effect of the electric field on the TBR process. The kinetics of this process was also monitored using temporal measurements of the transmitted intensity. Figures 3.12 (a)-(c) display the TBR process from the photodriven I, N, and SmA to the equilibrium N, SmA, and $N_{re}$ phases, respectively. Here again, we analyze the data in terms of two time scales: a delay time $\tau_{d2}$ and a response time $\tau_{OFF}$, defined in a fashion similar to that for the ON process. It is obvious from the figures that whereas the durations have comparable values for the I-N and N-SmA transitions, the recovery of the $N_{re}$ phase occurs with nearly an order of magnitude longer delay as well as the response times. Quantitative values of these durations are shown in Table 3.3. The values for the delay seems ($\tau_{d2}$) to suggest that although the variation is large, it could simply be a temperature-dependent one, being least for I-N and maximum for $N_{re}$-SmA transition. However, it was noted that the Z isomer concentration obtained from optical absorption measurements increases by about 1.7 times over the temperature range covering the isotropic to $N_{re}$ phase. Such an increase may just be owing to reduced thermal fluctuations lowering the back conversion of Z isomers. As it varies by more than an order of magnitude between the I and $N_{re}$ phases, $\tau_{d2}$ may be very sensitive to the Z isomer concentration. The response time $\tau_{OFF}$ also shows such a large increase from its value in the I phase to that in the $N_{re}$ phase, the minimum value seen was for the intermediate transition N-SmA.

In the previous section, we pointed out that the photochemical SmA-N transition
Table 3.3: The delay and response for the Thermal back relaxation for the three transitions.

<table>
<thead>
<tr>
<th>Transition</th>
<th>τ_{off} (s)</th>
<th>τ_{OFF}</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-I</td>
<td>526</td>
<td>1679</td>
</tr>
<tr>
<td>SmA-N</td>
<td>812</td>
<td>1102</td>
</tr>
<tr>
<td>N_{re}-SmA</td>
<td>9032</td>
<td>12950</td>
</tr>
</tbody>
</table>

shows an additional step in its response. Such a feature is seen in the TBR process also for not only the N-SmA, but the SmA-N_{re} transformation as well (Figure 3.12). The TBR profiles also make it clear that the step is always closer to the nematic phase involved. In the hybrid geometry wherein the two surfaces have antagonistic ordering requirements, the SmA-N transition is often mediated by a stage where stripe (or chevron) textures are observed. Such textures arise owing to the tendency of layer thinning and strong temperature dependence of the smectic penetration length [46]. Therefore the photoinduced transformation seen here provides a convenient way to study the kinetics of the formation of such a texture under equilibrium (thermal) as well as nonequilibrium (isothermal but photo-driven) conditions.

### 3.3.3 Possible causes for the photodriven N_{re}-SmA transition

We consider here the possible scenario for the photo-driven N_{re}-SmA transition to be a combination of the light-driven nanophase segregation and a frustrated spin gas situation. To begin with, it may be worth recalling that the formation of the smectic phase is considered to be due to the separation, on a microscopic scale, of the mesogenic cores and the flexible tails [See e.g., Ref [47]]. Now, let us look at the molecular scenarios for the photo-stimulated transformation of different phases. Since the host molecules (C_{8} and C_{10}) are non-photoactive, consider the situation for EPH molecules only, which have a rod-like shape in the E form, but after isomerization to the Z form assume a bent conformation. This shape change plays an important role as the rod-like E conformation supports the formation of the LC phase of the host, whereas the bent Z conformation destabilizes it and can even
cause isothermal transitions, generally lowering the order of the system. In fact, a mere
reorientation of the host molecules, followed by the shape change of the guest photoac-
tive molecules, is sufficient to bring about the N-I transition. In contrast, for the transition
between the N (or N_{re}) and the SmA phases, the structural change of the system is not
associated with a simple reorientation of the molecules, but rather a physical translation to
cater to the layer structure of the SmA phase.

**Light-driven nanophase segregation**

To analyze the increase in the smectic layer spacing caused by photoisomerization of
azobenzene molecules [48] in a host environment of strongly polar molecules, structurally
not different from the ones used in the current study, the Boulder group [38] performed
molecular dynamics simulations and proposed a **“nano-phase segregation”** mechanism.
The principle behind this mechanism, schematically shown in Figure 3.13, is essentially
that along the layer normal direction, the position of the photoactive molecules can depend
on its conformation: the $E$ form with its rod-like shape is easily accommodated inside the
smectic layers, but the photoisomerized bent $Z$ form is expelled from within the layers oc-
cupying a separate (segregated) region between the neighboring layers of host molecules.
Such a segregation results in a small increase in the overall layer spacing value.

**Frustrated spin-gas model**

This model (although a 2-dimensional one) [49-51], proposed for mesophases of polar
molecules, has been especially successful in explaining the appearance of reentrant nematic
and smectic phases. Like other microscopic theories it incorporates intermolecular steric
hindrance and van der Waals attraction but emphasizes the dipole-dipole forces, which are
important for strongly polar molecules. The main aspect of the model is that since the
system is close packed, on a local level it can be approximated with a triangular (hexago-
nal) structure. The system would favor antiparallel dimer formation in order to reduce the
Before UV
trans-azobenzene
cis-azobenzene
t
Cyano biphenyl

Figure 3.13: Representation for the nanophase segregation discussed in this work. The cyanobiphenyl molecules are represented as arrows. Before UV illumination the azobenzene molecules are present in the host smectic layers. After UV exposure, they are expelled to a region between the two smectic layers (representation taken from [38]).

dipolar contribution to the free energy, but when a third polar molecule comes near such a dimer, its orientation cannot be antiparallel to both the molecules in the dimer leading to frustration (Figure 3.14). When dipolar forces between two molecules cancel, a third dipole experiences no force and is free to permeate (diffuse) from layer to layer “frustrating” smectic order, favoring the reentrance of the nematic phase. On the other hand, if the cancellation is not complete a population of triplets stabilizes the smectic order through short-range dipolar interactions. Creating a series of ‘energy notches’ which stabilize a
particular triplet configuration (Figure 3.15), the model accounts for multiple reentrant sequences [52] involving a variety of smectic A phases (Figure 3.16).

Figure 3.15: The frustrated spin-gas model [39].

Figure 3.16: The theoretical P-T diagram in the spin-gas model for quadrupole reentrance.
Now we combine the above two ideas to explain the observed light-driven appearance of the smectic phase and the associated dynamics. Upon UV irradiation in the $N_{re}$ phase the guest azobenzene molecules in their bent form and the rod-like host molecules are not favored to mix with each other. Owing to this antipathy between the two, the azobenzene molecules are moved to a separate region along the director direction so as to reduce their interaction with the host molecules. Since the concentration of the azobenzene molecules is low, such a segregation takes place only on a molecular scale. This causes a difficulty for the permeation of the host molecules along the director direction, effectively creating a layered structure. The reduction in the freedom to permeate makes the situation less conducive for the system to remain in the $N_{re}$ phase resulting in the transformation to the SmA phase.

For the static case, the photodriven nanophase segregation mechanism manifests as an extended range for the smectic phase (Figure 3.6 and 3.9). In the dynamic sense, it makes the escape from the $N_{re}$ phase faster (faster $\tau_{ON}$ for the $N_{re}$-SmA phase) and retards the recovery of the $N_{re}$ phase (slower TBR). This tendency to avoid the $N_{re}$ phase is so strong that substantial effects are seen even for very low powers of the UV intensity. In principle, this argument should be applicable for the transition to the high temperature N phase. However, increase in thermal fluctuations can help to overcome this problem and when the illumination is done the SmA (at temperatures not far from the transition temperature for the non-irradiated case) can transform to the high temperature N phase. Owing to the competition between the thermal fluctuations to have the N phase and the effect of light to retain the SmA phase, the photoinduced shift in the transition temperature is small for the SmA-N transition as compared to those for the N-I and $N_{re}$-SmA transitions. The thermal fluctuation mechanism does not favor the retention of the SmA phase since such fluctuations always mimic a higher temperature situation, but the $N_{re}$ phase occurs at a temperature lower than the SmA phase. Of course, when the UV radiation is switched off, the reverse isomerization takes place and the photoactive molecules regain their rod-
Figure 3.17: Schematic representation of the molecular arrangements in the equilibrium (left panels) and photodriven (right panel) states.
like form, slip back into the layers of the host molecules (now their shape is comparable with that of the hosts) create frustration in packing allowing the recovery of the N<sub>re</sub> phase.

However, the nanophase segregation may still dominate given a chance, and perhaps is the cause for the faster $\tau_{\text{OFF}}$ seen for the N-SmA transition, in comparison to that for the I-N transition. As far as the dynamics is concerned, in the case of the relaxation of N from the photodriven I phase, shown in Figure 3.17 (a), the host molecules need to simply change their orientation. In the SmA-N case, the back relaxation from the fluid N phase to the one-dimensionally ordered state of SmA may be relatively easier, since the bent photoactive molecules are present in a fluid environment [Figure 3.17 (b)]. In contrast, the nanophase segregated SmA phase photodriven from the fluid N<sub>re</sub> phase has the bent azo molecules trapped in a one-dimensional periodic potential of the layered structure [Figure 3.17 (c)]. Therefore, the recovery of the N<sub>re</sub> phase can be visualized to be more complicated, involving first the transformation of the Z conformers to the E form and then sliding down to random positions along the director direction to get rid of layering. This may be the reason for the longer duration of TBR.

The presence of the azobenzene molecules, having weak polarity in the E configuration alters the process of interaction between the molecules. The triplet-molecule-induced frustration mentioned above could be reduced if one of the molecules in the triplet is a non-polar one [Figure 3.14 (a)]. A further parameter that should be considered is the charge transfer complex that can get formed [53] between strongly polar host molecules which act as acceptors and the weakly polar photoactive molecules as donors. However, the enhanced dipole moment, ~5 debye, of the Z isomer coupled with its packing constraint owing to the bent shape, perhaps plays a major role. 1. At least in the situation when segregation

---

1Azobenzene is a stereo-isomeric molecule. In the E form the two phenyl rings are located on opposite sides of the molecular axis along the azo-group. Owing to the high symmetry, in the planar E configuration this isomer exhibits a vanishingly small dipole moment. On the other hand, the Z form is three-dimensional due to steric effects between the phenyl rings, wherein the planes of the two rings are rotated by 60° with respect to each other. Further, the two lone pair of electrons located on the same side of the nitrogen double bond results in the Z isomer having a large dipole moment ~5 debye perpendicular to the molecular axis [54, 55].
occurs, the Z conformers would want to pack such that their bend direction is along the layer normal and therefore effectively interacting with the host polar molecules aiding the frustration [Figure 3.14 (b)] and consequent phase sequences in the medium. This may be the cause for the enhancement of the smectic range upon photoisomerization. Probably due to the low concentration of the photoactive molecules, these effects would be perturbative in nature.

3.3.4 Electric field effect

In this section we look at the influence of the electric field on the dynamics of the photoinduced transitions. The temporal variations in the transmitted intensity during the back relaxation process of the three transitions, upon application of voltage of different magnitudes are shown in Figure 3.18. A common feature seen for all the three transitions is that the presence of the electric field generally accelerates the recovery of the equilibrium situation and appears to have a limiting behavior at larger voltages. A second feature to be noted is that the profiles become sharper and change their appearance also with voltage. The former indicates that not only the delay time, but also the response time is affected by the voltage. The latter is due to the fact that the system has a positive dielectric anisotropy and therefore the molecules would want to get oriented along the field direction at sufficiently high voltages. The third feature is that, unlike for the I-N transition, the transitions associated with the SmA phase exhibit, in comparison to the no-voltage thermal back relaxation, longer delay as well as response times when the voltage applied is 1 V. This is seen clearly from the plots of $\tau_{d2}$ and $\tau_{OFF}$ as functions of the applied voltage [Figures 3.19 (a) and (b)].

The influence of the voltage is not only on the duration of the delay, but also on the response time. This is at variance with the behavior observed when a surface field is dominant, a point that will be discussed in the next section. For all the transitions, when the voltage is 20 V, $\tau_{d2}$ reduces to about 8 seconds, a value which is close to the time interval
Figure 3.18: Temporal behavior of the transmitted intensity as a function of the time elapsed since the UV is turned off and simultaneously the voltage of different magnitudes is turned on during the thermal back relaxation of the I-N, N-SmA, and SmA-N$_{re}$ transitions. It is seen from the diagram that with increasing voltage the process is hastened, with the effect being large for the SmA-N$_{re}$ transition. However, the 1 V data for the latter two transitions deviate from this behavior.

At which the data are collected (6 seconds). The effect of the electric field in diminishing $\tau_{d2}$ is maximum in the case of the N-SmA transition: even at a voltage of 5 V, it achieves this limiting value, as compared to the values of 55 and 909 seconds for the I-N and SmA-N$_{re}$ transitions. However, the largest acceleration in $\tau_{d2}$ is seen for the SmA-N$_{re}$ transition at larger voltages: at least three orders of magnitude. In contrast, the improvement in the response times upon application of voltage is more modest. In the absence of any theoretical model that describes the influence of an applied electric field on TBR, the data has been fitted, by excluding the value obtained for 1 V, to an exponential decay function.
This function fits the data reasonably well, as shown by the solid lines in the Figures 3.15 (a), and (b). The reason for both the features, namely, that the exponential form describes the data and that there is an increase in the value for 1 V, are not clear to us.

**Possible causes for the acceleration of the back relaxation with electric field**

First, it has to be recalled that when a photoresponsive liquid crystal material is confined in a polymer matrix a drastic diminution in the delay time (although not in the response time) has been observed for the recovery of the equilibrium N phase from the photoinduced I phase, an effect argued to be due to the presence of virtual surfaces at each liquid crystal-matrix interface [43]. The virtual surfaces create a surface field that is known to enhance the nematic ordering [56]. In the photoinduced isotropic case, the surface field produces a paranematic-like (in analogy with paramagnetism, the isotropic liquid with field induced
orientational order is called paranematic) situation and thus reduces the delay time in the return to the equilibrium N phase, but does not alter the process once the first nematic droplets appear, and consequently the response time is unaltered. This is the essential difference between such a virtual surface field and the external electric field of the present case, with the latter reducing the delay as well as the response times. Since the virtual surface field appeals to the molecular anchoring at such interfaces, the chemical nature of the host molecules also become important. In the electric field case, it has been previously observed [32] that strong as well as weakly polar host molecules get significantly influenced. This provides the first clue that perhaps the dielectric coupling between the host molecules and the electric field may not be a central factor. Also, as mentioned already (§3.3.1), the influence of the electric field is limited to dc and very low frequency electric fields, a behavior not expected if the dielectric coupling were to be the reason. These arguments are further supported by the fact that the other two transitions, N-SmA and SmA-Nre, behave essentially in the same fashion, although the difference in the order parameter across these transitions is not the nematic order parameter. Owing to the fact that the acceleration of the TBR process is seen in the equilibrium isotropic phase also [32] rules out a flexoelectric origin (an effect possible especially because of the bent shaped Z isomers). Prasad et al [32] also suggested that the electrode polarization arising under the experimental conditions used is perhaps the underlying cause for the acceleration of the TBR. While this may still be operative in the present case, the different magnitudes of acceleration for the three transitions and also the values being nonmonotonical with temperature indicates that there could be other influences also. An important outcome of these analyses is that perhaps the electric field directly influences the azobenzene molecule itself with the host molecules hardly playing any role.

A theoretical model that is under consideration in this regard is the density-functional-theory-based calculations by Füchsel et al [57], which proposes that it is possible to induce the isomerization of azobenzene in the gas phase by an electric field; this model has been
used to explain the electric-field-induced isomerization of an azobenzene derivative on the gold surface by a scanning tunnelling microscope (STM) tip [58, 59]. The theory considers that in the presence of an electric field, the potential-energy surface related to a reaction path can be deformed, thus leading to an effective lowering of the isomerization barrier, and is argued to depend on the orientation of an intrinsic dipole moment (if present) and also on the polarizability of the molecule. The essential point is that application of an electric field reduces the potential barrier between the E and Z isomers and therefore favors a quicker return of the photoactive molecule to the equilibrium form. Qualitatively this theory can explain the influence of the electric field on the static as well as dynamic properties that has been observed in our experiments. If the reduction of potential barrier is exponentially dependent on the applied voltage, then the form of the $\tau_{\text{OFF}}$ and $\tau_{d2}$ variation with voltage can be explained. A point that should however be emphasized is that the actual electric field in our experiments (even at the highest voltage of 20V) is three orders of magnitude smaller than in the STM experiments.

**Effect of the sign of the voltage on the back relaxation of the SmA-N$_{re}$ transition**

Finally, we describe an observation that the TBR features could be dependent on the sign of the applied voltage. Here the positive or negative sign is defined with respect to the electrode kept closest to the UV source. The transmitted intensity during the back relaxation process from the photoinduced SmA to the N$_{re}$ phase for positive and negative signs of the applied voltage of fixed magnitude of 5 V is presented in Figure 3.20. The asymmetric behavior with the sign of the voltage is obvious. In fact, both the delay and response times are nearly halved for the negative voltage in comparison with the positive voltage. Similar behavior is seen for the I-N and the N-SmA transitions also, with the actual changes in $\tau_{d2}$ and $\tau_{\text{OFF}}$ being different. These features are interesting since the density-functional theory [57] predicts an asymmetric response in the Z-E isomerization with the electric field, with the situations corresponding to the model, in which the intrinsic and induced dipole moments
Figure 3.20: Temporal dependence of the back relaxation process associated with the recovery of the $N_{re}$ phase from the photostimulated SmA phase, exhibiting asymmetric behavior for the opposite signs of the applied voltage, with the delay time ($\tau_d$) and response time ($\tau_{OFF}$) being shorter for the negative voltage.

3.4 Conclusions

The influence of an applied electric field on the phase diagram and dynamic properties of photostimulated transitions in a reentrant nematic liquid crystal have been discussed in this Chapter. The mapped out temperature-electric field phase diagrams reveal that the electric field influences all the transitions, but its effect is maximum on the equilibrium reentrant nematic to the photoinduced SmA transformation. The dynamics of both the photochemical and back relaxation processes across the different transitions have been studied under photoinduced nonequilibrium conditions. The electric field accelerates the thermal back re-
laxation in each case with the recovery of the reentrant phase being about 1000 times faster. The possible causes for the acceleration have been explored. A suggestion has also been made that the observed acceleration may be associated with the phenomenon predicted by the density-functional theory.
References


