

Kinetics of the thermal back relaxation time of the photoinduced nematic-isotropic transition

V. Jayalakshmi, Geetha G. Nair, and S. Krishna Prasad

Centre for Liquid Crystal Research, Jalahalli, Bangalore 560 013, India

(Received 3 November 2006; published 30 March 2007)

We report on the temperature dependence of the response time for the photochemical and thermal back relaxation processes observed in a material exhibiting a photostimulated, isothermal nematic-isotropic phase transition. It is found that the time required for the system to achieve the photostationary state as well as to recover the original state after photoirradiation with a uv beam is a smooth function of the absolute temperature of the sample, except in the vicinity of the transition. The duration of the recovery can be split into two parts: delay time and response time. Using a simple description based on the Maier-Saupe model, we show that the temperature dependence of the response time can be understood in terms of the order parameter excess between the equilibrium and photostimulated states.

DOI: [10.1103/PhysRevE.75.031710](https://doi.org/10.1103/PhysRevE.75.031710)

PACS number(s): 61.30.-v, 64.70.Md

I. INTRODUCTION

Isothermal phase transitions have been actively studied in a variety of systems [1–4], with special attention being paid to biological cases [5–8]. In liquid crystalline materials such transitions, induced by a beam of light of proper wavelength, have attracted significant interest in recent times [9]. The photoisomerization and associated shape change of certain molecules, e.g., azobenzene, is a convenient but powerful mechanism that has been exploited for such studies. The molecules containing the azobenzene moiety show reversible isomerization transformations upon irradiation with uv and visible light [10]. Upon absorption of uv light (typically 365 nm) the energetically more stable *E* configuration with an elongated rodlike molecular form, changes its shape to a bent bananalike *Z* configuration. The reverse transformation of the *Z* isomer into the *E* isomer can be brought about by irradiation with visible light (in the range of 400–500 nm) or spontaneously through a process termed “thermal back relaxation” even when the system is kept in the dark. When the azobenzene entities are integrated into a liquid crystalline medium, either by physical mixing with a nonphotoactive host system or by chemical bonding, the photoisomerization can lead to interesting effects. For example, owing to its rodlike shape the *E* form stabilizes the liquid crystalline phase but the photoinduced *Z* isomer with its bent shape acts like an impurity, destabilizing the phase, and can even lead to a photoinduced isothermal transition from a liquid crystalline phase, say, the nematic phase to the isotropic phase [11–15].

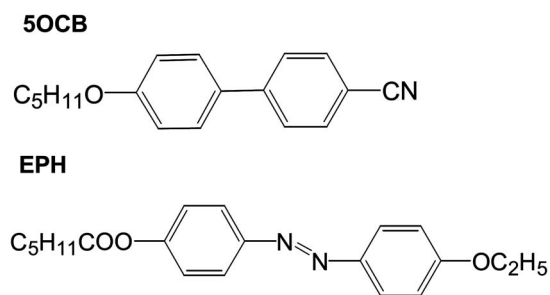
Such transitions can be considered to be nonequilibrium transitions given the fact that the systems are driven out of equilibrium by creating impurities (*Z* isomers) *in situ*. In fact, as happens for simple fluids [16], the driven phase—photodriven isotropic phase—appears no different from the equilibrium isotropic phase occurring above the nematic phase in the thermal cycle. The dynamics of the isothermal change involves the response for the system to (i) undergo the nematic to isotropic transition consequent to *E-Z* isomerization (which we refer to as the photochemical process) and (ii) recover the nematic phase through the thermal back relaxation mechanism (referred to as the thermal process). Systematic studies of the response time have been very few, but

it is known that the thermal process takes a much longer time than the photochemical process. Here we report simultaneous absorption and dielectric constant measurements which bring out the finer features, particularly of the thermal process. It is found that the dynamics of this process involves a delay and an actual response time. The temperature dependence of these time scales are found to be nontrivial and are seen to be related to the order parameter (orientational) excess between the equilibrium and photodriven situations.

II. EXPERIMENT

The liquid crystalline host compound is the nematogen 4-*n*-pentyloxy cyanobiphenyl (5OCB), procured from E-Merck. The uv-active guest compound is 4-(4'-ethoxyphenylazo)phenyl hexanoate (EPH). The mixture used in all the experiments discussed in this paper contains 2 wt % EPH in 5OCB. The molecular structures of the host and the guest compounds are given in Fig. 1. The isotropic-nematic (*I-N*) transition temperatures (T_{I-N}) obtained by polarizing microscopy observations for the two compounds as well as for the mixture are shown in the same figure.

The anisotropy of a physical property of liquid crystals, such as magnetic or electric susceptibility can be used to define the microscopic orientational order parameter *S*. Conversely, the magnitude of these anisotropies can be used to extract the magnitude of the orientational order in the medium. Hence, the measurement of the principal dielectric constants in the nematic phase can be employed to conveniently depict the orientational order parameter. For dielectric studies the samples were sandwiched between indium tin oxide- (ITO-)coated glass plates treated either with a polyimide solution and unidirectionally rubbed to get uniform planar alignment of the molecules or with a silane solution to get homeotropic alignment. The geometries thus corresponded to the dielectric constant perpendicular (ϵ_{\perp}) and parallel (ϵ_{\parallel}) to the nematic director, respectively. Dielectric constant measurements were done using an impedance analyzer (HP4194A). Data were collected at a fixed frequency of 10 kHz, which is well below the relaxation frequency of any dielectric mode for the materials under study. Photoabsor-



Sample	T_{I-N} (°C)
5OCB	66.8
EPH	128.1
2%EPH in 5OCB	68.7

FIG. 1. Molecular structures of the guest uv-active dopant EPH and host compound 5OCB. The transition temperatures obtained on cooling, for the guest and host compounds as well as for the 2 wt % mixture of EPH in 5OCB are also given.

balance measurements were carried out in the nematic and isotropic phases as a function of wavelength in the range of 300 to 700 nm, with the same ITO-coated glass cells mentioned above using a uv-visible spectrophotometer (Ocean Optics). The photoisomerization was brought about by employing the uv radiation from an intensity-stabilized uv source with a fiber-optic guide (Hamamatsu L7212-01) along with a uv bandpass filter (UG 11, Newport). 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, falling on the sample, and measured with a uv power meter (Hamamatsu, C6080-03) kept in the sample position was 1 mW/cm².

III. RESULTS AND DISCUSSION

The starting point of the present investigations is the data given in Fig. 2 showing the temperature dependence of the dielectric constants ϵ_{\parallel} and ϵ_{\perp} without and with uv irradiation. Under both conditions ϵ_{\parallel} increases and ϵ_{\perp} decreases at the $I-N$ transition, indicating that the dielectric anisotropy is positive. This feature in conjunction with the fact that the changes are substantial is characteristic of materials having a strongly polar group at one end of the molecule, like 5OCB, the host compound used here. For the mixture the value of the anisotropy decreases slightly as compared to that for pure 5OCB, owing to the fact that the guest compound EPH present in the mixture is a nonpolar compound. Also to be seen is that the values of both ϵ_{\parallel} and ϵ_{\perp} of the set obtained with uv approach those recorded under no-uv condition, deeper in the nematic phase. The important features to be noted, however, are the following. Upon uv illumination the transition temperature shifts by $\Delta T=6$ °C. This happens ow-

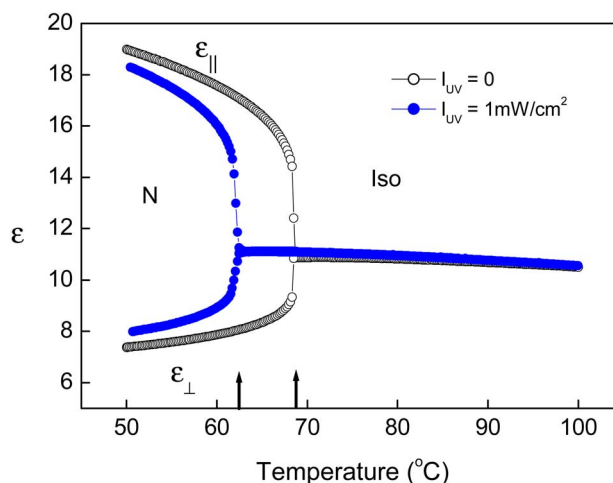


FIG. 2. (Color online) Temperature dependence of the two principal dielectric constants ϵ_{\parallel} and ϵ_{\perp} without (○) and with (●) the uv radiation. The two arrows indicate the transition temperatures $T_{no\ uv}$ and $T_{with\ uv}$, before and after uv irradiation.

ing to the fact that consequent to uv illumination photoisomerization of the EPH molecules from the E to Z form reduces the stability of the liquid crystalline phase resulting in a diminution in the transition temperature. Considering the fact that the concentration of EPH is only 2% in the mixture the magnitude of the shift seen here is substantial. The second salient feature is the behavior of the dielectric constant in the isotropic phase upon illumination. To highlight the observations the data in the isotropic phase for the two cases—with and without uv—have been plotted on an enlarged scale in Fig. 3 and as a function of reduced temperature $T-T_c$, with T_c being the transition temperatures $T_{no\ uv}$

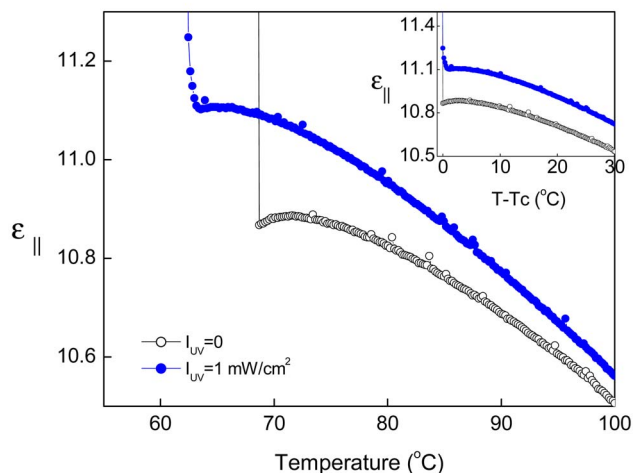


FIG. 3. (Color online) Temperature-dependent dielectric constant data collected in the homeotropic configuration shown on an enlarged scale in the isotropic phase without (○) and with (●) the uv radiation. The inset shows the same data as a function of reduced temperature $T-T_c$, T_c being the transition temperatures $T_{no\ uv}$ and $T_{with\ uv}$ for the two cases, respectively. Notice that at a given temperature the dielectric constant increases upon uv illumination.

and $T_{\text{with uv}}$ for the two cases, respectively, in the inset of Fig. 3. (It must be mentioned that the width of the transition, i.e., the coexistence of the region, is less than 1°C in both cases and thus much smaller than ΔT , the photoinduced shift in T_c .) There is an enhancement in the value of ϵ_I , the dielectric constant in the isotropic phase, upon uv illumination. A similar feature was recently reported by us for a nonpolar liquid crystal [17]. The reason for the increase is the following. Molecular modeling of azobenzene molecules in their *E* and *Z* conformations has shown that the dipole moment of the *E* isomer is only ~ 0.1 D whereas for the *Z* isomer it is very high, being about 3 D [18]. Therefore photoisomerization from the *E* to the *Z* form enhances the dipole moment of the photoactive molecules, causing the dielectric constant to increase. Far away from the transition to the *N* phase, the dielectric constant in the *I* phase is expected to follow the $\mu^2/k_B T$ relationship, where μ is the dipole moment and k_B is the Boltzmann constant. Therefore the enhancement in ϵ_I should be proportional to the square of the increase in the dipole moment. But keeping in mind that the μ of the *Z* isomer of the EPH molecule is comparable to that for the polar 5OCB molecule, and that EPH forms only 2% of the constituent molecules, the $\sim 2\%$ increase in ϵ_I can be accounted for by the photoisomerization process.

In both cases the temperature dependence of ϵ_I has a convex shape reaching a maximum at a temperature slightly above the *N-I* transition. Such a behavior is known for polar compounds of the kind used as the host material in the present investigations and has been explained to be due to the antiparallel near-neighbor correlations developed even in the *I* phase [19,20]. In fact, in the vicinity of the *N-I* transition the appearance of such correlations is expected to result in a crossover from the inverse linear temperature dependence characteristic of a liquid, which makes ϵ_I to increase with decrease in temperature, to the behavior wherein ϵ_I decreases with decreasing temperature. Although the reversal is seen in both the cases the dip just before the transition is less prominent for the with-uv case. The reason could be that the presence of the *Z* isomers of the EPH molecules interspersed between the host molecules reduces the near-neighbor (antiparallel) correlations. It could also have been caused by the broadening of the transition in the uv-illuminated situation. Owing to the large contribution due to the orientational ordering the enhancement of the dielectric constant is difficult to see in the *N* phase.

Figure 4 shows the temporal variation of ϵ upon uv illumination and subsequent switch off in the *I* phase (90°C), well in the *N* phase (55°C), and in the temperature range in which there is a photostimulated *N-I* transition (65°C). Upon uv illumination the dielectric constant increases in the *I* phase, but decreases for the scans taken in the *N* phase for reasons mentioned above. To compare the data in the different phases, we define three different response times τ_{on} , τ_{off} , and τ_{delay} : τ_{on} and τ_{off} are the durations taken for the dielectric constant to change between 10% and 90% of the total response upon switching the uv on (due to the photochemical process) or off (owing to the thermal back relaxation) respectively. It is seen that the sample response does not change immediately after the uv light is switched off. We quantify this feature by defining a parameter termed τ_{delay} . It is the

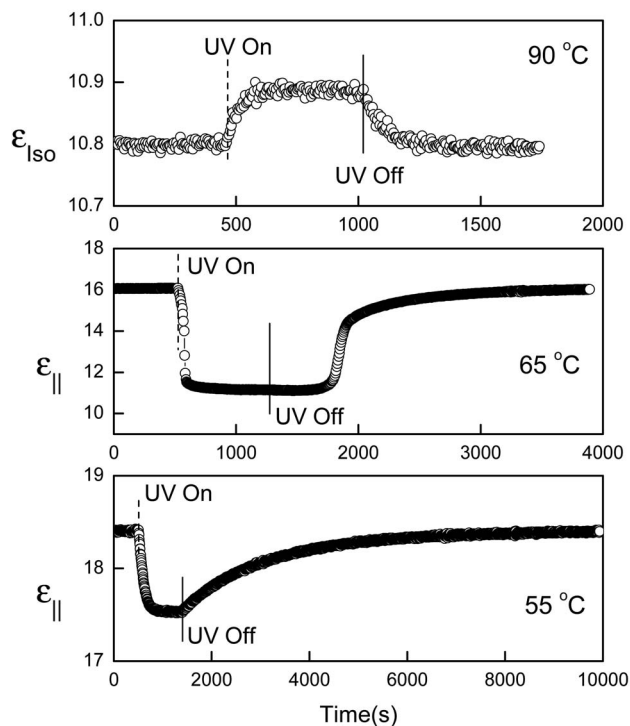


FIG. 4. Temporal variation of the dielectric constant upon uv illumination and subsequent switch off in the *I* phase (90°C), well in the *N* phase (55°C), and in the *N* phase but within the ΔT region (65°C).

duration between the instance at which the uv illumination was switched off and the instance at which ϵ starts changing. The detailed temperature dependence of the three response times, shown in Figs. 5(a), 5(b), and 5(d), although corroborates these features, presents some surprises as well. Both τ_{on} and τ_{off} have a nonmonotonic thermal variation with three clearly identifiable regions. Region I is the *I* phase where the response times for the uv-on and thermal back relaxation processes are comparable, a feature not seen in the *N* phase. Region II is bracketed by the transition temperatures with and without uv, in which there is a substantial delay in the response during the thermal back relaxation. Region III is the *N* phase well away from the transition, where the overall dynamics is slower than in the *I* phase and in particular τ_{off} is an order of magnitude larger than τ_{on} . In regions I and III, the two response times τ_{on} and τ_{off} exhibit an Arrhenius behavior that can be described with an activation energy of 82 ± 4 kJ/mol. The most interesting feature observed occurs in region II: compared to the background Arrhenius behavior there is a large (factor of 3) reduction in both the response times. Additionally, τ_{delay} , the delay in the response of the system after the uv is switched off, exists only in region II. In fact, the delay rises exponentially on moving away from $T_{\text{with uv}}$ indicating that the appearance of the nematic from the isotropic phase gets retarded. Outside region II, since the system remains in the equilibrium *N* (for $T < T_{\text{with uv}}$) or *I* (for $T > T_{\text{no uv}}$) phase before as well as after uv illumination, the question of appearance of one phase in another does not arise.

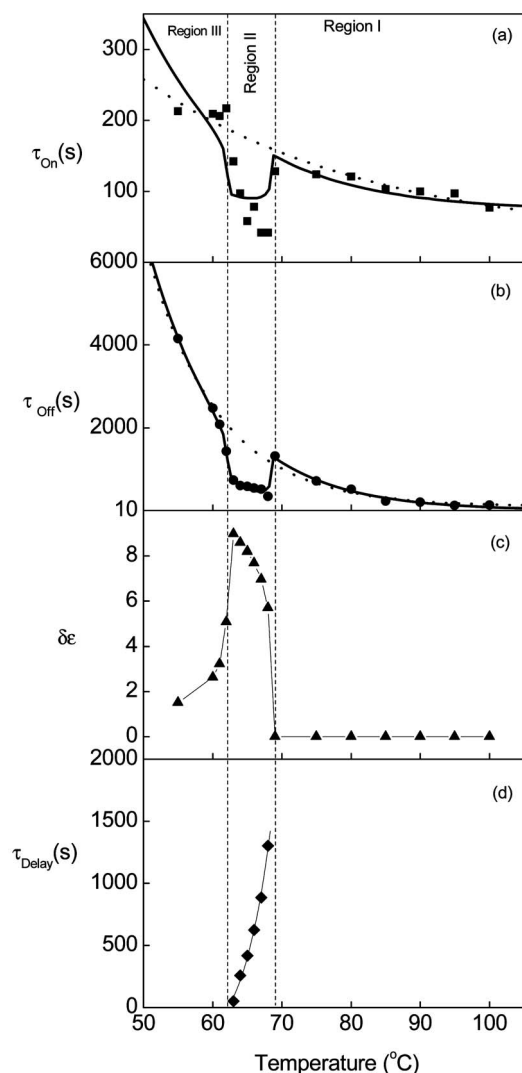


FIG. 5. Thermal variation of the response times (a) τ_{on} , (b) τ_{off} , and (d) τ_{delay} for uv intensity 1 mW/cm^2 . (c) shows $\delta\epsilon$, the difference in the dielectric anisotropies for the no-uv and with-uv cases. The solid line in (b) is a fit to Eq. (7) and the dotted line represents Arrhenius behavior. The description of regions I, II, and III and the definitions of different response times are given in the text.

Now we look at a possible explanation for the reduction in the values of τ_{on} and τ_{off} in the transition region (region II). This region is characterized by an equilibrium N phase which upon photostimulation transforms to the I phase. Since the I phase thus formed is in a nonequilibrium state it should eventually return to the N phase in the absence of any stimulus (uv radiation here). The larger the difference in ordering between the equilibrium and nonequilibrium states, the greater should be the effect of the system returning to its original state in the absence of the stimulus. Such a difference should be largest in the region where the system undergoes a photostimulated transition to the I phase since the order parameter changes from a finite value to zero value. Thus one can expect the response time to be dependent on the order parameter change in the presence of the uv radiation. Figure 5(c) shows the temperature dependence of $\delta\epsilon$,

the excess in the dielectric anisotropies ($\epsilon_a = \epsilon_{\parallel} - \epsilon_{\perp}$) between the equilibrium (no uv) and the photostimulated (with uv) states. Of course, $\delta\epsilon$ is identically zero in the I phase. Also, well in the N phase, $\delta\epsilon$ hardly exists but increases on approaching region II. When $\delta\epsilon$ is large τ_{on} and τ_{off} decrease below their purely temperature-dependent values (Arrhenius behavior). In fact, the behavior of τ_{on} and τ_{off} is just the mirror image of the trend shown by $\delta\epsilon$. It is well known that the dielectric anisotropy ϵ_a can be taken to be proportional to the nematic orientational order parameter S [21]. According to Maier-Saupe theory the two principal dielectric constants can be written as [22]

$$\epsilon_{\parallel} - 1 = \frac{NhF}{\epsilon_0} \left(\bar{\alpha} + \frac{2}{3} \Delta\alpha S + \frac{F}{k_B T} \mu_{\parallel}^2 \right) \quad (1)$$

$$\epsilon_{\perp} - 1 = \frac{NhF}{\epsilon_0} \left(\bar{\alpha} - \frac{1}{3} \Delta\alpha S + \frac{F}{k_B T} \mu_{\perp}^2 \right) \quad (2)$$

where N is the number of molecules per unit volume, h and F are the cavity and reaction field factors, $\bar{\alpha}$ and $\Delta\alpha$ are the mean and anisotropy of the polarizability, k_B is the Boltzmann constant, ϵ_0 is the permittivity of free space, μ_{\parallel} and μ_{\perp} are the longitudinal and transverse components of the molecular dipole, and S is the Maier-Saupe orientational order parameter. Using Eqs. (1) and (2) the dielectric anisotropy can be written as

$$\epsilon_a = \frac{NhF}{\epsilon_0} \left(\Delta\alpha S + \frac{F}{k_B T} (\mu_{\parallel}^2 - \mu_{\perp}^2) \right). \quad (3)$$

Substituting for the known behavior of μ_{\parallel} and μ_{\perp} ,

$$\epsilon_a = \frac{NhF}{\epsilon_0} \left(\Delta\alpha - \frac{F\mu^2}{2k_B T} (1 - 3 \cos^2 \omega) \right) S \quad (4)$$

where ω is the angle the permanent dipole makes with the polarizability axis.

Leaving out the parameters that are weakly dependent on temperature, it is seen that the temperature dependence of ϵ_a is controlled by the induced polarization, which in turn is proportional to S , and the orientation polarization, which varies as S/T . In materials for which $\Delta\epsilon$ is strongly positive (as in the present case), its behavior is dominated by S/T . Applying this to the results of the photoinduced experiments, we can write

$$\begin{aligned} \delta\epsilon &= \epsilon_a(\text{no uv}) - \epsilon_a(\text{uv}) \\ &= \frac{NhF}{\epsilon_0} \left(\Delta\alpha - \frac{F\mu^2}{2k_B T} (1 - 3 \cos^2 \omega) \right) S_{\text{no uv}} - S_{\text{uv}}. \end{aligned} \quad (5)$$

For the 5OCB molecule (serving as the host in the binary system used here), the cyano dipole is along the long molecular axis and therefore the angle ω can be taken to be zero. We can also neglect the contribution of the polarizability anisotropy owing to the dominant contribution of the permanent dipole moment of the biphenyl molecules. Since the other parameters like N , h , μ , and F are not expected to change upon uv illumination, the change in the dielectric anisotropy should be just dependent on the photoinduced change in the order parameter and the temperature. Thus,

$$\delta\epsilon \propto \frac{\delta S}{T}. \quad (6)$$

Here δS is the excess in the orientational order parameter between the equilibrium and the photostimulated cases. For 5OCB, Heeks and Luckhurst [23] showed that the temperature dependence of the order parameter S can be described by a power law with 0.196 as the exponent. Since the dielectric anisotropy is proportional to the order parameter we fitted the data obtained with and without uv to the power law expression $\epsilon_a = A(T_{NI} - T)^\gamma$. The γ values obtained with and without uv were 0.21 and 0.20, respectively, indicating that at least at the uv power employed and low concentration of the EPH molecules in the mixture the critical behavior of the transition is hardly altered. As shown in Fig. 5(c) $\delta\epsilon$ increases by 16% when the reduced temperature changes from $(T_{no\ UV} - 3)^\circ\text{C}$ to $(T_{no\ UV} - 6)^\circ\text{C}$ in region II. The data taken from Ref. [23] show that the order parameter increases by 15% over the same temperature range for 5OCB, suggesting that the uv-induced change in the dielectric anisotropy must be almost entirely due to the change in S . Also, the exponent for the dielectric data is comparable to that from the NMR measurements [23], further confirming the correlation between the order parameter and the dielectric anisotropy.

Now let us look at the temperature dependence of τ_{off} [Fig. 5(b)]. The data in regions I and III can be quite well described by an exponential expression, characteristic of an Arrhenius behavior, but there is a substantial deviation for the results in region II. It is in this region II, the primary effect of the photoisomerization would be to induce large changes in the order parameters between the no-uv and with-uv conditions. Keeping these two factors in mind, the following simple expression may be written for the temperature dependence of τ_{off} :

$$\tau_{off} = A + B \exp\left(\frac{-W}{k_B T}\right) - C \delta\epsilon. \quad (7)$$

Here A , B , and C are constants and W is the characteristic parameter for the Arrhenius behavior. The first two terms on the right-hand side describe the background variation of the response time valid in the absence of the substantial change in the order parameter owing to isomerization, while the third term is the important one for the present discussions. The fitting to the data was carried out in the following fashion. To retain the temperature as the only one independent variable, for each temperature the values of $\Delta\epsilon$ (for the no-uv and with-uv cases) were calculated using the power law expressions with the two exponents mentioned earlier and the difference $\delta\epsilon$ determined. All the parameters A , B , C , and W/k_B were allowed to float. The best-fit values obtained from the least-squares fitting are $A = -39 \pm 63$ s, $B = (3.6 \pm 5.3) \times 10^{-10}$ s, $C = 153.3 \pm 8.2$ s, and $k_B/W = -1.01 \times 10^{-4} \pm 5 \times 10^{-6} \text{K}^{-1}$. (It may be noted that the errors in the fitting for the two important parameters C and k_B/W are quite small. It is also to be noted that the activation energy value determined from this fit using the value of k_B/W is identical to that obtained by fitting the data, excluding those in region II, to a simple Arrhenius expression.) Figure 5(b)

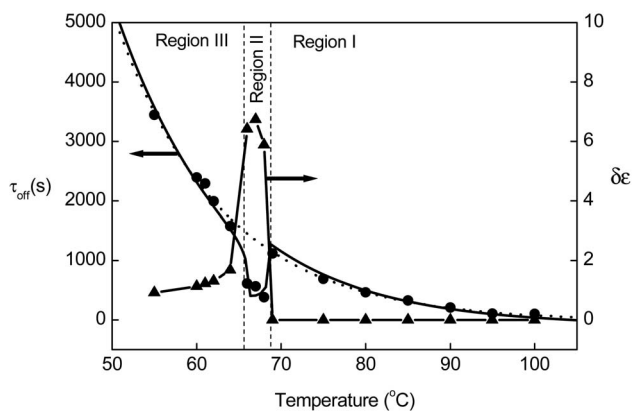


FIG. 6. Thermal variation of τ_{off} (●) and $\delta\epsilon$ (▲) when the uv intensity is lowered to 0.1 mW/cm^2 showing very similar features as seen for data obtained at higher intensity of 1 mW/cm^2 (see Fig. 5). The solid line through τ_{off} data is a fit to Eq. (7) whereas the dotted line represents Arrhenius behavior.

shows that Eq. (7) describes the data well demonstrating that the reduction in τ_{off} value as compared to the Arrhenius background can be modeled by considering the order parameter variation with and without uv radiation. Figure 5(a) shows that the τ_{on} data can also be described by a similar expression although the quality of fit is quite poor. Even when the intensity of the uv radiation was reduced by an order of magnitude (0.1 mW/cm^2) the model describes the situation quite well (see Fig. 6).

Finally, a comment regarding the reverse isomerization and the thermal back relaxation. Figure 7 shows the absorbance at 370 nm corresponding to the $\pi-\pi^*$ electronic transition of the EPH molecule present in the mixture, and $\epsilon_{||}$ in the N phase (at a temperature of 65°C) collected simultaneously as a function of time after the uv illumination is switched off. Notice that the absorbance value continuously increases (indicating the recovery of the E isomers) up to a certain point (~ 1800 s), then suddenly dips before increasing again, although at a much slower rate. Except in the vicinity of the dip the data can be fitted to a first-order ki-

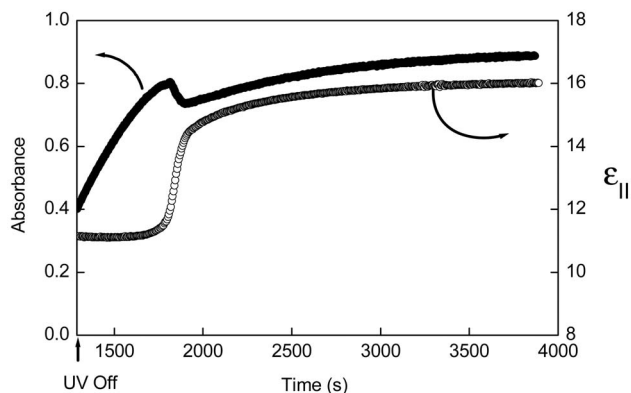


FIG. 7. Temporal variation of the sample absorbance and dielectric constant simultaneously determined after turning the uv radiation off in the N phase at 65°C .

netics. The dielectric constant remains at the isotropic value till the instant at which the absorbance shows a dip and then increases abruptly to the value in the N phase. Thus it appears that a minimum number of E isomers of EPH are required for the N phase to reappear. As the temperature is decreased even with a lower number of E isomers, the N phase is recovered, indicating that the influence of the isomerization in altering the properties of the medium is maximum near the equilibrium (no-uv) transition. For example, at 65 °C the reappearance of the N phase requires 91% of the EPH molecules to be in their E form whereas at 63 °C, 70% E isomers are sufficient.

In summary, we have shown that in the isotropic phase of a nonphotoactive host–photoactive guest mixture, the photo-induced increase in the dielectric constant can be accounted for by the change in the dipole moment between the E and the Z isomers of the photoactive molecule. Investigation of the dynamics of the response upon turning the uv light on and subsequently off reveal that the latter process involves both a delay time and an actual response time. The delay

time is finite only in the temperature region that lies between the transition temperatures for the no-uv and with-uv cases. The response time which follows an Arrhenius behavior away from this region becomes substantially smaller within this region. Using a simple argument based on the association between the dielectric anisotropy of strongly polar molecules and the nematic orientational order parameter, we have shown the data of the response times can be described by the temperature dependence of the difference in the order parameter between the no-uv and with-uv situations. This description is quite interesting since it can be applied to other isothermal transitions also.

ACKNOWLEDGMENTS

The work described here has been carried out under an Indo-Italian collaborative project [INT/ITALY/POCMST-03/05] and a SERC project (Grant No. 93357) of the Department of Science and Technology, New Delhi.

-
- [1] A. A. Wheeler, W. J. Boettinger, and G. B. McFadden, *Phys. Rev. A* **45**, 7424 (1992).
- [2] E. Bonetti, E. G. Campari, M. D' Astuto, and M. Marangolo, *Phys. Rev. B* **51**, 1249 (1995).
- [3] M. V. Kozlovsky, J. G. Meier, and J. Stumpe, *Macromol. Chem. Phys.* **201**, 2377 (2000).
- [4] W. Hu, *J. Chem. Phys.* **115**, 4395 (2001).
- [5] G. D. Fidelio, B. Maggio, and F. A. Cumar, *Biochim. Biophys. Acta* **854**, 231 (1986).
- [6] D. C. Carrer and B. Maggio, *J. Lipid Res.* **40**, 1978 (1999).
- [7] K. Brandenburg, A. David, J. Howe, M. H. J. Koch, J. Andra, and P. Garidel, *Biophys. J.* **88**, 1845 (2005).
- [8] J. S. Ishay, Z. Joseph, D. V. Galushko, and D. J. Bergman, *Curr. Nanosci.* **1**, 125 (2005).
- [9] For recent reviews on this topic see T. Ikeda, *J. Mater. Chem.* **13**, 2037 (2003); S. Krishna Prasad, Geetha G. Nair, Gurumurthy Hegde, K. L. Sandhya, D. S. Shankar Rao, Chethan V. Lobo, and C. V. Yelamaggad, *Phase Transitions* **78**, 443 (2004); R. P. Lemieux, *Soft Mater.* **1**, 348 (2005).
- [10] See, e.g., H. Rau, in *Photochemistry and Photophysics*, edited by J. F. Rabek (CRC Press, Boca Raton, FL, 1990), Vol. II, p. 119.
- [11] H. Knobloch, H. Orendi, M. Buchel, T. Seki, S. Ito, and W. Knoll, *J. Appl. Phys.* **77**, 481 (1995).
- [12] L. M. Blinov, M. V. Kozlovsky, M. Ozaki, K. Skarp, and K. Yoshino, *J. Appl. Phys.* **84**, 3860 (1998).
- [13] A. Stracke, J. H. Wendorff, D. Goldmann, and D. Janietz, *Liq. Cryst.* **27**, 1049 (2000).
- [14] Y. Yu, M. Nakano, and T. Ikeda, *Nature (London)* **425**, 145 (2003).
- [15] Geetha G. Nair, S. Krishna Prasad, and C. V. Yelamaggad, *J. Appl. Phys.* **87**, 2084 (2001).
- [16] John Bechhoefer, in *Spatio-Temporal Patterns in Nonequilibrium Complex Systems: A NATO Advanced Research Workshop*, edited by P. Cladis and P. Palffy-Muhoray (Addison-Wesley, Reading, MA, 1995).
- [17] Gurumurthy Hegde, Geetha G. Nair, S. Krishna Prasad, and C. V. Yelamaggad, *J. Appl. Phys.* **97**, 093105 (2005).
- [18] V. Borisenko, D. C. Burns, Z. Zhang, and G. A. Woolley, *J. Am. Chem. Soc.* **122**, 6364 (2000); also see C. Ruslim, L. Komitov, Y. Matsuzawa, and K. Ichimura, *Jpn. J. Appl. Phys., Part 2* **39**, L104 (2000).
- [19] B. R. Ratna and R. Shashidhar, *Mol. Cryst. Liq. Cryst.* **42**, 113 (1977).
- [20] M. J. Bradshaw and E. P. Raynes, *Mol. Cryst. Liq. Cryst.* **91**, 145 (1983).
- [21] See, e.g., S. Chandrasekhar, *Liquid Crystals* (Cambridge University Press, Cambridge, U.K., 1992).
- [22] See, e.g., G. Vertogen and W. H. de Jeu, *Thermotropic Liquid Crystals, Fundamentals* (Springer-Verlag, Berlin, 1988).
- [23] S. K. Heeks and G. R. Luckhurst, *J. Chem. Soc., Faraday Trans.* **89**, 3783 (1993); also see S. Urban, B. Gestblom, W. Kuczynski, S. Pawlus, and A. Wurflinger, *Phys. Chem. Chem. Phys.* **5**, 924 (2003).