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Influence of a long-chain alkane on the photoinduced nematic-isotropic transition

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We investigated the phenomenon of photoinduced nematic-isotropic (N-I) transition for different concentrations of a long-chain alkane, viz., octadecane (OD), and a host liquid crystalline material having a small quantity (4.5 mol %) of a photoactive azo compound. As expected, the N-I transition temperature diminishes with increasing concentration of OD. Data of time-resolved measurements of the dielectric constant through both the UV-activated *trans-cis* transformation and the thermal back relaxation process are presented. With increasing concentration of OD, although the response time for the former process increases slightly by less than a factor of 2, the thermal back relaxation shows a greater increase by more than an order of magnitude. As a possible explanation for this surprising result, we discuss an argument based on the structural incompatibility of the constituents of the system investigated.

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INTRODUCTION

Molecules containing an azobenzene moiety are well known to show reversible isomerization transformations upon irradiation with UV and visible light [1]. Upon absorption of UV light (~ 365 nm) the energetically more stable *trans* configuration, with an elongated rodlike molecular form, transforms into a bent banana-shaped *cis* configuration. The reverse transformation of the *cis* isomer into the *trans* isomer can be brought about by irradiation with visible light (in the range of 400–500 nm). The latter change also occurs in the "dark" by a process known as "thermal back relaxation" in a period ranging from minutes to tens of hours depending on the system. Photoinduced effects reported in the literature [1–4] are on liquid crystals in which the azobenzene group is either chemically attached to the molecule of interest or used as a dopant in a liquid crystal host material. In the case of the latter, guest-host systems, the *trans* form of the azo dopant, as it is rodlike, is favorable for the stabilization of the liquid crystalline phase. On the other hand, the *cis* form, which is in bent form, acts like an "impurity" and therefore destabilizes the liquid crystalline phase. The destabilization can be significant enough even to cause an isothermal photoinduced transition from a liquid crystalline phase, say, the nematic phase to the isotropic phase [5]. This phenomenon has attracted attention, not only from a basic point of view, but also for possible applications in optical switching and image storage [6]. Photoinduced effects have been well studied in systems exhibiting nematic-isotropic (N-I) [1,5,7] and smectic C^*–smectic A [8–10] transitions. Very recently we reported a photoinduced disorder-order phase transition [11].

The time taken for the phase transition to take place following the isomerization of the photoactive molecules is not only of significant interest from a basic point of view, but of concern for applications also. For example, in both monomeric and polymeric samples, τ_{on}, the time required for the photoinduced nematic-isotropic transition to occur, depends on the temperature at which the UV illumination is done, and with a conventional type of UV source the typical duration required is of the order of a few minutes [5,7]. (Of course, with a pulsed laser source very fast time scales—submicrosecond level—can be achieved [11]). In contrast, τ_{off}, the thermal back relaxation time restoring the nematic phase, takes much longer (an order of magnitude more). We report here that addition of a long-chain alkane to the liquid crystalline material results in more than a factor of 15 increase in the τ_{off} value, whereas τ_{on} shows only an increase by less than a factor of 2. A necessary condition in creating optical storage devices is to employ materials with a large value of τ_{off} such that the optically generated pattern lasts longer. The obvious contenders for such an application have been liquid crystalline polymers and systems that exhibit a glassy state. In the light of this the present article provides a path for the exploration of systems for obtaining long-term storage devices.

EXPERIMENT

Materials

The liquid crystalline host material is a mixture of hexyloxycyanobiphenyl (6OCB) and the UV-active dopant compound (5 wt %) p-(p-ethoxyphenylazo)phenyl hexanoate (EPH). 6OCB was used as obtained, while EPH was purified by standard chemical methods to decrease the ionic conductivity. We investigated several mixtures of this host material with octadecane (OD), a long-chain alkane. The chemical structures of the compounds 6OCB, EPH, and OD, along with their transition temperatures as obtained by differential scanning calorimetry (Perkin Elmer DSC 7), are given in Fig. 1.

Measurements

Photoabsorbance measurements were carried out as a function of wavelength in the range of 300 to 600 nm, using a UV-visible spectrophotometer (Shimadzu 3100 UV-PC). For these measurements the samples were sandwiched between two optically flat quartz plates, separated by Mylar spacers, for measurements in the nematic and isotropic phases. For dielectric studies the samples were sandwiched between indium tin oxide (ITO) coated glass plates treated

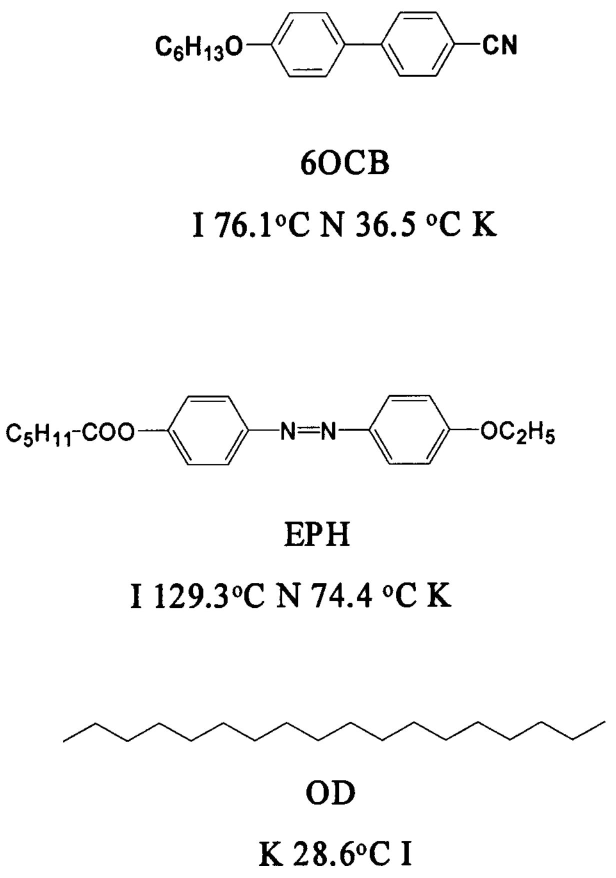

FIG. 1. Molecular structures of 6OCB, the UV-active dopant EPH, and the alkane OD.

with a polyimide solution and unidirectionally rubbed to get uniform planar alignment of the molecules. This geometry gives the dielectric constant perpendicular ($\varepsilon_\perp$) to the nematic director. Dielectric constant measurements were done using an impedance analyzer (Hewlett-Packard 4194A). 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. The UV apparatus used for inducing photoisomerization is described in an earlier publication [7]. Briefly, the UV radiation from an intensity stabilized UV source with a fiber-optic guide (Hamamatsu L7212-01) was used along with a UV-bandpass filter (Newport, UG 11). 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 1.1 mW/cm^2.

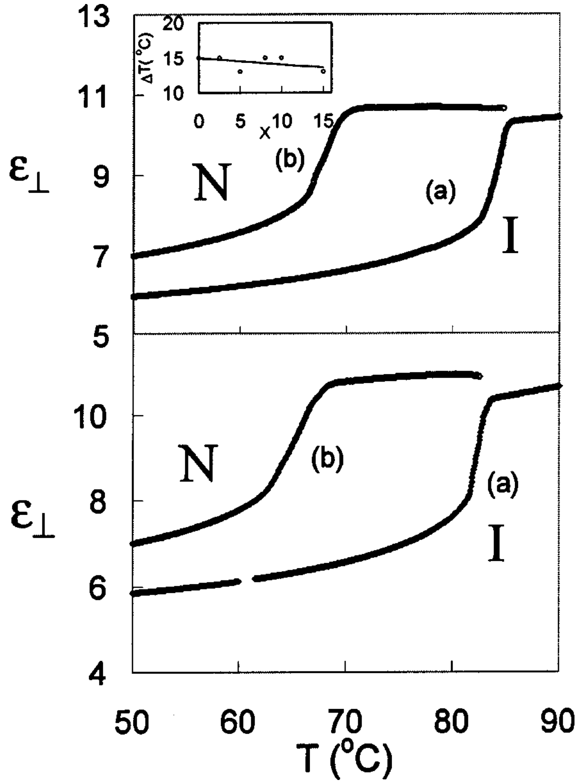

FIG. 2. Temperature dependence of the dielectric constant $\varepsilon_\perp$ (a) without and (b) with UV radiation for the host material (top panel) and the mixture of the host material with 5% OD, i.e., $X=5$ (bottom panel). ΔT, the photoinduced shift in the transition temperature, given by the difference in the transition temperatures with and without the UV radiation, is shown in the inset of the top panel and exhibits a weak dependence on the concentration of OD in the mixture.

RESULTS AND DISCUSSION

Temperature-dependent dielectric constant

It is known that the dielectric anisotropy of the nematic phase arises from the cooperative ordering of the rodlike molecules. Hence a decrease in the nematic order parameter, say by the *trans-cis* isomerization, should decrease the dielectric anisotropy, which should become zero in the isotropic phase. The host material used in the present investigations has a strong positive dielectric anisotropy, i.e., $\varepsilon_\parallel - \varepsilon_\perp > 0$, where $\varepsilon_\parallel$ and $\varepsilon_\perp$ are the dielectric constants parallel and perpendicular to the director. Thus the magnitude and thermal behavior of the dielectric constant of the mixture are essentially determined by those of the host material. Hence, as for any material with a positive dielectric anisotropy, the onset of the N-I transition is marked by an abrupt increase in $\varepsilon_\perp$. With this background, we look at the $\varepsilon_\perp$ data presented in Fig. 2 showing the temperature dependence of $\varepsilon_\perp$ in both the unirradiated and the irradiated states for $X=0$ and 5 mixtures [here X indicates the concentration (wt %) of OD in the mixture]. In the latter experiments, to ensure that there is no effect of thermal back relaxation during the measurements, the radiation was kept on throughout. In both cases the UV-induced shift in the transition temperature is quite clear. The magnitude of ΔT, the shift in the N-I transition temperature, is comparable to that reported in the literature [5,7]. The inset of Fig. 2 shows that ΔT diminishes slightly as the concentration of OD is increased. The second feature to be noticed is that, upon irradiation, the magnitude of change in $\epsilon_\perp$ between the UV on and UV off measurements decreases on moving deeper into the nematic phase. This is to be expected, since with increasing nematic order parameter the

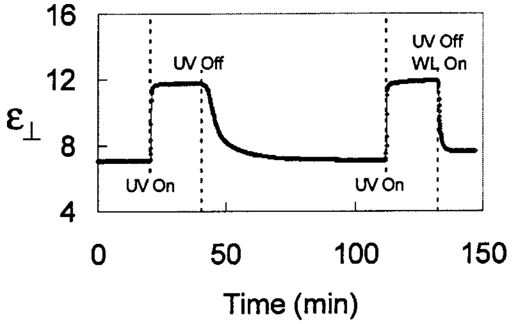

FIG. 3. The time-resolved variation of $\varepsilon_\perp$, measured at a constant temperature for the $X=5$ mixture. The dashed lines indicate the instant at which the UV radiation was turned either on or off. The *trans-cis* isomerization due to the UV radiation leads to an isothermal nematic-isotropic transition, causing the $\varepsilon_\perp$ values to increase. After the UV radiation is switched off, the reverse isomerization takes place either through a slow thermal back relaxation process or quickly in the presence of white light and changes the isotropic phase back to the nematic phase, also isothermally.

efficiency of the *trans-cis* conversion by a given intensity of the radiation should decrease. We also notice that the change in $\varepsilon_\perp$ on approaching the isotropic phase is more gradual in the UV on case compared to the unirradiated case. This is because of the enhanced biphasic region as explained in a previous paper [7].

Dynamics of the photoinduced transition

Figure 3 shows the time-resolved dielectric constant data for a representative mixture, viz., $X=5$; the profile obtained for the other mixtures was qualitatively similar. Before irradiation, the sample is in the nematic phase. Turning the UV radiation on, the value of $\varepsilon_\perp$ starts increasing rapidly and saturates within about 1 min of exposure and achieves a "photostationary" state. When the radiation is switched off and the sample is left in the dark, reverse isomerization takes place with the sample transforming back into the nematic phase, and consequently $\varepsilon_\perp$ decreases. The switching kinetics for this reverse transformation (thermal back relaxation) is, however, very slow compared to that induced by the *trans-cis* isomerization. Notice that even ~ 20 min after switching off the radiation the recovery is not complete. Also shown in the plot is the effect of irradiating the sample with white light on the time taken for the back relaxation process. The presence of the white light accelerates the reverse transformation by a factor of ~ 5.

Thus we get three different response times: τ_{on}, the time taken for the $\varepsilon_\perp$ value to change from 10% to 90% of the final value upon irradiation, and τ_{off} and τ_{wl}, the times for $\varepsilon_\perp$ to relax from 90% to 10% of the UV-saturated value in the absence and presence of white light, respectively. The temperature dependence of the different response times obtained for $X=2.5$ are shown in Fig. 4. Notice that while τ_{on} and τ_{wl} have hardly any temperature dependence τ_{off}, the response time for the thermal back relaxation time in the absence of any radiation, shows a substantial increase as the temperature is lowered (i.e., $T_{\text{NI}}-T$ increased). This is because both τ_{on} and τ_{wl} are controlled by radiation-induced (UV or white light) isomerization-driven torques but τ_{off} owes its origin to thermal fluctuations and therefore is viscosity dominated. In fact, the temperature dependence of τ_{off} can be described by the Arrhenius law and a fit to the expression $\tau_{\text{off}}=\tau_0 \exp(W/k_BT)$, where k_B is the Boltzmann constant, T the absolute temperature, and W the activation energy, yields a value of $W=0.4$ eV, which is comparable to the activation energy associated with the relaxation modes of the nematic director [12].

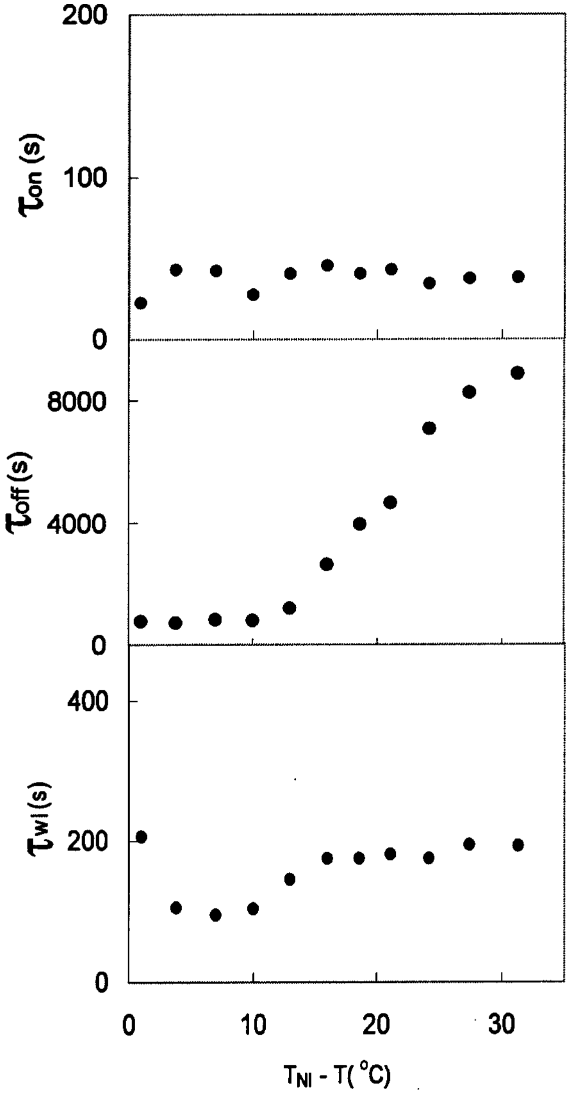

FIG. 4. Plot of the three response times τ_{on}, the time taken for the $\varepsilon_\perp$ value to change from 10% to 90% of the final value upon irradiation, and τ_{off}, and τ_{wl}, the time for $\varepsilon_\perp$ to relax from 90% to 10% of the UV-saturated value in the absence and presence of white light, respectively, in the nematic phase as a function of the reduced temperature $T_{\text{NI}}-T$ for the mixture $X=2.5$.

Concentration dependence of the dynamics

The effect of adding OD, a long-chain alkane, on the dynamics of the photoinduced transition is shown in Fig. 5. The feature to be noted is that, although the time response for the UV-induced N-I transition does not seem to be affected

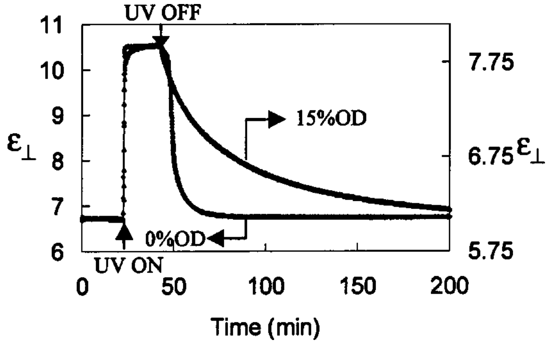

FIG. 5. UV on (up arrow) and UV off (down arrow) dynamics for $X=0$ (host material) and the $X=15$ mixture. Notice that the UV on dynamics takes about the same time for both the materials, but the thermal relaxation process takes much longer for the $X=15$ mixture.

much by the addition of OD, there is a strong influence on the thermal back relaxation process; the material with OD relaxes far more slowly than the one without it. Figure 6 shows the effect of the concentration of OD in the mixture on the three response times, τ_{on}, and τ_{off}. We find the surprising result that with increasing concentration of OD τ_{on} increases only marginally (by less than a factor of 2) whereas τ_{off} exhibits a dramatic increase of more than an order of magnitude. It may be pointed out that δ, the temperature range of the biphasic region, increases slightly as the concentration of OD is increased (in the presence of UV, $\delta=4.6\,^{\circ}\mathrm{C}$ and $5.7\,^{\circ}\mathrm{C}$ for $X=0$ and $X=15$ mixtures, respectively), a feature commonly observed in multicomponent systems. Further, a thermal hysteresis was also observed between the heating and cooling scans, being about 1 °C for the different concentrations studied. Since τ_{on} has only a small increasing trend with increasing X, we can safely conclude that, even if either the hysteresis or the width of the biphasic region were to affect the τ_{off} data, its magnitude would be limited to the magnitude of variation seen for τ_{on}, and thus is negligible for the data for τ_{off} taken at 8 °C away from the transition in each case.

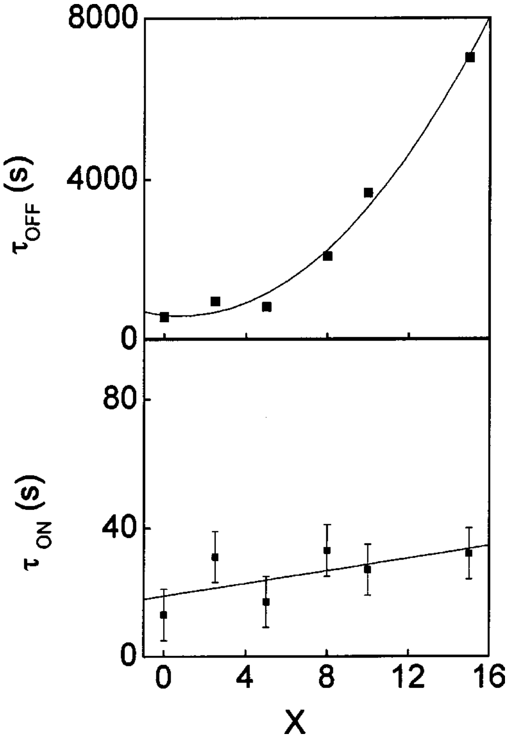

FIG. 6. Dependence of the response times τ_{off} (top panel) and τ_{on} (bottom panel) on the concentration of OD in the mixture. The line shown is only a guide to the eye. In the top panel the error bars are of the same magnitude as in the data shown in the bottom panel, but are smaller than the symbols used.

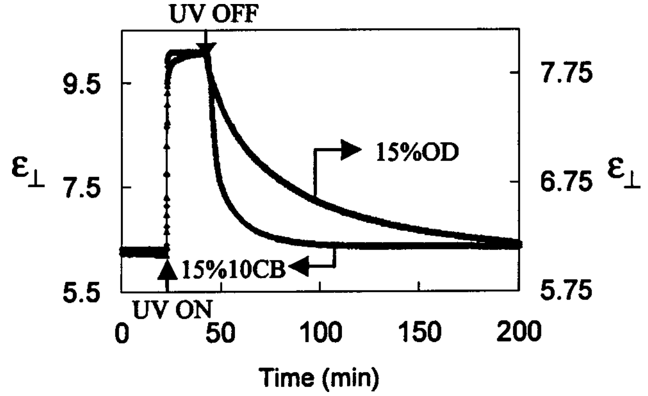

FIG. 7. UV on (up arrow) and UV off (down arrow) dynamics for the mixture with 15% OD and for that with 15% 10CB. While the UV on dynamics takes about the same time for both the materials, the thermal relaxation process takes much longer for the OD mixture.

Now let us explore the possible cause for such a slowdown in the thermal back relaxation process. A trivial cause could be that the molecular length of OD is more than that of the other two materials in the mixture, viz., 6OCB and EPH, and therefore its addition slows down the relaxation process. The measured molecular lengths for 6OCB, EPH, and OD in their most extended all-*trans* configurations are 2.04 nm, 2.41 nm, and 2.55 nm, respectively. Thus the effective molecular length of the host 6OCB+5% EPH mixture is 2.06 nm and that of the mixture with 15% OD in the host material is 2.13 nm, the latter being only ~3% more than that for the host material and therefore far too small to explain the magnitude of the observed increase in τ_{off}. To further confirm this aspect, we replaced OD with another compound, namely, decylcyanobiphenyl (10CB), having a comparable molecular length. The time dependence of $\varepsilon_{\perp}$ in the mixture with 15% 10CB in the host material upon turning the radiation on and subsequently off is shown in Fig. 7. For the purpose of comparison the data for the 15% OD mixture are also shown. While the τ_{on} values are comparable, the τ_{off} value is much smaller (faster relaxation) for the 10CB mixture; in fact, the value is just about the same as that for the host material. Thus the longer molecular length of OD cannot be the cause for the large τ_{off} values of the OD mixtures.

Another possibility could be that the viscosity of the host material increases on adding OD. To find whether this could be the reason for the slow relaxation of the OD mixtures, we carried out Freedericksz transition measurements [13]. In this measurement, the sample cells used were the same as that for the photoinduced transition studies. In the planar geometry of the cell used, since the materials under study have a positive dielectric anisotropy, an electric field, greater than a threshold value, applied along the normal to the substrate orients the molecules along the electric field direction. When the electric field is switched off the molecules relax back to the original planar configuration. The response time for both the electric field on and off processes increased only marginally with increasing concentration of OD, and even for the 15% OD mixture the increase was less than a factor of 2 compared to that of the mixture without any OD. Notice that the relaxation of the molecules when the electric field is switched off is dictated by the viscosity of the medium. The absence of a dramatic increase in the response time for the electric field off case rules out viscosity as the reason for the large increase in τ_{off} with UV off.

In the following, we attempt an explanation, which, in our opinion, could be causing the observed behavior of τ_{off}. Octadecane and other such similar long-chain alkanes have only flexible units and thus *per se* cannot and do not support the formation of liquid crystalline phases. Even when added to materials that already exhibit liquid crystalline phases, they tend to destabilize the liquid crystallinity [14]. For example, in the system studied here, the addition of 15% OD brings down the temperature range of the nematic phase by as much as 16 °C, as compared to that for the host material. It may be recalled here that a detailed analysis of phase diagrams involving a liquid crystalline material and long-chain alkanes has been done [15] by taking into account the structurally incompatible rodlike form of liquid crystalline molecules and the coil form of the alkanes [16]. The not very large biphasic region in our systems suggests that, at the concentration level of OD used in these studies, the structural incompatibility is still tolerable on a macroscopic scale. In order to determine whether the microscopic level incompatibility affects at least the dynamics of the process of photoisomerization itself, we carried out time-dependent absorbance measurements in both the nematic and isotropic phases at a wavelength matching the absorption peak of the *trans* isomer of the photoactive molecule. The data were obtained by irradiating the sample with UV radiation and collecting the data as a function of time. For the sake of better comparison, measurements were done for the mixture with 15% OD as well as for the mixture with 15% 10CB. These time-dependent absorption data [for the sake of comparison, the value of absorbance has been normalized as $\eta=(A_\infty-A_t)/A_\infty$, with A_∞ being the absorbance long after the UV is switched off, and A_t the instantaneous absorbance after irradiation] given in Fig. 8 shows that, while in the isotropic phase both systems have approximately the same relaxation behavior, in the nematic phase the 10CB mixture relaxes (i.e., recovers the *trans* isomer from the *cis* form) much faster compared to the OD mixture. (Note that $\eta=0$ corresponds to the full recovery of the *trans* isomers.) As mentioned above, the alkane molecules prefer the coil form. Consequently, in the isotropic phase there would be less difference between the local order in the vicinity of the alkane and the entire medium. In contrast, in the nematic phase, to be compatible with the environment the alkane molecule is forced to deviate from the coil form. Indeed, experimental studies have shown that the alkane molecule is not totally disordered in the host nematic phase. But, given a chance to deviate from this situation, the alkane molecules may perhaps hinder the liquid crystalline molecules in the vicinity from achieving nematic order. For the temperature-dependent transition, such an influence will lower the transition temperature, a feature generally observed for mixtures of liquid crystalline molecules and alkanes. In the case of the photoinduced transition, the process is an isothermal one. Thus a possibility is that in the absence of any isomerization-driven torques (e.g., presence of white light) the local disorder of the OD molecules will retard the relaxation of the system from the photoinduced isotropic phase, thereby increasing the thermal back relaxation time τ_{off}. The magnitude of the effect increases, naturally, with increasing concentration of the alkane.

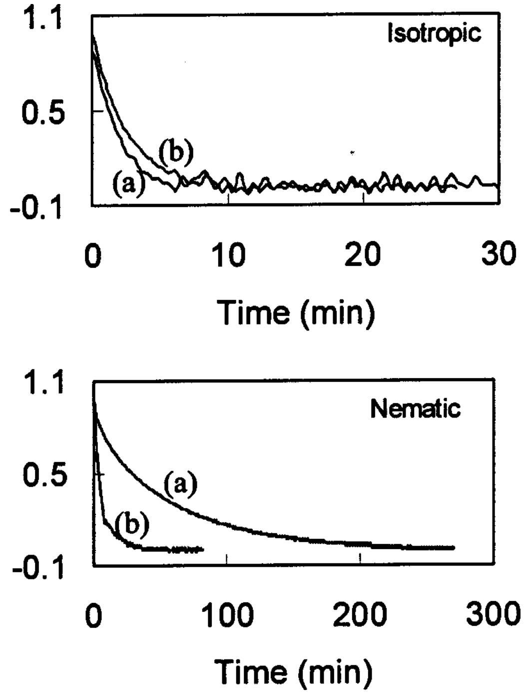

FIG. 8. Time dependence of the absorbance $\eta=(A_\infty-A_t)/A_\infty$ at 365 nm (with A_∞ being the absorbance long after the UV is switched off and A_t the instantaneous absorbance) after irradiation in the isotropic phase (top panel) and nematic phase (bottom panel) for (a) the 15% OD mixture and (b) the 15% 10CB mixture.

SUMMARY

We have investigated the influence of adding octadecane, a long-chain alkane, on the photoinduced nematic-isotropic (N-I) transition of a host material having a small quantity of a photoactive compound. A surprising finding of these studies is that the relaxation time involved for the restoration of the nematic phase from the photoinduced isotropic phase is markedly affected by the concentration of octadecane.

ACKNOWLEDGMENT

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