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Photoinduced effects in the vicinity of the smectic-C_α^*–smectic-A transition

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We report the first results of photoinduced effects near the smectic-C_α^*-smectic-A transition in a binary liquid crystalline material. Dielectric dispersion measurements show that the softening of the tilt fluctuation mode in the vicinity of the transition gets enhanced in the presence of the UV light.

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I. INTRODUCTION

Owing to many promising features for practical applications, the phenomenon of reversible photoinduced shape transformation of chromophoric molecules, such as azobenzenes, has been extensively studied [1]. The phenomenon is all the more interesting when associated with mesogenic properties of liquid crystals [2–6], the underlying principle of which is briefly outlined in the following. In the absence of UV radiation, the azobenzene molecules exist in their energetically more stable *E* (also known as trans) configuration, which has a rodlike form and thus supports the formation of liquid crystalline phases. Upon illumination with UV light (~360 nm wavelength, corresponding to the π-π^* band of the azo group), a shape transformation takes place to the *Z* (or cis) form. The *Z* form due to its bent shape results in the destabilization of liquid crystalline phases or more specifically, in the lowering of the phase transition temperatures. The reverse transformation can be brought about by illuminating with visible light (~420 nm, corresponding to the n-π^* band). This latter change can also occur spontaneously in the ‘‘dark’’ by a process known as thermal back relaxation. All these features provide a new tool to study phase transitions in which the transformation takes place isothermally, but is photocontrolled. Photoinduced effects have been well studied in systems exhibiting nematic-isotropic [2,6,7] and smectic-C^*–smectic-A [8,9] transitions. Very recently we reported [10] a reentrant nematic–smectic-*A* transition induced by light (notice that in this case, contrary to all earlier observations, the photoinduced phase is more ordered). The discovery in 1989 of the antiferroelectric chiral smectic-*C* (Sm-C_A^*) phase [11], led to intense activity in the field and resulted in the identification of the other variants of the previously discovered ferroelectric chiral smectic-*C* (Sm-C^*) phase. One of these variants is the smectic-C_α^* (Sm-C_α^*) phase. This phase has an incommensurate short-period ferroelectriclike structure [12]. Although there have been numerous studies on a variety of materials exhibiting these phases [13], only one report exists, to our knowledge, on the photoinduced phenomenon in the Sm-C_A^* phase [14]. In this paper, we describe results of the first detailed dielectric study of the photoinduced phenomenon in the vicinity of the Sm-*A* to Sm-C_α^* phase transition of a binary mixture of 4-1-(methylheptyloxycarbonyl) phenyl 4′-octyloxy biphenyl-4-carboxylate (well known [13] as MHPOBC), the first compound reported to exhibit the Sm-C_α^* phase, and a photoactive azobenzene compound.

II. EXPERIMENT

The liquid crystalline host material is MHPOBC, a chiral material exhibiting the following sequence of phase transitions:

$$\text{Iso-Sm-}A\text{–Sm-}C_\alpha^*\text{–Sm-}C^*\text{–Sm-}C\gamma^*\text{–Sm-}C_A^*\text{–Crystal.}$$

The guest, UV-active dopant compound, p-(p-Ethoxyphenylazo)phenyl Hexanoate [C_5H_{11}-COO-ϕ-N=N-ϕ-OC_2H_5, where ϕ indicates a phenyl ring], hereafter referred to as EPH, is from Eastman Organic Chemicals and is also liquid crystalline exhibiting a nematic mesophase. All the results described in this paper have been obtained on a mixture of 4.7 wt % of EPH in MHPOBC. This mixture exhibits a Sm-*A*–Sm-C_α^* transition at 107.7 °C. The presence of the Sm-C_α^* phase was established by polarizing microscopic observations and from the current response of the sample to applied electric fields.

III. RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of the low frequency dielectric constant without and with an UV illumination of 5.5 mW/cm^2 magnitude. The dielectric constant increases from both the sides on approaching the Sm-*A*–Sm-C_α^* transition and reaches a maximum at T_c, the transition temperature. Such a feature has been reported [13] across the Sm-*A*–Sm-C_α^* transition for many compounds including pure MHPOBC also. It has been attributed to the presence of the soft mode associated with the tilt fluctuations, a feature that we shall discuss in detail later. The behavior with and without UV appears qualitatively the same, but there are quantitative differences. In the presence of UV, (a) the transition temperature decreases by ~5 °C and (b) there is a slight increase in the maximum value (i.e., the value at T_c). The first feature is not uncommon in the area of photoinduced phase transitions, although in the present case the magnitude is somewhat large considering the fact that the transition is between layered phases and that the level of the UV intensity used is not high. As a possible cause for the second feature, namely, that in the presence of the UV illumination the value of the dielectric constant at T_c increases

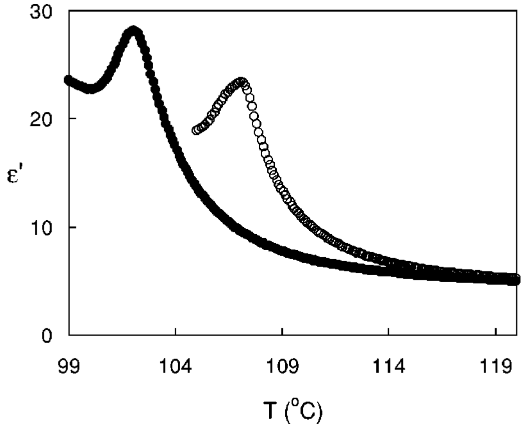

FIG. 1. Temperature dependence of the dielectric constant at 100 Hz in the vicinity of the Sm-A–Sm-C_α^* transition. The open circles represent the data collected in the absence of UV radiation and the filled circles are data obtained by illuminating the sample with a UV radiation of 5.5 mW/cm^2 magnitude. The peak point in both the traces signifies the transition point. Notice that the value of the dielectric constant increases upon UV illumination, the increase being quite large near the transition.

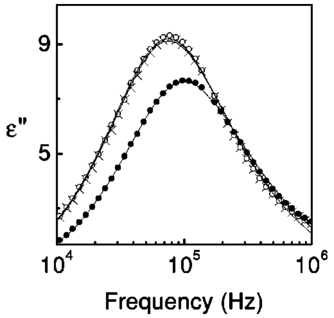

FIG. 2. Dielectric dispersion scans taken in the Sm-C_α^* phase, obtained before (open circles), during the process of illumination with UV radiation (filled circles) and after switching the radiation off (crosses). Notice that on UV illumination, the frequency of the peak point, corresponding to the relaxation frequency, shifts to a higher value, but the maximum value of ϵ'', corresponding to the dielectric strength decreases. After the radiation is switched off, the original values are recovered. The solid lines indicate the fit to expression (1).

by $\sim$21%, one can think in terms of the reported large increase in the dipole moment of the azobenzene molecules as a result of trans-cis isomerization [15]. For this purpose, we determined the dipole moment for EPH, the photoactive molecule used in the present study, using the MOPAC module in CHEM3D software (CambridgeSoft). We found that the value of the dipole moment along the short axis of the molecule gets doubled upon isomerization from the trans to the cis form. However, notice that the azobenzene molecules constitute only about 5% of the material and further, the extent of isomerization, calculated using the absorption peaks due to the π-π^* and n-π^* bands was estimated to be only $\sim$10%. Hence, any change in the dielectric constant, owing to the isomerization of azobenzene molecules, should at best be only about 1%, and is, thus, much smaller than the observed change. We shall see later, that the observed behavior is caused by the slower dynamics of the system.

Figure 2 shows representative dielectric dispersion scans taken at $T = 106.7\,^\circ\mathrm{C}$ in the absence of UV light and after turning it on. A substantial increase in the relaxation frequency, induced by the radiation is seen. Also significant is the fact that when the radiation is turned off, the system recovers the original peak. To extract the parameters characterizing the relaxation process, the data were fit to a Havriliak-Negami expression [16],

$$\epsilon''(f) = \frac{\sigma}{2\pi\epsilon_o f^m} + \mathrm{Im}\frac{\Delta\epsilon_s}{[1+(if/f_s)^\alpha]^\beta}. \tag{1}$$

Here f is the measuring frequency, σ is the specific conductivity of the sample, ϵ_o is the vacuum permittivity, $\Delta\epsilon_s$ and f_s represent the dielectric strength and relaxation frequency of the mode under consideration. The parameters α and β describe the shape of ϵ'' vs f profile; $\alpha,\beta = 1$ describes the shape for a Debye type of relaxation. We found that over the entire temperature range of measurement, the value of β was very close to 1, indicating that the profiles are symmetric about the maximum in the dielectric loss factor. The parameter α was found to take a value between 0.85 and 0.99, signifying that the distribution of the relaxation times is quite narrow. The values extracted from the fit for the data in Fig. 2 are $\sigma = 3.07\times10^{-10}$ S/m, 3.45×10^{-10} S/m; $f_s = 76.96$ kHz, 97.12 kHz; $\Delta\epsilon = 18.6$, 15.2 in the absence and presence of UV, respectively.

Figure 3 shows the variation of f_s and $\Delta\epsilon_s$ in the vicinity of the transition without and with steady state UV illumination. (As shown in Fig. 1, the transition temperature shifts to a lower value upon UV illumination. Hence, to facilitate a better comparison between the two sets, the data are plotted in terms of the reduced temperature $T - T_c$.) In the Sm-C_α^* phase the molecules are tilted with respect to the smectic layer normal, just like in the Sm-C^* phase. In contrast, in the Sm-A phase they are along the layer normal direction. Thus, in the vicinity of the transition, thermal fluctuations cause fluctuations in the amplitude of either long-range (Sm-C_α^*) or local (Sm-A) tilt. But in both the phases, an associated stiffness (elastic) constant governs the magnitude of such fluctuations. This elastic constant softens on approaching the transition and, therefore, the amplitude of the fluctuations should increase. This in turn increases the contribution to the dielectric strength and a concomitant decrease in the relaxation frequency, and, therefore, $\Delta\epsilon_s$ has a maximum and f_s a minimum at the transition. Now, let us look at the effect of UV illumination. As seen in Fig. 3, at any given reduced temperature $T - T_c$, $\Delta\epsilon_s$ has a higher value in the presence of UV light, the difference in the value with and without UV increasing as $T - T_c \rightarrow 0$, i.e., as the transition is approached. This feature is in agreement with the behavior of the low frequency dielectric constant shown in Fig. 1. As we saw earlier, any photodriven enhancement in the magnitude of the dipole moment of the azobenzene molecules is unable to account for the observed effect. Also significant is the fact that the value of f_s is lower in the presence of UV as com-

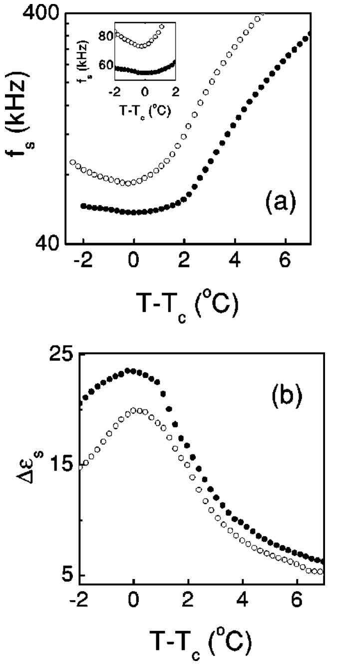

FIG. 3. Plot showing the behavior of (a) the relaxation frequency f_s and (b) the dielectric strength $\Delta\epsilon_s$ of the soft mode as a function of the reduced temperature in the presence (solid symbols) and absence (open symbols) of UV radiation. The data clearly demonstrate that at any given reduced temperature, UV illumination enhances the softening of the mode by lowering the relaxation frequency and increasing the dielectric strength. Another feature that may be noticed [see inset of (a)] is that the transition gets broadened in the presence of UV radiation. The magnitude of the radiation used here 6.4 mW/cm^2.

pared to the one in the absence of it. These features seem to suggest that the system softens more in the presence of UV. In other words, at any given reduced temperature the UV light enhances the magnitude of the tilt fluctuations. This is the opposite of the effect induced by ordering fields such as electric or magnetic fields [17]. In fact, we have recently described the photoinduced nematic-isotropic transition in the framework of a random field model where UV light plays the role of a disordering field [18].

In Fig. 4 the value of f_s at T_c is plotted as a function of I_{UV}, the amplitude of the UV intensity, and is seen to exhibit a quadratic dependence on I_{UV}, suggesting that the mode softening gets strongly enhanced by the UV light. But the concomitant increase in $\Delta\epsilon_s$ is a much weaker function of I_{UV}. To get a clue about the factor responsible for this photoinduced behavior, we borrow the expressions derived using a mean-field model and commonly employed to analyze the dielectric data in the vicinity of the Sm-*A*–Sm-*C** transition. (Although the detailed structure is different, Sm-C_α^* is similar to the Sm-*C** phase [19].) According to the mean-field model, the values of $\Delta\epsilon_s$ and f_s at the transition can be expressed as

$$f_s = \frac{Kq_o^2}{2\pi\eta_s}, \tag{2}$$

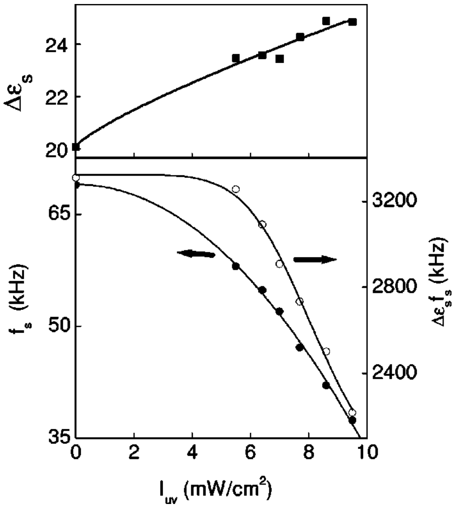

FIG. 4. Effect of the magnitude of the UV illumination on the value of the relaxation parameters at the transition: f_s (filled circles, bottom panel), $\Delta\epsilon_s$ (filled squares, top panel) and the product $\Delta\epsilon_s f_s$ (open circles, bottom panel).

$$\Delta\epsilon_s = \frac{\epsilon_o(\epsilon C)^2}{Kq_o^2}. \tag{3}$$

Here K is an elastic term, related to the bend elastic constant K_3, q_o is the wave vector corresponding to the helical pitch of the Sm-C_α^* phase, ϵ and ϵ_o are the high temperature and free space permittivities, respectively. C is a coefficient representing the linear coupling between polarization and tilt angle.

First let us look at the behavior of f_s, namely, that its value decreases as I_{UV} is increased. A possible reason for this behavior could be the lowering of the value of K_3 upon UV illumination. It may be recalled that decrease in K_3 values by the addition of bent molecules has recently been reported [20]. Thus we can expect K_3 to decrease owing to the bending of the photoactive molecules in the presence of the UV radiation. From Eq. (3) we see that $\Delta\epsilon_s$ is inversely proportional to K_3 and, therefore, we should expect an increase in its value upon illumination. Although this is qualitatively true, the increase in $\Delta\epsilon_s$ is only about 25%, while f_s decreases by about 46%. To eliminate the parameter K_3 from the expressions we take the product of the two quantities $\Delta\epsilon_s$ and f_s from Eqs. (2) and (3) we get

$$\Delta\epsilon_s f_s = \frac{\epsilon_o(\epsilon C)^2}{2\pi\eta_s}. \tag{4}$$

If the parameter K_3 alone is responsible for the changes then $\Delta\epsilon_s f_s$ should be independent of I_{UV}. This product is also plotted in Fig. 4 and is seen to be strongly dependent on I_{UV}, indicating that K_3 alone is not responsible for the observed behavior. From Eq. (4) we see that the variation of $\Delta\epsilon_s f_s$ with I_{UV} could be either because of a reduction in the magnitude of the polarization-tilt-coupling coefficient C or due to an enhancement in η_s, the soft mode viscosity. It is not clear as to why the viscosity gets enhanced in the presence of UV, although it is possible that the dynamic disorder created by the cis entities reduces the cooperative tendency of the system and hinders the dielectric relaxation. A more plausible cause is the UV-induced decrease in C. In this connection it may be recalled that a photoisomerization-driven decrease in polarization was observed [21] in a system of bent-core achiral molecules and was explained to be due to a ''local'' racemization. Such a process, if were to occur in the present system also, would lead to a reduction of the coefficient C. Detailed studies on the temporal behavior of the relaxation mechanism are in progress and are expected to throw more light on this interesting phenomenon.

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