

Effect of pressure on the photoinduced nematic-isotropic phase transition

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We report the results of high-pressure studies on the photoinduced nematic-isotropic phase transition. It is observed that pressure has a significant influence on the shift in the transition temperature caused by uv radiation. We propose a possible mechanism to explain the observed results.

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I. INTRODUCTION

It is well known that photochromic molecules like, for example, those containing azo groups undergo a reversible shape transformation when irradiated with light of suitable wavelength [1]. In the ground state the azo molecules exist in the *E* (also known as *trans*) form which has a rodlike shape. Upon illumination with uv radiation (~ 360 nm) photoisomerization takes place resulting in a transformation to the *Z* (or *cis*) form with a bent shape. When such azo entities are incorporated into a liquid crystalline medium, either by physical mixing or by chemical bonding, the photoisomerization can lead to spectacular results. For example, the *E* form, due to its rodlike shape, stabilizes the liquid crystalline phase while the photoinduced *Z* isomer with its bent shape acts like an “impurity” destabilizing the phase. The destabilization can even be significant enough to cause an isothermal photoinduced transition from a liquid crystalline phase, say, the nematic phase, to the isotropic phase [1,2]. This phenomenon has attracted attention, not only from a basic physics point of view, but also for possible applications in optical switching and image storage. Photoinduced effects

have been well studied in systems exhibiting nematic-isotropic (*N-I*) [1,3,2] and smectic *C**–smectic *A* [4,5] transitions. Very recently we reported [6] 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). Over the years, a variety of probes have been used to investigate photoinduced effects [7]. However, to our knowledge, the effect of pressure has not been studied. In this paper we report the results of high-pressure studies on the photoinduced nematic-isotropic phase transition.

II. EXPERIMENT

The liquid crystalline host material is 4-*n*-octyloxycyanobiphenyl (8OCB) from E-Merck and exhibits nematic and smectic *A* mesophases. The guest uv-active dopant compound, is *p*-(*p*-ethoxyphenylazo)phenyl hexanoate (EPH) from Eastman Kodak and is also liquid crystalline, exhibiting a nematic mesophase. All the results described in this paper have been obtained on a mixture of 3 mol% of EPH in 8OCB, which we refer to as mixture 1 hereafter. The *N-I* transition temperatures (T_{NI}), as obtained

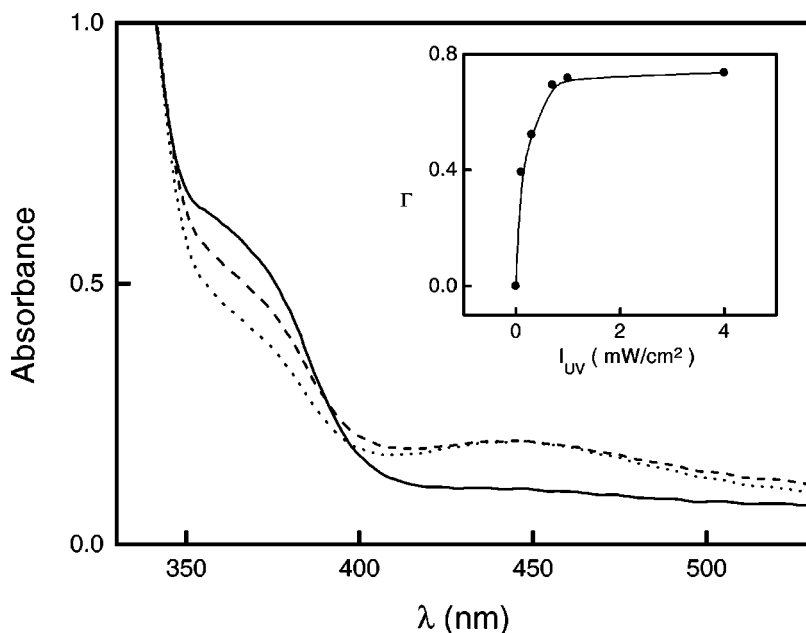


FIG. 1. Absorption spectra obtained in the nematic phase (at 72.9°C) of mixture 1 before (solid line) and after exposing to uv radiation of intensity 0.3 mW/cm^2 (dashed line) and 4 mW/cm^2 (dotted line). The maxima at ~ 374 nm and ~ 450 nm correspond to the π and π^* transitions of the *E* isomer and the n - π^* transition of the *Z* isomer, respectively. As expected, on exposure to uv radiation, the strength of the maximum due to the former decreases. The inset shows the efficiency Γ of the *E* isomer to *Z* isomer conversion as a function of the incident uv intensity. After a sharp increase at low intensities, a “saturation” behavior is seen at higher intensities. The line is meant as a guide to the eye.

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by differential scanning calorimetry (DSC 7, Perkin Elmer) for EPH, 8OCB, and mixture 1 are 125 °C, 79.8 °C, and 81 °C, respectively. The slight increase in the N - I transition temperature T_{NI} for mixture 1 with respect to pure 8OCB is to be expected as the T_{NI} for EPH is about 40 °C higher.

Photoabsorbance measurements were carried out using a uv-visible spectrophotometer (Lambda 20, Perkin Elmer). The samples were contained between two optically flat glass plates, separated by Mylar spacers, for measurements in the mesophase. The high-pressure setup employed has been described elsewhere [8]. It essentially consists of the sample sandwiched between two optically polished sapphire rods enclosed in an elastomeric tube, which not only serves as a container but also isolates the sample from the liquid pressure-transmitting medium. The transitions were detected by monitoring the intensity of a He-Ne laser beam transmitted by the sample. The uv apparatus used for inducing photoisomerization is described in an earlier publication [6]. Briefly, the uv radiation from an intensity stabilized uv source with a fiber-optic guide (Hamamatsu L7212-01, Japan) was used 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 (I_{UV}) of the radiation 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.

III. RESULTS AND DISCUSSION

Plots of absorbance as a function of wavelength obtained in the nematic phase at 72.9 °C before and after irradiation with uv light of different intensity levels are shown in Fig. 1. Upon irradiation there is a drastic decrease in the absorbance level at 374 nm indicating that the E - Z photoisomerization, the extent of which is dependent on the value of I_{uv} , has taken place. It is observed that there is a large background variation particularly below 340 nm. This is due to the absorbance from the biphenyl moieties of 8OCB and the contribution from the glass plates. The apparent efficiency of photoisomerization (or the disappearance of the E form of the azo molecule) can be determined [9] by $\Gamma = (A_0 - A_1)/A_0$, where A_0 and A_1 correspond to absorbance at 374 nm before and after irradiation. Values of Γ obtained for different I_{uv} levels are plotted in the inset of Fig. 1. Γ saturates for $I_{uv} \geq 1$ mW/cm², with an efficiency of 0.73, indicating that above that intensity 73% of all the E isomers are converted to their Z form.

As mentioned in the Introduction, the Z isomer, due to its bent shape, acts like an impurity for the rodlike host molecules. This causes a destabilization of the nematic phase leading to an isothermal transition to the isotropic phase. Figure 2(a) is a trace of the transmitted laser intensity as a function of temperature at room pressure obtained when there is no uv and when the sample is irradiated with uv illumination of 16 mW/cm². The N - I transition is signified by a sharp variation in the intensity. It is seen that uv illumination and the resulting photoisomerization depresses the transition temperature by as much as 11.4 °C. It should be

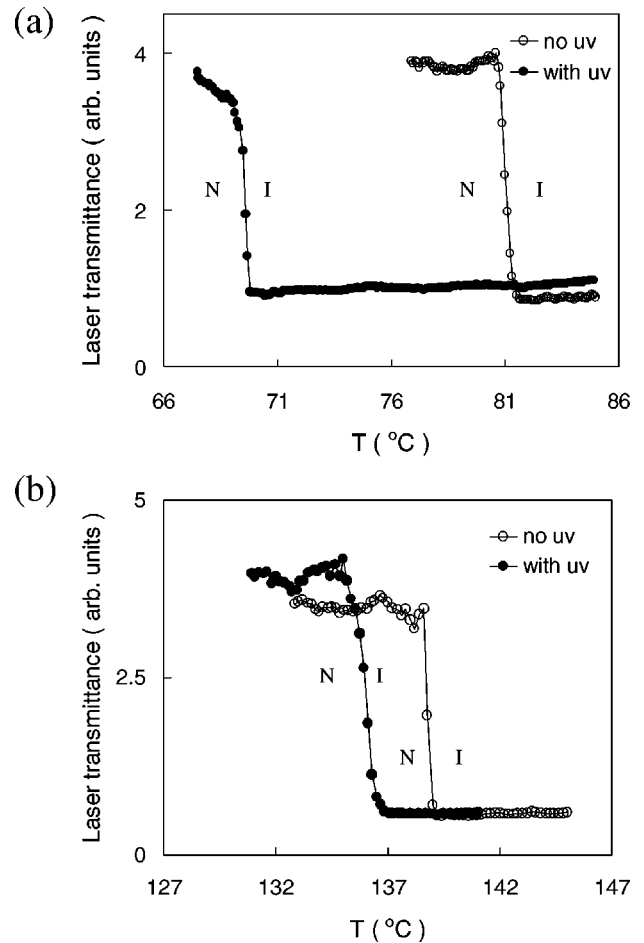


FIG. 2. Raw isobaric traces of the laser transmission as a function of temperature obtained at (a) room pressure and (b) a pressure of 2.2 kbar. In both the plots data represented by open and solid circles correspond, respectively, to scans taken in the absence of uv irradiation and when the sample is illuminated with uv radiation of 16 mW/cm² intensity. The E - Z isomerization caused by the uv radiation is responsible for the decrease in the transition temperature. Notice that the shift in the transition temperature diminishes substantially on application of pressure. The lines are meant as guides to the eye.

emphasized that on switching off the radiation, the reverse isomerization took place due to the thermal back relaxation process. A scan taken after the completion of the relaxation showed that the value of the transition temperature was identical to the one before the irradiation. In fact, this reversible and reproducible nature of the transition was observed at all pressures as well as for the different magnitudes of the uv intensities used in the experiments. One can perhaps argue that the reason for the shift in the transition temperature is due to local heating effects caused by the uv radiation. As already mentioned we took precautionary steps to reduce/eliminate such a possible effect by introducing an ir-block filter between the sample and the uv source. As a further independent check to confirm that the local heating effect is negligibly small/nonexistent, room pressure measurements were done in which the temperature measuring probe was located very close to the sample in the beam path. The actual

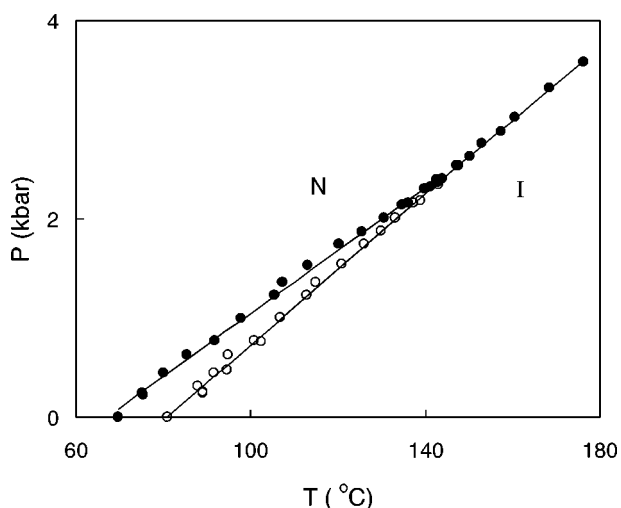


FIG. 3. Pressure-temperature phase diagram showing the nematic-isotropic (N - I) boundary obtained when there is no uv radiation (\circ) as well as in the presence of 16 mW/cm^2 uv radiation (\bullet). The uv-induced shift in the transition temperature decreases as the pressure is increased. Beyond a pressure $P_0 \sim 2.5$ kbar the uv radiation does not cause any change in the transition temperature. The lines are meant as guides to the eye.

temperature measured using such a probe showed hardly any difference between the uv on and off states. Thus, we can safely state that the isothermal transitions seen upon irradiation are solely caused by the E - Z photoisomerization. The trace obtained [Fig. 2(b)] when the applied pressure is 2.2 kbar clearly shows that the depression in the transition temperature $\Delta T (= T_{no\ uv} - T_{uv})$, decreases as the pressure is increased. The complete pressure-temperature (P - T) diagram is given in Fig. 3 and shows that the difference in the transition temperature with and without uv decreases with increasing pressure and goes to zero at a value of 2.5 kbar. In

order to check the effect of the magnitude of the uv radiation (I_{uv}), we performed measurements at different uv intensity settings. A plot of the calculated ΔT against the applied pressure for different values of I_{uv} is shown in Fig. 4. Three salient features to be noted are (i) at all uv intensities, ΔT decreases as pressure is increased and goes to zero at a certain pressure, which we denote as P_0 ; (ii) for each I_{uv} setting, ΔT has a weak pressure dependence at pressures well below P_0 , but decreases strongly close to P_0 ; (iii) P_0 increases as I_{uv} is increased. At low intensities P_0 is a strong function of I_{uv} , but has a saturation type of behavior for higher values of I_{uv} (inset of Fig. 4). This trend is qualitatively similar to the variation of ΔT with I_{uv} at room pressure (also shown in the inset of Fig. 4). Obviously, the behavior of ΔT is directly related to the dependence of Γ on I_{uv} as the magnitude of ΔT should depend on the number of Z isomers present in the system. As we shall see presently, the observed pressure dependence of ΔT should be over and above this effect.

In the following, we attempt to provide an explanation for the effect of pressure on the photoinduced phenomenon described above. As has been repeatedly stated, the photoinduced isothermal N - I transition occurs because of the fact that the Z isomer of the azo molecule has a bent shape and therefore acts like an impurity in the midst of rodlike host molecules. Measurements at constant temperature have established that there is a decrease in the specific as well as transition volumes as one moves up to higher transition pressures and temperatures [10,11]. Such a reduction in volume means that the intermolecular space available for the azo molecule to take a bent shape decreases as the pressure is increased. In other words, the system opposes the formation of the Z isomers. Consequently, the photoinduced shift in the transition temperature caused by the Z isomer also becomes smaller as the pressure is increased, and finally vanishes.

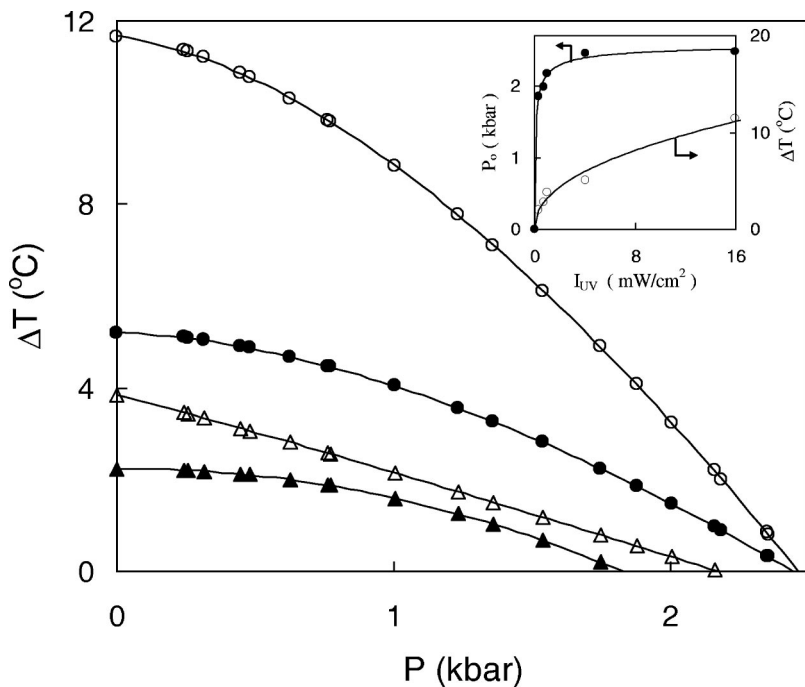


FIG. 4. Plot showing the effect of the magnitude of the uv intensity on the pressure dependence of the shift in the transition temperature ΔT . The different symbols represent data obtained at different uv intensities: solid triangle, 0.3 mW/cm^2 ; open triangle, 1 mW/cm^2 ; solid circle, 4 mW/cm^2 ; and open circle, 16 mW/cm^2 . The solid lines through the symbols are meant only as guides to the eye. Inset: uv intensity (I_{uv}) dependence of ΔT at room pressure and the pressure P_0 , beyond which there is no shift in the transition temperature. Both ΔT and P_0 increase sharply with increasing I_{uv} at low uv intensities, but show a much weaker dependence at high intensities. The behavior of P_0 , in particular, is qualitatively quite similar to the trend shown by Γ , the efficiency of the E - Z isomer conversion.

This opposition due to reduction in the intermolecular space can be countered, at least to a certain extent, by increasing the energy of the uv radiation pumped into the system. If this argument is true, then a higher intensity level of the radiation will force the *E* isomer of the azo to transform to the *Z* isomer. This will then lead to at least a partial restoration of the photoinduced shift in the transition temperature, as has indeed been seen in the experiments. The balance between these two opposing forces decides the pressure P_0 at which the shift becomes zero for a given intensity of the uv radiation. Volumetric measurements as a function of pressure with and without uv radiation would help in obtaining evidence for this hypothesis.

In summary, we have presented a report of the effect of pressure on the photoinduced nematic-isotropic transition. It is observed that the application of pressure reduces the shift in the transition temperature induced by photoisomerization.

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