

Photopyroelectric Investigation of the *trans-cis* Isomerization Effect on the Nematic-Isotropic Phase Transition of a Liquid Crystalline Azobenzene

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Abstract

Photopyroelectric calorimetry has been applied to the study of the effects of different concentration of photo-induced *cis* isomeric molecules on the characteristics of the nematic – isotropic phase transition in p,p'-diheptylazobenzene (7AB) samples. The investigations could be carried out by monitoring the behavior of the thermal diffusivity over the phase transition before and during the sample irradiation with UV light of varying intensity. Among other, it is shown that the monitoring of the time dependence of the thermal diffusivity at fixed sample temperature enabled the comparative study of the dynamics of the *trans-cis* and *cis-trans* isomeric transitions. It was shown that the increasing *cis* isomers concentration caused an increase in the fraction of material undergoing the phase transitions and increased the *cis-trans* conversion rate. Finally, polarization microscopy observations of the sample texture, which could be carried out together with the calorimetric evaluations proved useful for a more comprehensive analysis of the obtained results.

Keywords Azobenzene liquid crystal \cdot Phase transition \cdot Photopyroelectric technique \cdot Photoisomerization

1 Introduction

Liquid crystals (LCs) are broadly classified into different categories depending on how the phase transition between their mesophases are stimulated, being such transitions most often induced by variations in the LCs temperature. However, in a novel class of LCs, known as phototropic (PLC) [1–4], it has been observed that such phase transitions can be stimulated by light irradiation in isothermal conditions. Owing to such a circumstance, PLCs have attracted considerable attention because

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of the possibility to vary their macroscopic properties by optical means, thus opening up the possibility of designing light-driven devices such as optical modulators [5] or image recorders [6].

PLCs contain molecules that undergo transformation between two isomeric forms upon light absorption. Among others, p,p'-diheptylazobenzene (7AB) [7-10] has been one of the most widely investigated PLC because of the significant change in its molecular shape associated with the light-induced trans-cis isomerization. In fact, the 7AB molecule possesses an elongated trans ground isomer that, upon UV irradiation, converts into the metastable bent cis form. The reverse transformation into the trans ground state can occur either by visible light irradiation or through thermal relaxation in the dark [10]. Owing to the incompatibility between the cis isomer shape and the molecular orientational order, the presence of UV induced cis isomer often results in a destabilization of the mesophases that, under some circumstances, may possibly lead to an isothermal phase transition from more to less ordered mesophases.

7AB normally undergoes phase transitions from the crystalline (K) to the nematic (N) phase and, upon further heating, from the N to the isotropic (I) phase [11]. It has been found that, upon UV irradiation operated with a beam intensity of about 8 mW/cm², the I phase converts directly into the K one [11], being the intermediate ordered phases not able to form because of the presence of a sufficiently large number of cis isomeric molecules. Comparative analysis of the effects obtained at different cis molecule concentrations on the occurrence of the phase sequence in 7AB has however not yet been carried out.

In this work, the influence of the cis isomer concentration on the nucleation of the nematic phase upon cooling from the isotropic one has been investigated considering that the extent of the hindrance by the cis isomers to the onset of the N orientational order is expected to depend on their concentration. The rate equations for the trans-cis isomerization reported in Ref. [12] result in steady state values of the cis concentration that depend on the UV irradiation intensity. Accordingly, the I to N phase transition in 7AB samples for varying UV light intensities has been investigated by calorimetric evaluations. In particular, the photopyroelectric (PPE) calorimetric technique [13–22] has been adopted, which has been shown to be an effective tool for the characterization of phase transitions in PLCs [11, 22] since, unlike other calorimetric techniques, it enables the photoisomerization of the molecules to be induced by the UV light even during the calorimetric evaluations. In this respect, it is worth mentioning that a previous Nuclear Magnetic Resonance (NMR) investigation [23], also aimed at characterizing the disorder introduced by the cis isomers in the N phase in 7AB, could be carried out only after the UV light inducing the photoisomerization of the molecules had been switched off. In this way only phenomena concerning the relaxation from cis to trans states could be investigated and only with relatively small relaxation rates, while the trans to cis dynamics could not be probed. Moreover, the PPE characterization also enables the simultaneous optical microscopy study of the sample texture which, as shown later on, is of significant importance for a more comprehensive analysis of the results.

The study was carried out by monitoring the temperature dependence over the I-N phase transition of the thermal diffusivity D because it is related to the thermal

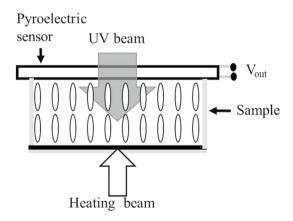


conductivity k and the specific heat capacity c through the expression $D=k/\rho c$, where ρ is the mass density. In fact, owing to the inverse proportionality to c which shows a peak over the phase transition, D correspondingly shows a minimum thus enabling the evaluation of the transition temperature T_{NI} that is expected to be significantly affected by the presence of the UV induced cis isomers. In addition, because of its proportionality to k, D proves to be sensitive to the average molecular alignment, which can occur when the nematic phase nucleates. This occurs because k is an anisotropic quantity whose value along a given direction may increase with the degree of the molecules orientation along that direction. Therefore, the comparison of the thermal diffusivity values obtained in the N range for different UV beam intensity values may allow the evaluation of the effect played by different concentrations of cis isomers on the onset of long range orientational order. Finally, we show that the time dependence of D can be usefully adopted to comparatively monitor the dynamics of both the trans to cis and cis to trans conversions as a function of the cis isomers concentration and sample temperature.

2 Experimental

Figure 1 depicts the scheme of the adopted experimental set up where PPE operates according to its back detection configuration of which a detailed description is given elsewhere [21]. As in Fig. 1, the sample is placed into a cell, 30 µm thick, where a modulated laser beam is absorbed by a metallic layer in contact with the sample surface so as to generate a thermal wave diffusing through the sample. A signal is then detected by a pyroelectric sensor in thermal contact with the opposite side of the sample. The induced temperature variation in the pyroelectric crystal gives rise to an output electric signal, V_{out}, that is then measured by means of a lock-in amplifier. Finally, the sample thermal diffusivity can be retrieved by processing the PPE signal phase data [21]. The sample cell is contained in an oven where the temperature was varied with a rate set at 0.01 °C/min.

Fig.1 Sketch of the experimental set up showing the modulated heating beam absorbed at the metallic layer (bottom) and the UV beam transmitted thorough the pyroelectric sensor and radiating through the sample (top)





The UV beam ($\lambda = 402 \text{ nm}$) [24] necessary to induce the trans to cis isomerization of the 7AB molecules could be introduced thanks to the optical transparency of both the pyroelectric transducer and of its ITO electrodes. Owing to the same reason, a linearly polarized visible light beam could also be directed through the sample to perform polarization microscopy observations of the sample texture.

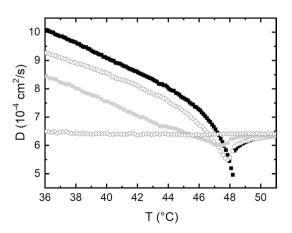
The sample cell walls have been treated with cetyl trimethyl ammonium bromide (CTAB) surfactant so as to promote the orientation of the 7AB molecules perpendicularly to the sample surface (homeotropic alignment) and, consequently, parallel to the induced heat flow. This condition corresponds to the maximum achievable values of k and therefore of D.

The 7AB sample was provided by AWAT Co Ltd, Poland and its molecular structure consist of two phenyl rings interconnected by a N=N bond with terminal alkyl C₇H₁₅ chains attached to each ring. Upon UV irradiation, the elongated trans isomer whose characteristic length is about 29 Å converts into the bent cis one characterized by a length of only about 16 Å.

3 Results and Discussion

Figure 2 shows the thermal diffusivity temperature dependence obtained with various UV irradiation conditions. In these measurements the UV illumination started in the I phase before cooling the sample and kept on throughout the sequence of the calorimetric runs. The position of the minima of the D profiles and, hence, the corresponding value of the transition temperature, are progressively downshifted with increasing UV intensity. In particular, values of T_{NI} =48.2 °C, T_{NI} =47.85 °C, and $T_{NI} = 47.5$ °C have been obtained for UV intensity of 0 mW/cm², 0.15 mW/cm², and 0.6 mW/cm², respectively. This is related to the progressive increase with intensity of the concentration of cis isomers [12] which, because of their bent shape, lead to the destabilization of the orientational order characteristic of the N phase. Moreover, there occurs a progressive increase of the D minimum value at T_{NI} , as well as an increase of the rounding of the profiles, reflecting the corresponding reduction of the

Fig.2 Temperature dependence of the thermal diffusivity in 7AB obtained with UV intensities of $0 (\blacksquare), 0.15(\bigcirc); 0.6 (\blacksquare)$ and 6 mW/cm² (\Diamond)





specific heat peak value at the transition temperature. This is related to the broadening of the transition region because of the presence of the cis isomers which act as impurities within a matrix of trans isomers. It is worth noting that the temperature dependence of D obtained for the largest value of the intensity (6 mW/cm²) is practically smooth over the investigated temperature range because of the absence of the formation of the N phase [11]. Also evident is the progressive decrease of the D values in the N phase, indicating a smaller degree of achieved mean molecular alignment. This is most likely related to the cis isomers preventing the occurrence of the orientational ordering of the LC molecules, with a significant percentage of the material remaining in the I phase, and a corresponding decrease of the thermal conduction efficiency across the sample and, consequently, of the thermal diffusivity value.

In order to gather further elements useful for the discussion of the results, the modifications of the sample texture induced by the UV irradiation have also been monitored by the polarization microscopy analysis of the sample. Such observations have been carried out after the sample had initially thermalized at 46.5 °C in the dark in the N phase. A birefringent texture of the N phase can be observed (see Fig. 3a) before the UV irradiation. In this respect, it is worth mentioning that the N phase in 7AB is biaxial [25] and, unlike the uniaxial compounds, it gives rise to birefringent patterns in the polarization microscopy images even with a homeotropic orientation of the sample [26].

With the UV irradiation, the sample part directly hit by the UV light first converts into the isotropic phase as shown in Fig. 3b where the bright and dark areas correspond to N and I domains, respectively. Finally, as the irradiation time increases, the N-I transition is induced also beyond the UV illuminated area (see Fig. 3c). The reason for such a result is that the cis isomers laterally diffuse beyond their generation region [27,28], with a consequent isothermal N-I transition occurring also in areas outside that hit by the UV light. After switching off the UV light, the sample converts back to the N phase progressing from the outer regions, where the cis isomer concentration is lower, toward the central area. Similar kind of results were observed at all the employed UV beam intensities, only with a considerable reduction of the I domain growth rate with the decreasing UV light intensity.

The dynamics of the conversions between the two molecular isomers and its dependence from the UV generated cis isomer concentration was further investigated by monitoring the time dependence of D following the start of the UV irradiation and its subsequent removal to inspect the likely dependence of the molecules



Fig. 3 Polarization microscopy images taken before UV irradiation \mathbf{a} ; at t=20 min \mathbf{b} and at t=170 min c after the onset of the UV irradiation obtained with at T=46.5 °C and a UV intensity of 0.15 mW/cm²



isomerization and relaxation rates from such parameters. In fact, according to the results reported in Ref. 8, the *cis* isomers concentration c_C , as well as their relaxation rate, are expected to depend on the UV beam intensity Φ according to the expression [12]:

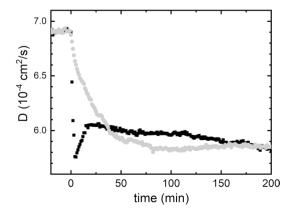
$$c_C(t) = c_{T0} \frac{K_{TC} \Phi \left\{ 1 - exp \left[- \left(\tau^{-1} + K_{TC} \Phi \right) t \right] \right\}}{\tau^{-1} + K_{TC} \Phi} \tag{1}$$

where c_{T0} is the initial trans isomers concentration, $K_{TC}\Phi$ is the UV induced rate for the trans to cis photoisomerization and τ is the characteristic time for the cis to trans thermal relaxation. For the cis to trans isomerization, the UV induced rate, i.e., $K_{CT}\Phi$, has been neglected since the UV quantum yield of such a process in 7AB can be considered negligible with respect to the *cis* to *trans* one.

In order to investigate the time dependence of D, before the beginning of the UV irradiation the sample was thermalized in the N phase at T=46.5 °C, being such a temperature close to the T_{NI}. With the sample in the N phase but at lower temperatures, the time dependence is expected to be similar to that observed at 46.5 °C only occurring with a slower rate because of the stiffer nature the N material exhibits at temperatures further away from the NI transition temperature [23].

In, Fig. 4 the time dependence of D is shown following the onset of the UV illumination (t=0). As regards such measurements, it must be mentioned that the calorimetric probing was performed over an area of approximately 1 mm² in the center of the UV illuminated area $(2 \times 3 \text{ mm}^2)$. With the maximum used intensity, $\Phi = 6 \text{ mW/cm}^2$ a rapid decrease initially occurs form the initial value of D and, after going through a sharp minimum, it reaches the value characteristic of the isotropic phase, as confirmed by the sample texture showing a dark pattern typical of such a phase. This isothermal phase conversion occurs because of the progressive increase of the concentration of the cis isomers occurring with increasing UV exposure time. A similar result is obtained with a smaller UV light intensity (0.15 mW/cm²) only with a considerably slower response time causing a broader minimum feature. This is consistent with a smaller value of the UV induced trans to cis conversion rate in

Fig. 4 Time dependence of the thermal diffusivity after the start of UV irradiation at t=0for UV light intensity of 6 mW/ cm^2 (\blacksquare) and 0.15 mW/cm² (\bullet) at $T = 46.5 \, ^{\circ}C$





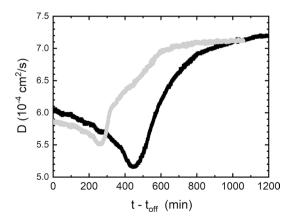
Eq. 1. It is useful to point out that the time dependence profiles of D in Fig. 4 corresponds to the specular images of those obtained in Fig. 2. This occurs because in both cases the thermal parameters are recorded as the sample temperature difference from $T_{\rm NI}$ is varied. In Fig. 2 the change is produced by varying the sample temperature at fixed $T_{\rm NI}$, (at each fixed cis isomers concentration) while in Fig. 4, at a fixed sample temperature, D is probed as the cis isomers concentration changes with time therefore producing corresponding changes of $T_{\rm NI}$. Therefore, the occurrence of the minima in the profiles of D in Fig. 4 are associated with the maxima in the specific heat capacity occurring during the nematic-isotropic phase transition.

In Fig. 5 the time dependence of *D* is shown following the switch off of the UV light at the two previously indicated intensities. In both cases the transition back to the N phase occurs with the value of *D* passing through a minimum, while the phase transition was occurring, and eventually reaching that characteristic of the N phase. The time required to reach such a value is shown to be larger for the sample previously illuminated with a larger intensity. This is likely related to the longer time required to convert back the initially larger induced concentration of *cis* isomers [23]. Finally, the minima of *D* over the phase transition time interval is shown to be smaller in the case of the larger UV intensity, corresponding to a larger value of the specific heat peak. This is consistent with the larger fraction of material isothermally switching to the N phase following the original generation of a larger concentration of *cis* isomers.

4 Conclusions

Photopyroelectric calorimetry has been applied to the investigation of the UV induced *trans* to *cis* isomerization effects over the I-N phase transition in 7AB liquid crystal. In this respect, the photopyroelectric calorimetry has been proven to constitute a unique tool since, unlike other calorimetric techniques, it enables the measurements to be carried out also while the sample is illuminated with the UV light to induce the sample molecules isomeric transformation. Such an ability has been

Fig. 5 Time dependence of the thermal diffusivity detected after the switch off ($t_{\rm off}$) of the UV light with intensities of 6 mW/ cm² (\blacksquare) and 0.15 mW/cm² (\blacksquare) at T=46.5 °C where the sample was in the I phase at $t_{\rm off}$





exploited for measuring the temperature dependence of the thermal diffusivity over the I-N transition for different values of the UV beam intensity and, consequently, of the concentration of the induced cis isomers. This because the thermal diffusivity can provide information on both the transition temperature and on the degree of average alignment of the liquid crystal molecules.

Upon increasing the UV light intensity, a progressive reduction of both the transition temperature value and in the attained orientational order of the 7AB molecules upon cooling over the N phase has been observed. These results have been ascribed to the shape of *cis* isomers being incompatible with the N phase orientational order, thus leaving a significant percentage of the sample in the I phase, and hindering the molecules orientational order in the N phase.

It has also been shown, by monitoring of the time dependence of the thermal diffusivity at fixed sample temperature, that the increase of the cis isomers concentration increased the *cis-trans* conversion rate. Finally, polarization microscopy observations of the sample texture, which could be carried out together with the calorimetric evaluations in the photopyroelectric set-up, proved useful for a more comprehensive analysis of the obtained results.

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Declarations

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