Photopyroelectric investigation of the *trans-cis* isomerization effect on phase transitions of a liquid crystalline azobenzene

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Over the recent period, photothropic liquid crystals (LC) have attracted considerable attention because of the possibility to very their properties by optical means. Such compounds may consist of photoactive molecules which possess self-ordering capabilities such as to give rise to LC mesophases. One example is constituted by p,p'-diheptylazobenzene (7AB) molecules that in their ground *trans* state do not significantly affect the LC ordering because of their elongated shape. Upon UV irradiation, the molecules convert into their bent *cis* form, thus destabilizing the LC phases to an extent that, under some circumstances, can possibly lead to an isothermal LC phase transition from a more to a less ordered phase. The reverse conversion into the *trans* ground state can occur either by visible light irradiation or through thermal relaxation in the dark. Despite the large number of investigations carried out in 7AB-LC mixtures, only few studies concerning the effect of UV irradiation on the phase transitions of pure 7AB have been reported in the literature [1,2].

Calorimetry has been proven a very effective technique for the analysis of phase transition in a wide range of different materials. However, as regards the investigation of photochromic LC, most of the calorimetric techniques suffer from severe limitations mainly because of the difficulty to introduce the optical beam in order to stimulate the phase transitions. Unlike such techniques, photopyroelectric calorimetry (PPE) has been demonstrated to be a very effective tool. In fact, thanks to the optical transparency of the pyroelectric transducer the UV beam to stimulate the *trans* to *cis* form isomerization can be directed onto the sample during the calorimetric measurements. Moreover, a linearly polarized white light beam can also be directed onto the sample to carry out reflection polarization microscopy observations of the sample texture simultaneously with the thermal properties measurements, being such a possibility of crucial importance for the interpretation of the experimental results.

In this study, PPE has been employed for the study of the transition between the nematic (N) and the isotropic (I) phase in pure 7AB upon varying degrees of UV sample irradiation so as to induce different concentrations of *cis* isomers. Beside the measurement of the temperature dependence of the thermal parameters for stationary values of the *cis* concentration, the dynamics of the *trans-cis* isomerization has been investigated by analysing the time-dependence of both the specific heat c and the thermal conductivity k following the onset of the UV irradiation and its subsequent switching off. As it can be seen in Fig. 1, right after the beginning of the UV irradiation, both c and k show a step decrease because of the progressive conversion of the N phase into the I one due to the disorder introduced by the *cis* isomers as confirmed by Fig. 2a where the bright and dark areas correspond to N and I domains, respectively. Upon further UV irradiation, the N-I transition is induced through the entire sample, even beyond the illuminated area (see Fig 2b). Finally, once the UV irradiation is turned off, the *cis* isomers covert into the ground *trans* ones over their relaxation period and, consequently, the transition from the

I phase to the N one takes place (see Fig.2c and 2d) as evidenced by the corresponding time–dependence of the thermal parameters.

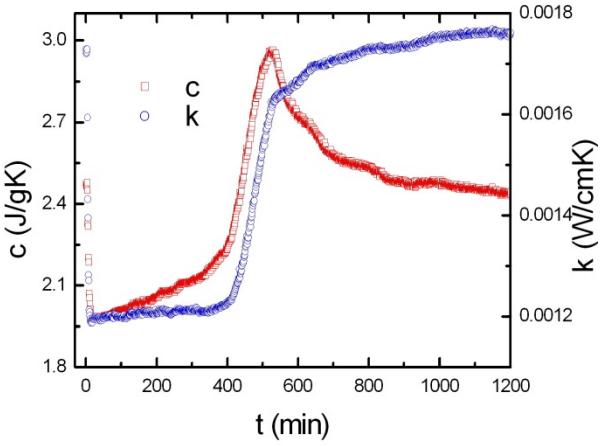

Fig. 1. Time-dependence of the specific heat (□) and the thermal conductivity (○) following the onset and the subsequent turning off of the UV radiation at t=3 min and t=16 min, respectively.

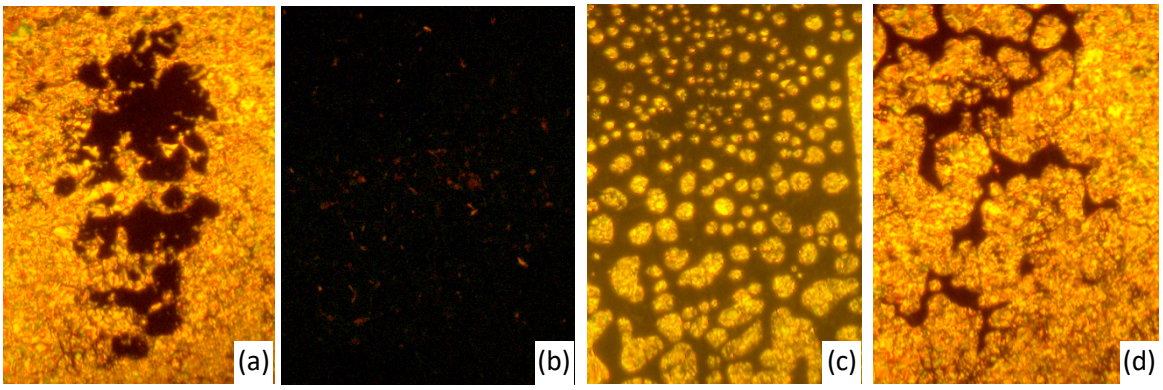

Fig. 2. Sample textures observed during the cis-trans isomerization shown in Fig. 1 at t=4 min (a), t=30 min (b), t=480 min (c), and t=520 min (d)

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References

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