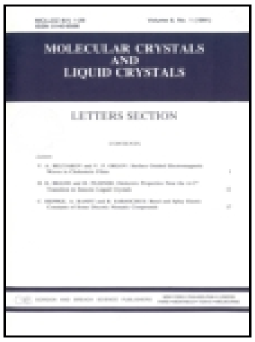

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Photopyroelectric Calorimetry for the Thermal and Optical Evaluations Over Phase Transitions in Liquid Crystals

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We report on calorimetric and optical evaluations performed by Photopyroelectric calorimetry on two phenomena involving changes in average molecular alignment. We first study the possibility to obtain permanent homeotropic single domain alignment in the smecticA phase by applying a “vertical” strain field in the volume of samples of 4-decyl-4′-cyanobiphenyl and of 4-octyl-4′- cyanobiphenyl, liquid crystals. We then report on the effects produced by the illumination by UV light on 4-octyl-4′- cyanobiphenyl samples hosting photochromic molecules in terms of the change induced to the phase transitions characteristics and the average molecular alignment.

Keywords Calorimetry; phase transitions; polarization microscopy; thermal transport

Introduction

The photopyroelectic technique (PPE), in the so called “back-detection” configuration, is a technique which enables the determination, with a high temperature resolution, of the specific heat, *c*, the thermal conductivity, *k*, and the thermal diffusivity, *D*, of a sample, and it is thus very useful for a complete study of the critical behaviour of the thermal parameters over phase transitions in solids and liquids [1, 2]. Its principle of operation is based on the photothermal techniques which consist in detecting the temperature oscillation at one surface of a sample induced by the absorption of modulated light. They have proved to be very sensitive techniques which allow an adequate signal to noise ratio to be achieved with little light induced heating. They are therefore extremely important when the temperature dependence of the thermal parameters must be obtained with a large temperature resolution, and also in all those situations where the optical absorption in the samples is limited, such as in the case of thin films [3]. Moreover, they have proved to be very useful even to study the frequency dependence of thermal parameters for the detection of glassy behaviour [4], and to detect latent heat [5, 6].

Recently, an upgraded setup has allowed to perform also polarization microscopy evaluations and optical transmittance evaluations, together with, and therefore with the same high temperature resolution, as the thermal parameters measurements [7, 8].

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The possibility to perform, in the upgraded PPE set-up, measurements of the thermal transport parameters (thermal diffusivity/conductivity), which are anisotropic in liquid crystals (LC), and polarization microscopy evaluations, enables the accurate monitoring of the degree of average molecular alignment in the LC samples. So in this work we report on the study of two different phenomena where the monitoring of the molecular alignment in the sample proves very useful. In particular, we report first on the study of the possibility to obtain permanent homeotropic single domain alignment in the smecticA phase of 4-octyl-4′- cyanobiphenyl (8CB) LC by applying a "vertical" strain field in the sample volume, similarly to what can be achieved by inducing shear flow [9] in the nematic phase of LC. We then report on the effects produced by the illumination by UV light on 8CB LC samples hosting photochromic molecules in terms of the change induced to the phase transitions characteristics and the average molecular alignment.

Experimental

The polarization microscopy observations and the thermal diffusivity determination were performed simultaneously in a photopyroelectric (PPE) calorimetric setup [7, 8, 10] where the LC samples were contained in quartz cells of calibrated thickness ranging between 10 and 100 μm. The cell side in contact with the LC was coated with a 300-nm-thick optically opaque Ti layer. The opposite sample side was in thermal contact with a 300 μm thick Z-cut $LiTaO_3$ pyroelectric transducer, constituting the cover of the cell, coated with transparent indium-tin oxide (ITO) electrodes. The light from a laser diode, modulated at frequencies which, depending on the cell thickness, ranged between 11 and 60 Hz, was absorbed by the metallic coating in contact with one side of the sample, and the temperature oscillations introduced in the sample were detected on the opposite side by the pyroelectric transducer. A two phase lock-in amplifier measured the signal amplitude and phase from which the specific heat c, the thermal conductivity k, and the thermal diffusivity $D = k/\rho c$, (ρ is the density) can simultaneously be retrieved by means of appropriate theoretical expressions [10, 11]. The power density and the temperature rate change were adjusted to minimize the thermal gradients in the sample which can induce smearing of the Vs temperature profiles of the observed quantities. Thanks to the transparent ITO electrodes of the pyroelectric transducer, the light from a lamp, transmitted through a polarizer, could be introduced in the sample and, after the reflection from the metalized side of the cell, it could be conveyed through a crossed analyzer to reach a CCD camera, so that polarization microscopy observations could be recorded [7, 8, 10].

During the calorimetric measurements on the 8CB mixed with the naphopyran (methyl 8-(49-pentylbiphenyl-4-yl)-2-phenyl-2-(4-fluorophenyl)-2H-naphtho[1,2-b]pyran-5-carboxylate) molecules, their switching from the "closed" form to a planar and more elongated "open" form [12] was obtained by introducing in to the sample also the UV light from a laser diode operating at 405 nm.

For the strain induced alignment studies, the homeotropic single domain samples was achieved by applying a strain on the LC molecules perpendicular to the cell walls, obtained by small vertical displacements of the pyroelectric transducer. In this way, because of the very effective wetting of the transducer wall by the surface molecular layer following the cooling down of the sample from the isotropic to the smectic phases, a vertical "stretch" could be applied to the sample molecules, which could promote a uniform molecular alignment along such a direction.

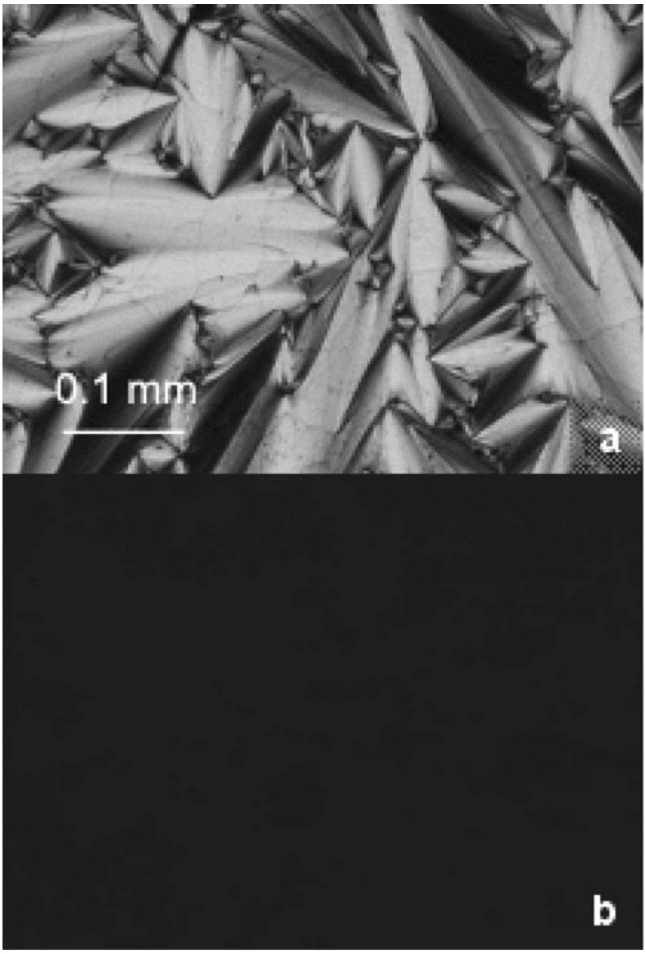

Figure 1. Polarization microscopy pattern of focal conics texture (a) and homeotropic sample (b) in the smectic phase of 10CB LC.

Results and Discussion

Stress Induced Alignment

In samples with the nematic (*N*) phase a permanent uniform molecular alignment can be achieved by inducing an anisotropy on the cell walls which can promote a common orientation direction in the molecular layer next to the substrate [13]. The field resulting from the aligned layer can then yield a common molecular orientation throughout the whole sample as it is cooled down from the isotropic (*I*) phase. This can occur because of the fluid like nature of the nematic phase. In nematics, optical induced orientation effects can also be achieved [14]. However, when the sample cools from the isotropic phase directly in the smectic*A* (*A*) one, with no intermediate nematic phase, the stiffer nature of the former prevents eventual surface ordering fields on the cell walls to produce the uniform alignment in the sample volume of both the molecular director and of the smectic planes. In this case the aligning field needs to be applied throughout the entire sample volume as when a

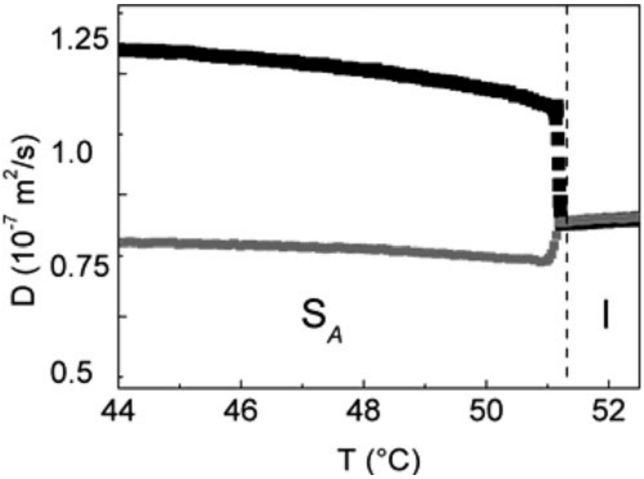

Figure 2. Thermal diffusivity profiles over the smectic-isotropic range in 10CB LC in a homeotropic sample (black) and focal conics texture (gray).

magnetic field is applied [15], but, in this case, the alignment can survive only as long as the field is maintained.

Another possible volume diffused field which could possibly achieve uniform alignment in the smectic*A* phase may be that associated with a uniform strain field induced in the sample volume, similarly to what occurs in the case of the flow induced alignment in nematics mentioned earlier on. Even in the smectic*A* phase, the resulting hydrodynamic torques acting on the molecules could induce a uniform orientation of their director and, possibly, also of the smectic planes. Figure 1a shows the polarization microscopy images of a 10 μm thick sample of 10CB LC showing a multi domain focal conics textured [16] smectic*A* sample, obtained after the cooling from the isotropic phase. Then, with the sample thermalized at 45°C in the smectic*A* phase, the vertical displacement, necessary to achieve the homeptropic single domain alignment, is applied to the pyroelectric transducer. This yields the uniform dark pattern, shown in Fig. 1b, which confirms the lack of birefringence typical of homeotropic single-domain samples (Fig. 1b). So, once the hydrodynamic torques associated with the volume diffused uniform "vertical" strain succeed in aligning the molecules in the smectic*A* phase, such an alignment proves to become permanent. After the sample is taken again to the isotropic phase and then cooled back over the *IA* transition, the formation of the focal conic texture occurs thus once again providing evidence that all memory of the previous single domain alignment is lost when re-entering the smectic*A* phase from the isotropic phase. Therefore, even though, as suggested in ref. 17, a homeotropically aligned molecular monolayer anchored to the cell walls may actually form during the alignment procedure and even survive in the isotropic phase, it would not succeed in the recovery of the alignment in the sample volume as the smectic*A* phase is entered from the isotropic one, as pointed out earlier on.

The good degree of homeotropic alignment in the single domain sample is also certified by the results reported in Fig. 2 which show the thermal diffusivity values in the smectic*A* phase considerably larger than those in the isotropic phase as observed earlier on [18, 19]. After the sample is taken to the isotropic phase, the subsequent cooling over the

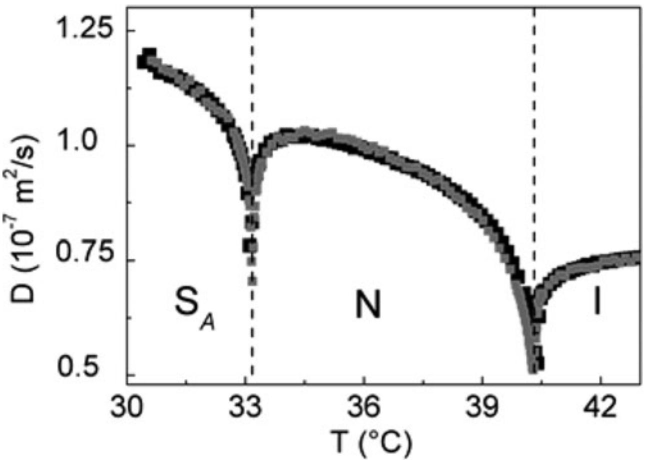

Figure 3. Thermal diffusivity profiles over the smectic-isotropic range in 8CB LC in a homeotropic sample during: heating (black) and subsequent cooling (gray).

AI transition leads to thermal diffusivity values close to that of the isotropic phase, typical of the non aligned focal conic textured sample.

The strain induced alignment was also produced in an 8CB LC sample, which displays an intermediate nematic phase between the isotropic and the smectic*A* ones. The strain is applied to the sample after the sample is cooled down close to 30°C in the smectic*A* phase. The thermal diffusivity profiles are reported in Fig. 3, as the aligned sample is subsequently heated up to the isotropic phase and then taken back to the smectic phase. Both the *NI* and the *AN* transitions are clearly detectable in the thermal diffusivity profiles by the minima displayed over both transitions. The larger diffusivity values found in the nematic and in the smectic*A* phases, with respect to the isotropic one, confirms a successful homeotropic single domain alignment in the former phases, as also witnessed by the correspondingly dark polarization microscopy pattern (not reported). In this sample, however, following the cooling through the nematic and smectic*A* phases, the thermal diffusivity profile typical of the single domain homeotropic alignment is fully recovered. Therefore, in this sample, the ordering field induced by the aligned molecular monolayer anchored to the cell walls, referred to in ref. 17 and produced following the application of the strain field, proves sufficient to promote the uniform homeotropic alignment in the whole sample volume as the “soft” nematic phase is entered from the isotropic one. Once the smectic*A* phase is subsequently entered, the uniform alignment of also the smectic planes is obtained back.

Effect of UV Illumination in LC with Photochromic Molecules

Naphtopyrans are a family of photochromic molecules which, under UV light illumination, change their configuration from a “closed” form to a planar and more elongated “open” form [12]. When hosted in a LC, their presence weakens the average ordering molecular field of the LC and therefore lowers the phase transition temperatures with respect to the pure material. When switching from the closed to the open configuration, because of the more elongated form of the latter, the disordering power of the naphtopyrans molecules is reduced and thus causes a correspondent reduction also of the depression, with respect to the pure LC, of the transition temperatures. Upon UV light exposure, such temperatures

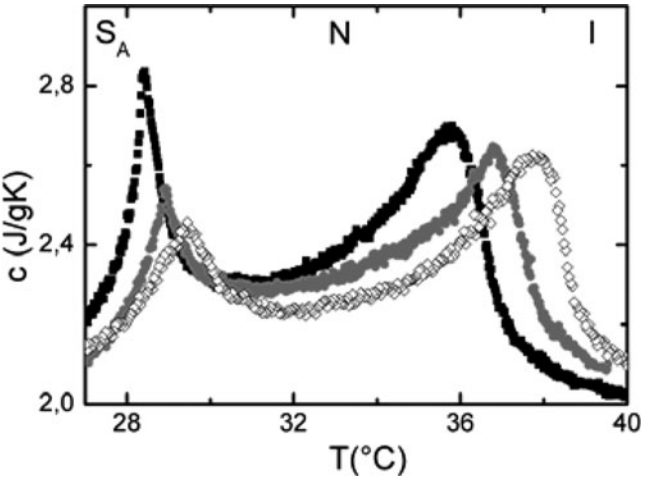

Figure 4. Specific heat profiles over the smectic- isotropic range in 8CB LC with 2% naphtopyran molecules: before (black), during (gray), after (open) UV illumination.

should therefore become larger than those before the illumination. So, if the naphtopyrans molecules are hosted, for example, in the isotropic phase of a LC close enough to the transition temperature to the more ordered nematic (N) phase, the illumination with UV light can cause the LC to switch to the N phase as showed by polarization microscopy observations in ref. 12. The transition temperatures can be evaluated by probing the specific heat temperature dependence which in turn requires calorimetric evaluations. To date, the only technique which can allow UV light access to the sample *during* the specific heat evaluation is PPE calorimetry which thus enabled such a characterization to be carried out.

Figure 4 shows the temperature dependence of the specific heat over the *NI* and *AN* phase transitions of an 8CB liquid crystal sample, containing a 2% mass concentration of naphtopyran molecules, before, during and after the UV light illumination, the data being collected only when cooling down the sample from the isotropic phase. The UV illumination conditions were changed with the sample in the isotropic phase and the data collection was started just minutes after the change. At this concentration, before the UV illumination, the *IN* and *NA* transition temperatures turn out to be, respectively, approximately 4°C and 5°C smaller with respect to the pure material [18]. As expected, the UV light causes both the transition temperatures to shift to larger values as the photochromic molecules switch to their more ordered open configuration because of the reduction of their disordering power. Finally, it can be observed that, after repeated cycling over the two transitions with the UV light on, after the light is turned off, the transition temperatures do not return down to the corresponding values obtained before the light had been switched on. This indicates that the prolonged (several hours) exposure of the photochromic molecules to the UV light, occurring during the cycling with the light on, causes irreversible effects in the molecules in their open form. Figure 5 shows the thermal diffusivity profiles for the 8CB sample with 2% naphtopyran molecules over the smectic*A* -isotropic temperature range, before, during and after the UV illumination. The substantially larger values in the nematic and the smectic*A* phases, before the UV illumination, with respect to the isotropic phase, indicate the good degree of homeotropic alignment having occurred in the sample in spite of the absence of any surface treatment of the cell walls. The alignment was confirmed

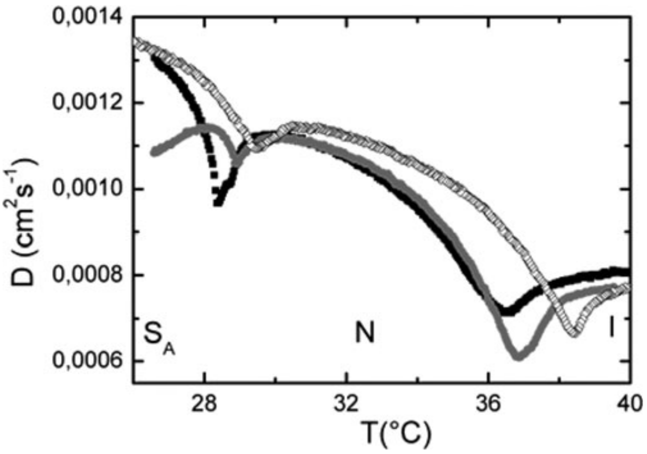

Figure 5. Thermal diffusivity profiles over the smectic-isotropic range in 8CB LC with 2% naphtopyran molecules: before (black), during (gray), after (open) UV illumination.

by the correspondingly obtained dark polarization microscopy pattern (not reported). It is seen that, after the UV light was switched on, the sample persisted in the homeotropic state throughout the entire nematic range, but, upon entering the smectic*A* phase, the thermal diffusivity showed a progressive decrease indicating a partial lost of such an alignment. Such a possibility could be readily verified in the correspondingly obtained polarization microscopy pattern, displayed in Fig. 6, which shows some focal conic texture nuclei embedded in a homeotropic (dark) matrix. It is therefore evident that the presence of open form naphpopyran molecules can disrupt the homeotropic alignment. It can also be seen that, after the repeated cycling over the two transitions, with the naphopyran molecules persisting in their open form even after the UV light is switched off, the homeotropic alignment is

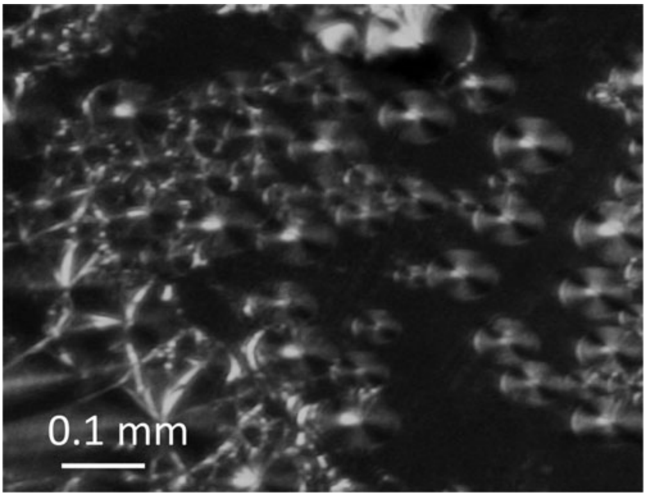

Figure 6. Polarization microscopy pattern, corresponding to the gray data in Fig. 5, showing focal conics texture nuclei embedded in homeotropic matrix.

eventually recovered even in the smectic*A* phase. The same kind of measurements were repeated with the cell walls treated with a surfactant, to induce a more effective homeotropic alignment in the nematic phase of the sample. No focal conics texture does form in this case as the smectic phase is entered from the nematic one with UV light on and, therefore, with the photochromic molecules in their open form. To possibly explain such results we must consider that reports have shown that [20], in the smectic*A* phase of LC, the hosted photochromic molecules in the disordered (closed) form become segregated between the LC smectic planes. They can become integrated within the planes only when they assume the more elongated open form. So it must be concluded that it is the process of inclusion of the photochromic molecules within the LC molecular smectic planes that can cause the formation of the focal conics texture. So, probably, when the LC molecules in the nematic phase are homeotropically aligned with sufficient effectiveness such as to induce alignment of also the open form photochromic molecules, then the latter can be hosted in the smectic planes without disrupting the existing alignment. This can occur when the sample walls are treated with a surfactant, or, in the sample without treated walls, following repeated cycling of the open form photochromic molecules in the nematic phase where their degree of homeotropic alignment can progressively increase.

Conclusions

By simultaneous photopyroelctric calorimetry and optical characterizations, we have shown that a permanent homeotropic single domain alignment can be induced in the smecticA phase of 10CB and 8CB LC samples by applying a “vertical” strain field in the sample volume. In the case of 10CB sample, when the sample is taken from the homeotropically aligned smectic phase, to the isotropic and then back to the smectic phase, the homeotropic alignment is lost. In the case of the 8CB sample, the same cycling, passing through the intermediate nematic phase, leads to a reformation of the homeotropic single domain.

Using the same technique we have shown that, in 8CB mixed with 2% naphtopyran photochromic molecules, their switching from the closed to the more elongated open form induced by UV light illumination, causes an upward shift of both the *NA* and *IN* transition temperatures of the LC due to the reduction of the disordering power of the naphtopyran molecules in their open form. Moreover such a structure change can cause the disruption of the initial homeotropic alignment in the smectic phase of the LC.

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