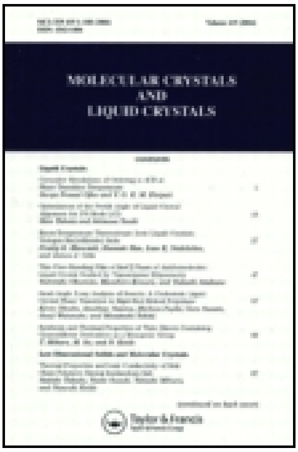

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Novel Application of a Photothermal Technique on Polymer/Liquid Crystal Mixtures

S. Delenclos [a], H. Sahraoui [a], M. Benmouna [a] [b], J.-M. Buisine [a] & U. Maschke [c]

[a] Laboratoire de Thermophysique de la Matière Condensée (Equipe de l'UPRESA N° 8024 du CNRS), Université du Littoral, MREID, Dunkerque, F-59140, France

[b] Laboratoire de Recherche sur les Macromolécules, Faculté des Sciences, Université Aboubakr Belkaïd, Bel Horizon, Tlemcen, 13000, Algeria

[c] Laboratoire de Chimie Macromoléculaire, UPRESA CNRS N°8009, Université des Sciences et Technologies de Lille, Villeneuve d'Ascq Cedex, F-59655, France

Version of record first published: 18 Oct 2010

To cite this article: S. Delenclos, H. Sahraoui, M. Benmouna, J.-M. Buisine & U. Maschke (2002): Novel Application of a Photothermal Technique on Polymer/Liquid Crystal Mixtures, Molecular Crystals and Liquid Crystals, 375:1, 353-361

To link to this article: http://dx.doi.org/10.1080/10587250210550

Mol. Cryst. Liq. Cryst., Vol. 375, pp. 353-361
Copyright © 2002 Taylor & Francis
1058-725X/02 $12.00 + .00

Novel Application of a Photothermal Technique on Polymer/Liquid Crystal Mixtures

S. DELENCLOS[a], H. SAHRAOUI*[,a], M. BENMOUNA[a,b],
J.-M. BUISINE[a] and U. MASCHKE[c]

[a]*Laboratoire de Thermophysique de la Matière Condensée (Equipe de l'UPRESA N° 8024 du CNRS), Université du Littoral, MREID, F-59140 Dunkerque, France*
[b]*Laboratoire de Recherche sur les Macromolécules, Faculté des Sciences, Université Aboubakr Belkaïd, Bel Horizon, 13000 Tlemcen, Algeria and*
[c]*Laboratoire de Chimie Macromoléculaire, UPRESA CNRS N°8009, Université des Sciences et Technologies de Lille, F-59655 Villeneuve d'Ascq Cedex, France*

The photopyroelectric technique (PPE) has been used to investigate phase transitions in polymer/liquid crystal systems. The sensitivity of measurements has allowed the detection of transitions from biphasic regions to isotropic single phase state. Equilibrium phase diagrams of these systems have been established on the basis of data recorded from the amplitude and phase of the PPE signal. Comparison was made with polarized optical microscopy (POM) results.

Keywords photopyroelectric technique; polymer; nematic liquid crystals; phase behavior.

INTRODUCTION

The photopyroelectric (PPE) method is now a well known photothermal technique used for measuring optical and thermal parameters of materials[1]. In recent years it has been introduced in the field of liquid crystals and proposed as a sensitive technique for phase transition detection[2]. In the standard configuration of the technique, a modulated incident light beam is absorbed at the front side of the sample generating temperature oscillations which propagate through the sample thickness and reach the opposite surface in thermal contact with a pyroelectric transducer. The subsequent temperature variation induced in the pyroelectric crystal generates an electrical signal whose amplitude and phase depend on optical and thermal properties of the sample. For phase transitions detection, this configuration was used almost exclusively because, in easily fulfilled conditions, both the amplitude and the phase of the PPE signal are sensitive to the critical anomalies of the thermal parameters. In the present work we show that the PPE technique is particularly useful to determine the transition from biphasic regions to isotropic single phase states. Many polymer/Low Molecular Weight Liquid Crystal (LMWLC) systems exhibit nematic + isotropic (N+I) / isotropic (I)- , (N+I) / (I+I)- as well as (I+I) / (I) transitions. Often the latter transition covers a broad range of composition and can hardly be observed by polarized optical microscopy (POM). The reason is that the contrast of the two phases is not sufficient to allow an easy observation of the image change from (I+I) morphology to a single isotropic phase texture. Note that the letter I stands for an isotropic phase while (I+I) designates a region where 2 isotropic phases are in equilibrium. The transition from (I+I) to I is accompanied by a very small energy exchange that is hardly identified in the DSC spectra. The present technique based PPE effects gives access to the specific heat and thermal diffusivity parameters and turns out to be quite sensitive to the (I+I)/(I) transition in contrast to the classical methods such as POM and DSC.

Two different systems were investigated : the first one is made of a crosslinked polymer/LMWLC system while the second is a poly(styrene) (PS) /5CB mixture. The equilibrium phase diagram was established by the PPE technique and compared to the results obtained by the conventional POM technique.

THEORETICAL ASPECTS

In the one dimensional heat propagation approximation the PPE response generated by periodic excitation of frequency f is given by[3]:

$$V(f,t) = V_0(f)\Gamma(f)e^{j2\pi ft} \tag{1}$$

where V_0 is an instrumental constant and the dimensionless complex quantity $\Gamma(f)$ contains all thermo-optical properties of the sample and other parameters of the PPE cell. The general expression of $\Gamma(f)$ is too complicated for direct experimental applications. Fortunately this general expression simplifies considerably in some special cases of practical interest, when mathematical approximation may be made

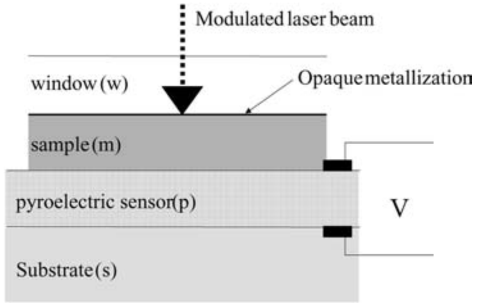

FIGURE 1 One dimensional geometry of the PPE cell.

according to the optical and thermal thickness of the PPE cell components (Figure 1) [gas (g); window (w); sample (m); pyroelectric sensor (p); substrate(s)].

At this stage it will be useful to define the optical penetration depth as $1/\beta_m$, where β_m is the sample optical absorption coefficient at the used wavelength and the thermal diffusion length as $\mu_m = (\alpha_m/\pi f)^{1/2}$, where α_m is the thermal diffusivity of the sample. The case where the sample and the pyroelectric transducer are optically opaque and thermally thick ($1/\beta_m \ll L_m; 1/\beta_p \ll L_p$; $\mu_m \ll L_m$; $\mu_p \ll L_p$, $L_{m,p}$ being their thicknesses) is particularly suitable for detecting phase transitions. In this case the amplitude of the PPE voltage is proportional to[4] :

$$|\Gamma(f)| = 2\exp\left(-\sqrt{\frac{\pi f}{\alpha_m}}\,L_m\right) \tag{2}$$

and its phase is:

$$\phi(f) = \varphi_0 - \sqrt{\frac{\pi f}{\alpha_m}}\,L_m \tag{3}$$

where φ_0 is the phase shift introduced by electronics.

Eqs. (2) and (3) indicate that both the amplitude and the phase of the signal depend on the thermal parameters of the sample. The signal amplitude depends exponentially on the thermal diffusivity of the sample. Consequently, a given heat capacity or thermal conductivity anomaly produces an enhanced signal anomaly. However, the exponential in Eq.(3) shows that the quality of the results is affected by two contradictory conditions: high enough frequency required in the case of thermally thick sample, and on the other hand, the necessity to keep a low frequency to prevent strong attenuation of the signal. Therefore, we have to adjust the modulation frequency f and / or the sample thickness L_m to achieve an optimum trade-off between signal-to-noise ratio and sensitivity.

EXPERIMENTAL AND RESULTS

The experimental set-up used in this work has been described elsewhere[5]. An Ar^+ laser with stabilized power output at λ=534 nm, modulated with an acoustooptical modulator (AOM-40, IntraACTION), was used as heating source. The pyroelectric sensor (p) (Figure 1) was a 300 μm-thick $LiTaO_3$ crystal with gold electrodes on both faces. Atop the sensor was mounted a thick quartz window (w) (Hellma Co.) having a calibrated 100 μm thick void that accommodated the sample (m). The (w/m) face of the window was made opaque by vacuum-deposited titanium metallization. The substrate (s) was a 2 mm thick glass plate in contact with the heating block itself, with a thin layer of silicone grease in between as thermal coupling fluid. A metallic lid with a small opening for the laser beam was placed on top in order to ensure homogeneous temperature throughout the PPE cell. The temperature controller type Linkam TMS 530 allowed for a minimum temperature variation rate of 10 mK/min. Typical scan rates were 0.1...0.5 K/min. The PPE signal was processed with a digital lock-in amplifier type Stanford SR830. A microcomputer was used for temperature programming and data acquisition. The POM used in this study is of type Leica DMRXP equipped with the heating-cooling stage described above.

PS and 5CB were dissolved in THF at 50 wt % (weight percent) and stirred mechanically for 12 h. A small amount of the mixture was cast on the quartz window, and the sample was left for 24 h to allow for a complete evaporation of the sample. The quartz window was put on the sensor, and the dry sample was sandwiched, with a known thickness, between the quartz window and the pyroelectric sensor.

Mixtures of tripropyleneglycoldiacrylate (TPGDA) and the nematic LC E7 were cured by using electron beam irradiation. Films of a given thickness were obtained consisting of micron sized LC droplets dispersed in a cross-linked polymer network.

Samples were heated at the rate 5°C/min from room temperature to 15 degrees above the transition temperature leading to the isotropic phase. Afterwards, the samples were cooled to room temperature. This procedure is followed by a heating ramp at a rate of 0.5°C/min. The PPE signal was recorded during the last heating ramp. Figure 2 shows the direct experimental plots of the phase of the signal in a temperature range covering the nematic–isotropic phase transition for three

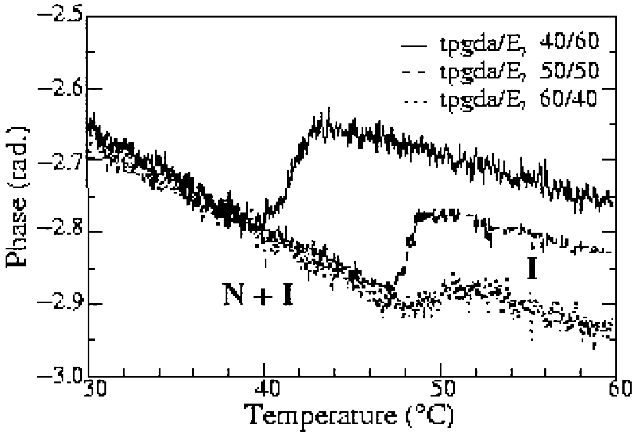

FIGURE 2 Photopyroelectric signal phase vs temperature for different compositions of TPGDA/E7 mixtures at the (N+I)/(I) transition (f=81 Hz).

(TPGDA)/E7 mixtures of different compositions. The signal shows a large minimum at the phase transition temperature.The results obtained for the (PS)/5CB system are shown in Figure 3. A small but detectable

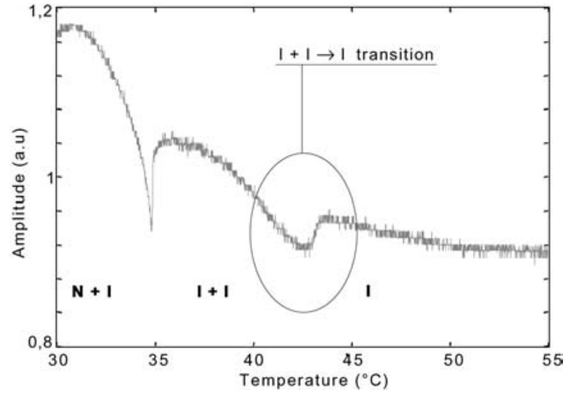

FIGURE 3 Photopyroelectric signal amplitude vs temperature for a PS/5CB mixture (20/80) (f=81 Hz).

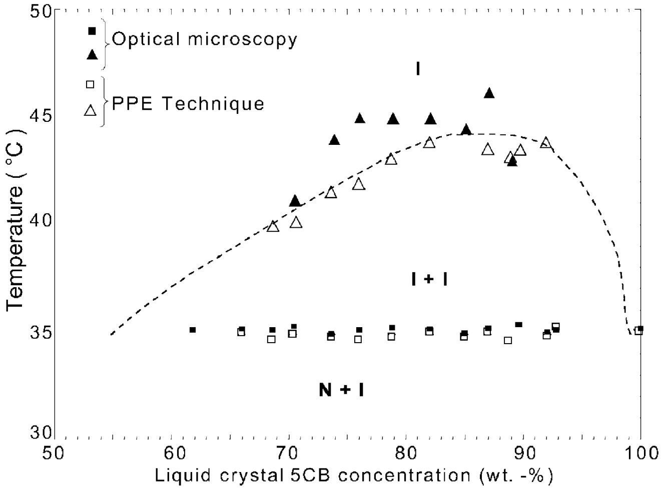

FIGURE 4 Equilibrium phase diagram of PS/5CB obtained by PPE and POM techniques.

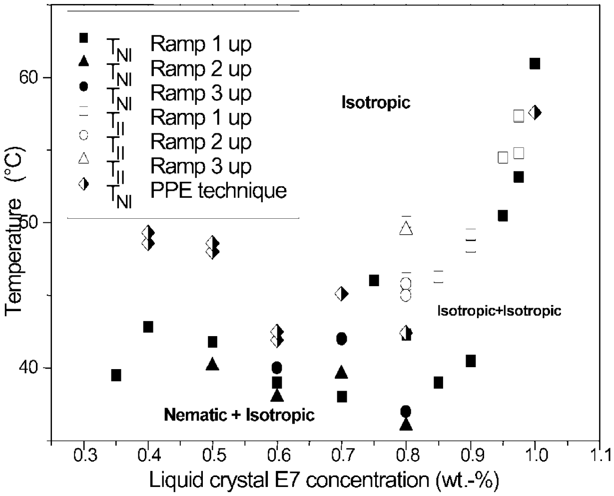

FIGURE 5 Equilibrium phase diagram of TPGDA/E7 obtained by PPE and POM techniques.

variation of the PPE signal is clearly shown around the (I+I) / (I) transition. This transition has not been observed when using differential scanning calorimetry.

Figures 4 and 5 show the phase diagrams of the two systems established on the basis of transition temperatures deduced from the amplitude and phase of the PPE signal and POM measurements for different composition mixtures. More details concerning the phase diagram of figure 5 are given elsewhere[6] especially the data obtained by POM observations. These data were obtained via thermal treatment with 3 scans of temperature up and down (i.e. Ramps up and down 1,2,3). The main point here is to show that the PPE technique is not only capable of detecting the transition (N+I) to (I+I) consistent with POM observations but detects also the transition from (I+I) to I while this was not possible with neither POM nor DSC. Figures 4 and 5 confirm the good agreement between PPE and POM data.

CONCLUSIONS

Phase diagram of polymer / liquid crystal mixtures has been established using PPE technique. This technique presents a large sensitivity to thermal parameters changes and therefore is suitable for evincing phase transitions even those where small anomalies in the temperature behaviour of the thermal parameters are observed. The phase transitions exhibited by the investigated systems have been detected on both the amplitude and phase of the signal. The (I+I) / (I) transition has been detected in contrast to the DSC technique where this transition has not been observed. The comparison made with the results obtained by the POM technique shows that the PPE technique is competitive with respect to the conventional ones.

References

[1] S. B. Peralta, Z. H. Chen, A. Mandelis, Appl. Phys. A **52**, 289 (1991).

[2] M. Marinnelli, U. Zammit, F. Mercuri, R. Pizzoferrato, J. Appl. Phys. **72**, 1096 (1992).

[3] M. Chirtoc, G. Mihailescu, Phys. Rev. B **40**, 9606 (1989).

[4] D. Dadarlat, M. Chirtoc, D. Bicanic, Appl. Phys. A **50**, 357 (1990).

[5] S. Delenclos, M. Chirtoc, A. Hadj Sahraoui, C. Kolinsky, J.-M. Buisine, Anal. Sci. **17**, 166 (2001).

[6] U. Maschke, F. Roussel, F. Benmouna, A. Daoudi, J.-M. Buisine, X. Coqueret, M. Benmouna, Mol. Cryst. Liq. Cryst. **365**, 287 (2001).