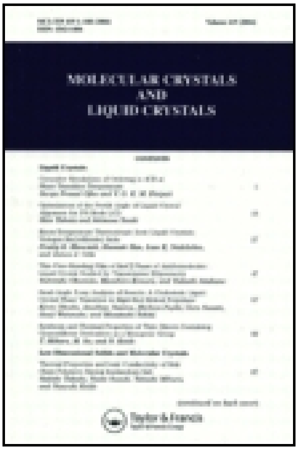

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Version of record first published: 18 Oct 2010

To cite this article: S. Delenclos, A. Hadj Sahraoui, J.-M. Buisine, M. Benmouna, C. Kolinsky & U. Maschke (2004): Photopyroelectric Measurements of Thermal Parameters over Phase Transitions in Polymer/Liquid Crystals Systems, Molecular Crystals and Liquid Crystals, 410:1, 163-170

To link to this article: http://dx.doi.org/10.1080/15421400490436269

Mol. Cryst. Liq. Cryst., Vol. 410, pp. 163/[691]–170/[698], 2004

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490436269

PHOTOPYROELECTRIC MEASUREMENTS OF THERMAL PARAMETERS OVER PHASE TRANSITIONS IN POLYMER/LIQUID CRYSTALS SYSTEMS

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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 the transition from biphasic regions to isotropic single phase state. Thermal diffusivity and specific heat changes that occur over this phase transition have been measured by using the PPE technique in the back detection configuration with a new normalisation procedure. Equilibrium phase diagrams of these systems have been established on the basis of data recorded from the amplitude and phase of the PPE signal.

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Keywords: liquid crystal; phase behavior; photopyroelectric technique; polymer; specific heat; thermal diffusivity

INTRODUCTION

Photothermal methods are well established for the study of optical and thermal properties of condensed matter. In recent years these methods have been introduced in the field of liquid crystals. In particular photopyroelectric (PPE) technique has been used together with liquid crystal materials exhibiting first- or second order phase transitions and have been proven to be very useful and competitive with respect to well established conventional techniques. Contrary to classical thermal analysis methods like Differential Scanning Calorimetry (DSC), ac-calorimetry or Adiabatic Scanning Calorimetry (ASC) where only a static thermal parameter (specific heat) is investigated, the PPE technique enables in addition the study of dynamic thermal parameters such as thermal conductivity (k), thermal diffusivity (α) and thermal effusivity (e). One of the usual schemes of a PPE experiment consists in generating thermal waves in the sample using modulated radiation. The temperature rise is detected by a pyroelectric sensor in thermal contact with the rear sample's surface (back detection configuration, BPPE). The BPPE signal is a function of α and e [1–3], having in mind that the four thermal parameters are connected by two relationships, this means that only two are independent, so measuring two, one has practically the values of all four thermal parameters.

In the present work we use the PPE technique to determine the transition from biphasic regions to the isotropic state. 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) /(I) transitions. For strongly interacting molecular species, the latter transition covers a broad range of composition. The PPE technique is quite sensitive to the (I + I)/(I) transition in contrast to the classical methods such as polarized optical microscopy (POM) and DSC. We also study and compare the behaviour of the thermal parameters over the transitions from biphasic regions to the isotropic state. An application to poly(styrene) (PS) /5CB (4-cyano-4′-*n*-pentyl-biphenyl) mixtures is reported.

THEORETICAL ASPECTS

The BPPE configuration used in this work is shown in Figure 1. The window (w) and the substrate (s) are assumed to be thermally thick. In the

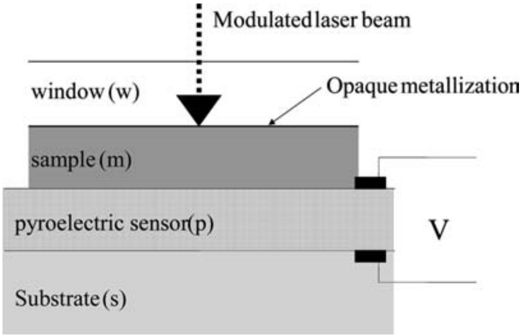

FIGURE 1 One dimensional geometry of the PPE cell.

one dimensional heat propagation approximation, the PPE response generated by periodic excitation of frequency f is given by [4]:

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

where the dimensionless complex quantity $\Gamma(f)$ contains all thermo-optical properties of the sample and other parameters of the PPE cell. If the signal is processed by an inverting current preamplifier having a feedback resistor R_f (or by the current input of a lock-in amplifier), the factor V_0 is independent of frequency and has the form [5]:

$$\mathrm{V_0} = \frac{-\mathrm{pI_0R_f}}{2\mathrm{L_p}c_p} \tag{2}$$

where p is the pyroelectric coefficient of the sensor, I_0 the intensity of the radiation and L_p and c_p the thickness and the volume specific heat of the sensor respectively.

For temperature-dependent measurements, one has to know the temperature dependence of each quantities appearing in V_0. A convenient way of avoiding this is to normalize the signal measured with the PPE cell to the one obtained with the sensor alone. In the case where the sample (m) and the pyroelectric transducer (p) are optically opaque and thermally thick, the normalized signal amplitude and phase are [5]:

$$|V_n(f,T)| = \frac{2(b_{gp}+1)}{(b_{wm}+1)(b_{mp}+1)}e^{-L_m/\mu_m} \tag{3}$$

$$\varphi_n(f,T) = -L_m/\mu_m \tag{4}$$

where $\mu_m = (\alpha_m/\pi f)^{1/2}$ the thermal diffusion length with $\alpha_\mathrm{m} = k_\mathrm{m}/\rho_\mathrm{m}c_\mathrm{m}$ the thermal diffusivity and k_m the thermal conductivity, c_m the mass specific heat, ρ_m the density and L_m is the sample thickness; $b_{ij} = e_i/e_j$

the ratio of thermal effusivities (i, j = g, w, m, p). For the study of temperature-dependent thermal parameters, the temperature is scanned at fixed frequency. From Eq. (4) one obtains $\alpha_{\mathrm{m}}(T)$ at a single fixed frequency by using the total phase shift $\phi_n(f, T)$:

$$\alpha_m(T) = \pi f L_m^2/\varphi_n^2(f,T) \tag{5}$$

The effusivity and its temperature-dependence can be obtained directly from Eqs. (3) and (4) by considering the quantity $\ln|V_n(T)| - \varphi_n(T)$ which is independent of frequency:

$$\ln|V_n(T)| - \varphi_n(T) = \ln\left[\frac{2(b_{gp}+1)}{(b_{wm}+1)(b_{mp}+1)}\right] \tag{6}$$

This last equation allows the determination of the thermal effusivity which is the only unknown parameter. Once α_{m} and e_{m} obtained, the thermal conductivity k_{m} and the mass specific heat c_{m} are calculated using the two relationships: $\mathrm{c_m} = \frac{\mathrm{e_m}}{\rho_{\mathrm{m}}\sqrt{\alpha_m}}$ and $\mathrm{k_m} = \mathrm{e_m}\sqrt{\alpha_m}$.

Experimentally one needs to carry out two temperature scans at a given frequency to obtain the normalized signal. The first one with the cell as it is; the second one with the sensor alone (in absence of the sample and with air as front medium and substrate).

EXPERIMENTAL PART

In our experimental set-up, an Ar^+ laser with stabilized power output at $\lambda = 534\,\mathrm{nm}$, modulated with an acoustooptical modulator (AOM-40, IntraACTION), was used as heating source. The pyroelectric sensor (p) (Fig. 1) was a 300 µm-thick $\mathrm{LiTaO_3}$ 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.

Polystyrene (PS) exhibiting a molecular weight $M_{\mathrm{w}} = 44{,}000\,\mathrm{g/mol}$ ($M_{\mathrm{w}}/M_{\mathrm{w}} = 1.05$) and the liquid crystal 5CB (4-cyano-4′-n-pentyl-biphenyl) were supplied from Aldrich (Saint Quentin Fallavier, France). They 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.

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 cooling ramp at a rate of −0.1°C/min.

RESULTS AND DISCUSSION

Figures 2 and 3 show the direct experimental plots of the normalized amplitude and phase of the signal respectively in a temperature range covering the (I + I)/(I) phase transition for a PS/5CB mixture (20/80). A 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. Figure 4 shows the phase diagram of the system established on the basis of transition temperatures deduced from the

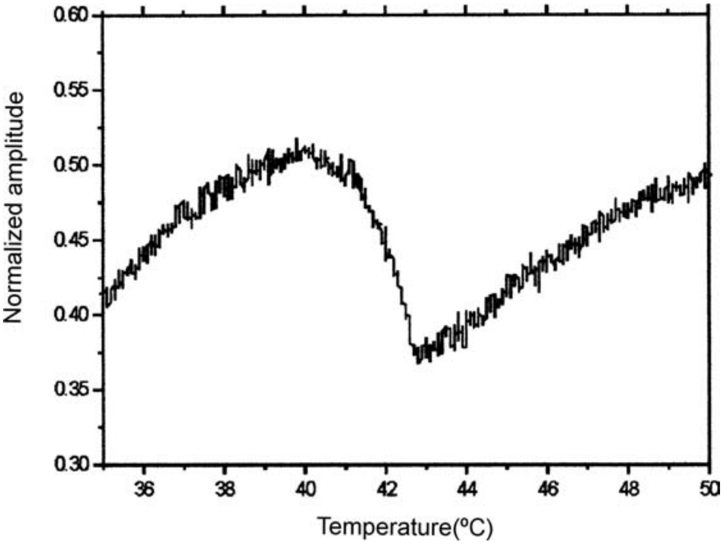

FIGURE 2 Photopyroelectric signal amplitude vs temperature for a PS/5CB mixture (20/80) (f = 111 Hz, $L_m = 100\,\mu m$).

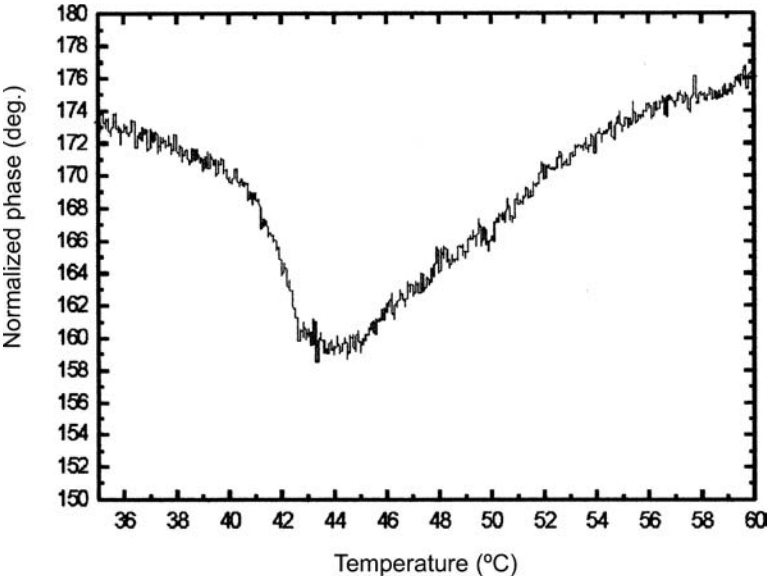

FIGURE 3 Photopyroelectric signal phase vs temperature for a PS/5CB mixture (20/80) (f = 111 Hz, $L_m = 100\,\mu m$).

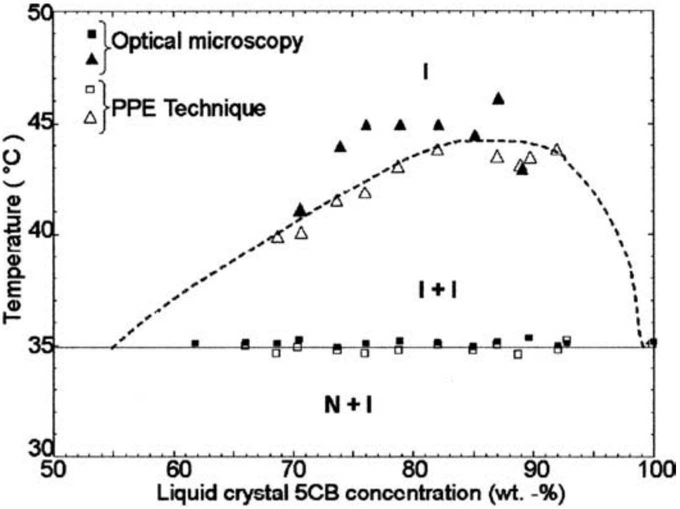

FIGURE 4 Equilibrium phase diagram of PS/5CB obtained by PPE and POM techniques.

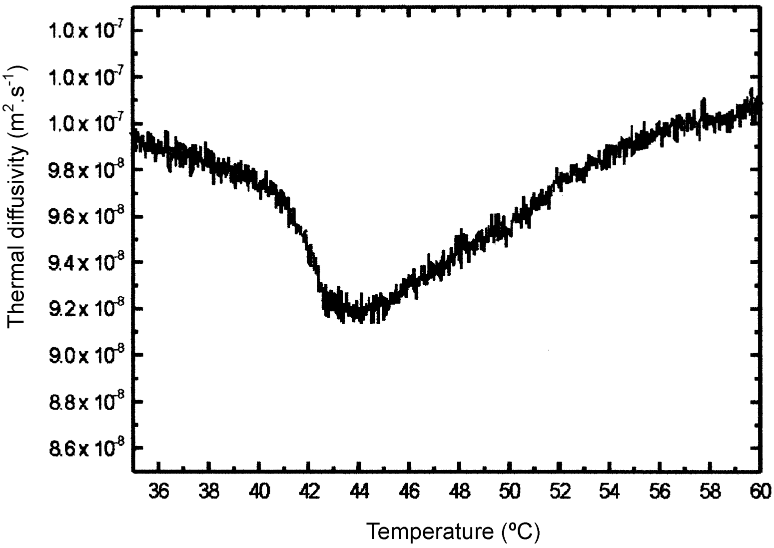

FIGURE 5 Thermal diffusivity vs temperature of PS/5CB mixture (20/80) at the (I + I)/(I) transition obtained with the photopyroelectric technique.

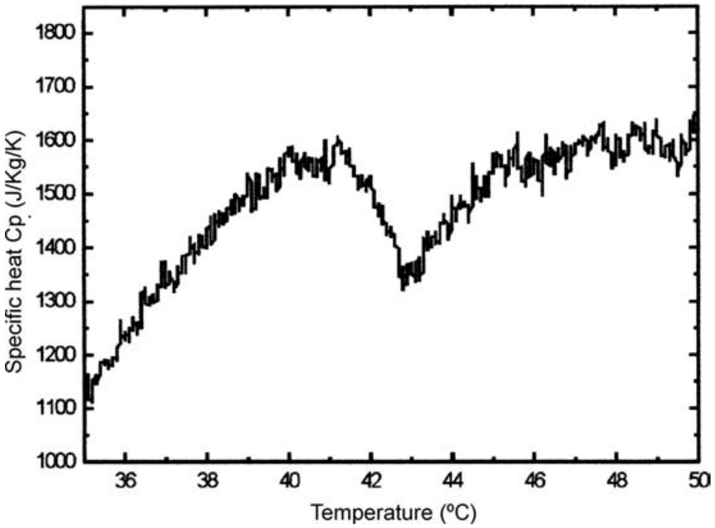

FIGURE 6 Specific heat vs temperature of PS/5CB mixture (20/80) at the (I + I)/(I) transition obtained with the photopyroelectric technique.

amplitude and phase of the PPE signal and POM measurements for different composition mixtures. One can observe the good agreement between PPE and POM data. The amplitude and the phase data shown in Figures 2 and 3 have been obtained in the conditions of thermally and optically thick samples for which Eqs. (3) and (4) apply. The temperature dependence of the thermal diffusivity α_m and the mass specific heat c_m around the (I + I)/(I) transition are derived from the data of Figures 2 and 3 by using Eqs. (3) and (4). Figures 4 and 5 show the results obtained for $\alpha_m(T)$ and $c_m(T)$, respectively. One can observe a relative variation of these parameters at the transition of about 8% for the thermal diffusivity and 12% for the heat capacity. This relatively small variation of the specific heat and the fact that the transition from (I + I) to I is accompanied by a very small energy exchange could explain why this transition is hardly identified in the DSC spectra.

CONCLUSIONS

The PPE technique allows, under particular experimental conditions, the simultaneous determination of specific heat, thermal conductivity and thermal diffusivity. Furthermore, this technique presents a large sensitivity to changes in these thermal parameters and therefore is suitable for evidencing phase transitions. This is true even when only small anomalies in the temperature behaviour of the thermal parameters are observed. The phase diagram of the PS/5CB system has been established including the (I + I)/(I) transition in contrast to the DSC technique where this transition has not been observed. Thermal parameter changes that occur over this phase transition have been measured by using the back detection configuration with a new normalisation procedure.

REFERENCES

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

[2] Thoen, J. & Glorieux, C. (1997). *Thermochimica Acta*, *304/305*, 137.

[3] Chirtoc, M., Dadarlat, D., Bicanic, D., Antoniow, J. S., & Egée, M. (1997). In: *Progress in Photothermal and Photoacoustic Science and Technology*, Vol. III, Mandelis, A. & Hess, P. (Eds.), SPIE Optical Engineering Press: Bellingham, Washington, USA.

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

[5] Delenclos, S., Chirtoc, M., Hadj Sahraoui, A., Kolinsky, C., Buisine, J.-M. (2002). *Rev. Sci. Instrum.*, *73*, 2773.