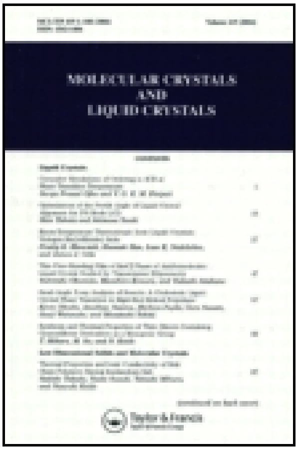


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Study of Ester-Type Liquid Crystals by TSDC and Optical Investigations

D. Manaila-Maximean [a], C. Rosu [a], I. Zgura [b], L. Frunza [b] & D. Stoenescu [c]

[a] Physics Department II, University “Politehnica Bucuresti”, Bucharest, Romania

[b] National Institute of Materials Physics, Magurele, Romania

[c] Nemoptic, Magny-les-Hameaux, France

Version of record first published: 05 Oct 2009

To cite this article: D. Manaila-Maximean, C. Rosu, I. Zgura, L. Frunza & D. Stoenescu (2009): Study of Ester-Type Liquid Crystals by TSDC and Optical Investigations, Molecular Crystals and Liquid Crystals, 512:1, 158/[2004]-166/[2012]

To link to this article: http://dx.doi.org/10.1080/15421400903050830

Mol. Cryst. Liq. Cryst., Vol. 512, pp. 158/[2004]–166/[2012], 2009
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400903050830

Study of Ester-Type Liquid Crystals by TSDC and Optical Investigations

D. Manaila-Maximean[1], **C. Rosu**[1], **I. Zgura**[2],
L. Frunza[2], **and D. Stoenescu**[3]
[1]Physics Department II, University "Politehnica Bucuresti",
Bucharest, Romania
[2]National Institute of Materials Physics, Magurele, Romania
[3]Nemoptic, Magny-les-Hameaux, France

We study ester-type liquid crystal, 4′-cyanophenyl 4-n-hexyl benzoate and its homologue 4′-cyanophenyl 4-n-pentyl benzoate. We used the Thermally Stimulated Depolarization Currents method and found information about phase transition temperature, and activation energies. The temperatures of phase transitions were compared to those obtained by classical DSC/DTA measurements. Simultaneously with the TSDC, we measured the optical transmission; we found a decrease of the optical transmission when it was measured after a greater pre-applied polarizing electric field.

Keywords: activation energy; cyanophenyl benzoates; liquid crystal; optical transmission; terminal cyano nematogens; Thermally Stimulated Depolarization Currents

I. INTRODUCTION

Liquid crystals of the cyanophenyl benzoate type are studied for fundamental reasons [1–4] and for their applicative properties [5,6] as well. They have molecules more flexible and with a higher degree of nonplanarity into the core than the well known related compounds with the same number of carbon atoms in the alkyl chain of cyanobiphenyl series, due to the ester group inserted between the two benzene rings of cyanobiphenyls. Besides, the cyanophenyl benzoates have a

The authors acknowledge the Romanian Ministry of Education and Research for financial support under the CEEX Program, Project CEX-05-D11-76.

Address correspondence to D. Manaila-Maximean, Physics Department II, University "Politechnica Bucuresti", Spl. Independentei 313, Bucharest, R-060042, Romania. E-mail: educmat2na@yahoo.com

rather good thermal stability and electro-optical properties which make them suitable for use as components in materials for liquid crystal displays (LCDs).

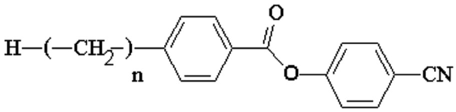
Recently, we studied the molecule dynamics in the bulk and 4′-cyanophenyl 4-*n*-hexyl benzoate and in its composites containing aerosil by broadband dielectric spectroscopy [7]. This work completes the dynamic behavior thus found with new results obtained by the method of Thermally Stimulated Depolarization Currents (TSDC) for 4′-cyanophenyl 4-*n*-hexyl benzoate and its homologue 4′-cyanophenyl 4-*n*-pentyl benzoate.

As it is known, TSDC method allows the determination of phase transitions that often present resolution difficulties by other techniques [8,9]. The TSDC spectra present several peaks indicating different processes occurred in the sample (depolarization of permanent dipoles, release of charges, polarization changes connected to phase transitions). Information regarding the conduction mechanism is obtained.

Optical transmission was measured simultaneously with TSDC spectra. Additional investigations by thermal analysis sustain the found results.

II. EXPERIMENTAL

Ester-type liquid crystals were commercially purchased (from Hoffmann La Roche) and are of cyanophenyl alkylbenzoate (CPnB) type, having the structure shown in the schema below:



where n = 5 for cyanophenyl pentylbenzoate (CP5B) and n = 6 for cyanophenyl hexylbenzoate (CP6B). The temperature of the phase transitions (in°C) as measured using a polarizing microscope method. are [2,10–16], as follows:

CP5B Cr 64.3 (N 55.3) I
CP6B Cr 44.3 N 48.5 I

where Cr-crystalline, N-nematic, I-isotrop. CP5B is monotropic. It melts to an isotropic phase that undergoes an isotropic-to-nematic transition on cooling. CP6B is enantiotropic with mesophases that are thermodynamically stable with respect to both, the isotropic and crystalline phases, within the temperature range from the melting point, to the clearing-point temperature.

The liquid crystal was filled in a 15 μm thick ITO covered glass cell.

The experimental set-up for TSDC measurements has been described in detail elsewhere [9,17]. Figure 1 illustrates the heating-cooling steps of the experiment. In the first heating step (0), from room temperature to a pre-established temperature (T_p), higher than the nematic–isotropic transition temperature of the liquid crystal, initial depolarization of the sample takes place. During the steps 1, 2, and 3 the polarizing field $E_p = 0$; these steps are performed to eliminate the eventually existing charges, due to previously treatments applied on the sample (manufacturing or previously applied heating cooling cycles and electric field).

During step 4, at T_p, the polarizing field $E_p = V_p/g$ is applied, (V_p is the voltage applied on the sample and g is the thickness of the sample) and it is maintained during the cooling down to T_0 (step 5). During the phase 6, the field E_p is cut-off and the sample is short-circuited to eliminate capacitive discharge. The depolarizing currents are registered during step 7. The heating-cooling rates were of 1 K/min and steps 2, 4, and 6 were of 15 minutes. In this experiment, the polarization temperature is $T_p = 80°C$ and $T_0 = 25°C$.

The optical beam from a light source is transmitted through the sample and measured by the photomultiplier; crossed polarizers have been used.

Additional measurements collected the curves of differential thermal calorimetry (DSC) using a Netzsch DSC 204F1 equipment, at scanning rates of 2, 5, or 10°C/min. Two to four heating-cooling cycles were applied for each sample. Differential thermal analysis

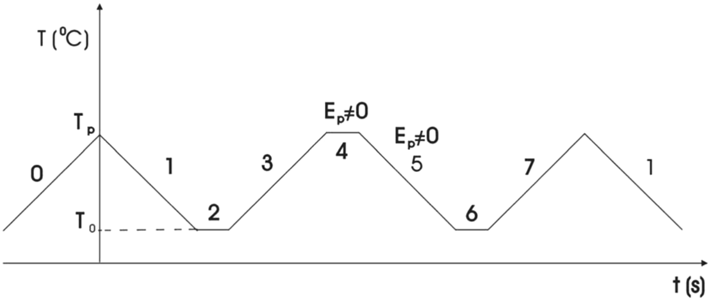


FIGURE 1 Heating-cooling cycles applied to the samples.

was also performed with a Diamond TG/DTA apparatus (from Perkin Elmer), with 2°C/min.

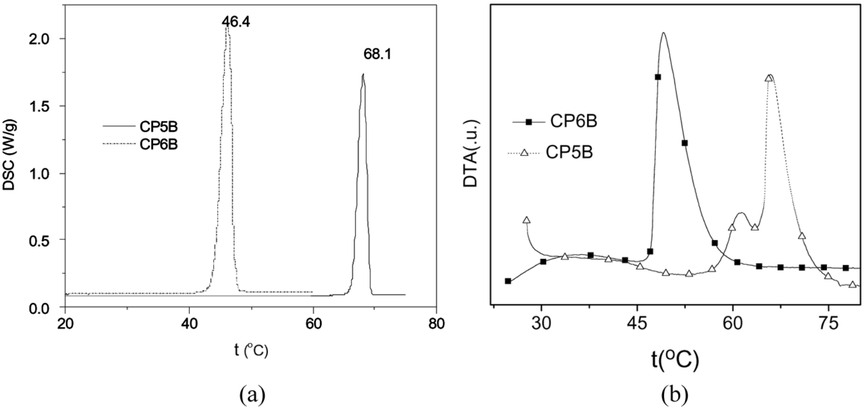
FTIR spectra were also registered with a Perkin Elmer Spectrum BX spectrometer. When necessary, the spectra were analyzed by fitting Gaussians to the data.

III. RESULTS AND DISCUSSIONS

DSC/DTA measurements were firstly performed in order to check the thermal behavior of the studied liquid crystals under conditions as much as possible close to those encountered in TSDC experiments. These data will be discussed firstly. Then the results obtained by the later method are presented. Finally the data concerning the optical transmission of the cells containing these phenyl benzoate LCs were discussed.

DSC/DTA Measurements

The temperatures of phase transitions in the original materials were checked by DSC and confirmed by DTA measurements. Figure 2 shows the corresponding thermograms obtained using the same reasonably low heating rate (2°C/min). CP5B shows only the crystalline-to-isotropic transition, while CP6B should indicate all the transitions involving the mesophase. However, even in this case one can observe only one peak, probably representing the overlap of the two peaks corresponding to the transition phases. In addition, both



(a) (b)

FIGURE 2 (a) DSC curves during the heating and (b) DTA curves for the investigated LC.

DSC and DTA thermograms show evidence for polymorphism and conformational changes, changes already discussed in the literature [18]. In fact, the peak for the nematic-to-isotropic transition of CP6B cannot be observed at higher heating rate owing to its proximity to the melting peak; that is why it appeared broad. The existence of several melting/solidification peaks or shoulders indicate that a process of conformational change is going on during (melting/)solidification; the solid associated with a solidification peak is of a different structure from that which melts at the upper temperature. Moreover, the conformational change gives rise to a disordered or "amorphous" solid.

TSDC Measurements

According to the heating–cooling cycles presented in Figure 1, the electrical field E_p is applied to the sample at the higher temperature T_p and it is maintained constant during cooling. The polarization of the dielectrics submitted to an external electric field is due to the mechanisms involving microscopic or macroscopic charge displacement. Since the internal friction and ionic mobility depend exponentially on temperature, heating a dielectric to a high temperature T_p enhances the response time of permanent dipoles and internal free charges to the applied electric field and allows the equilibrium polarization to be reached in short time. When the polarization field is maintained while cooling the sample to a temperature T_o sufficiently low to increase the relaxation times of the dipoles and ions to values of hours or more, these are practically "frozen" in the electrical configuration reached at T_p and consequently do not respond when the field is switched off. The equilibrium polarization $P_e(T_p)$ reached during the polarization phase 5 is consequently considered constant at the end of the cooling, when the heating step begins (step 7). This general presentation is complicated by the heterogeneous character of the studied system. Thus, the surface phenomena present at the LC-particle interface, mainly of dipolar origin, will render the electrical and optical effects more complicated.

In step 7 the Thermally Induced Depolarization Currents are measured. In Figures 3 and 4 we present the thermally stimulated depolarization currents versus temperature for the CP5B and for the CP6B liquid crystal, respectively.

Considering the charge given by the equation (1) [9]:

$$Q = -\int_{t_1}^{t_2} i(t) \cdot dt = -\frac{dt}{dT} \cdot \int_{T_1}^{T_2} i(T) \cdot dT \qquad (1)$$

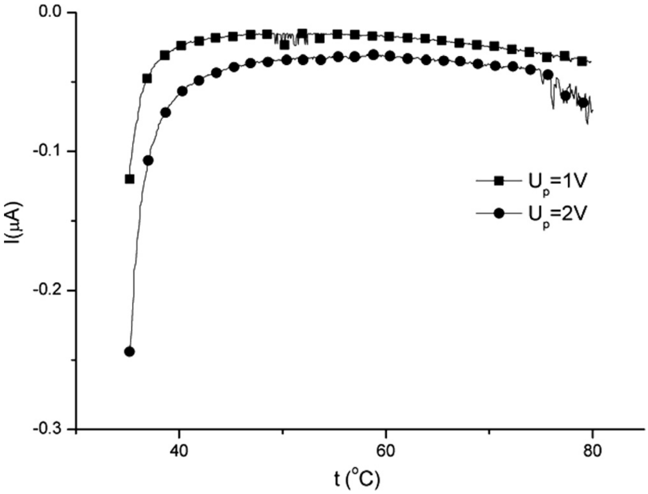


FIGURE 3 TSDC curve (step 7) for CP5B, for two polarizing voltages applied in previous step, 5.

where t_1 and t_2 represent the time moments between which the temperature varies from T_1 till T_2 with a linear constant rate. We notice that the sign of the charge depends on the sign of the current,

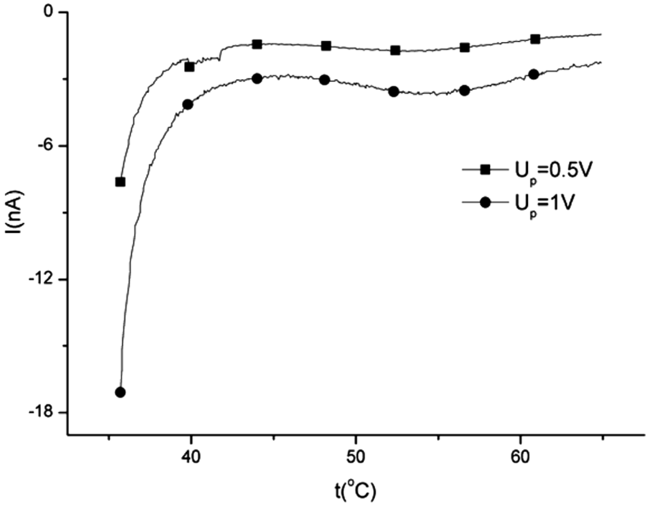


FIGURE 4 TSDC curve (step 7) for CP6B, for two polarizing voltages applied in previous step, 5.

respectively on the sign of variation of temperature dt/dT; for step 7, the last term is positive, because the temperature is increasing.

Considering the polarity of the voltage applied on the sample positive compared to the ground, it follows that if the current is positive, it is produced by a heterocharge (with a polarity opposing that of the electrode), and if the current is negative, it is due to a homocharge.

In our experiments, the TSDC diagrams have shown negative currents, due to homocharges.

The Arrhenius curves shown in Figure 5 for the CP6B liquid crystal present small variations at the Cr-N and N-I transition temperatures. The slope and the activation energy respectively, increase at higher temperatures at low voltages, but decreases at high voltages due to the increase of thermal movement that impedes the movement of the carriers.

For CP6B we have calculated the activation energy of 0,74 eV, at the polarizing voltage Up = 2 V, for a temperature lower than 44°C (Cr-N transition) and for a temperature higher than 52°C (N-I), the obtained activation energy is 0,515 eV. This is in agreement with the DSC data, mainly for the Cr-N transition, involving a greater energetic value. For the CP5B the activation energy calculated from step 5, at 2 V, is 0.503 eV for t > 47C and of 0.702 eV for t < 41°C.

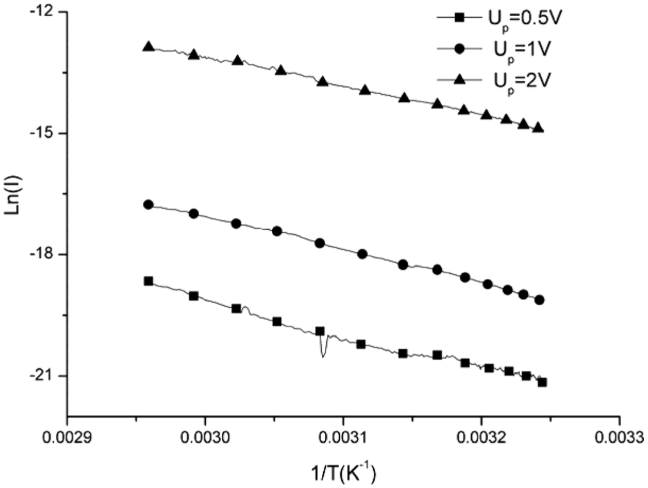


FIGURE 5 Arrhenius curves (ln(I) = f(1/T)) for CP6B in step 5, at the decrease of the temperature, for different polarizing voltages applied during the measurement.

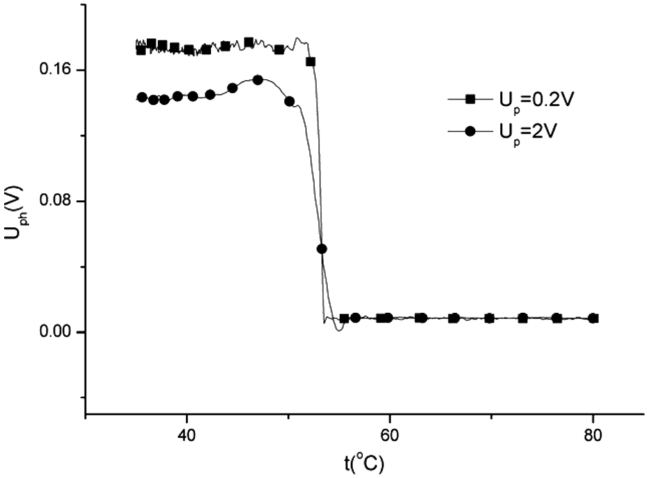


FIGURE 6 Optical transmission versus temperature measured in step 7 for CP5B, for two different previously applied electric field (in step 5).

Optical Transmission

In Figure 6 is presented the optical transmission for CP5B, measured in step 7, simultaneously with the depolarization currents. One observes the decrease of the optical transmission when measured after greater pre-applied polarizing electric fields. The optical transmission behavior of CP6B is qualitatively similar to that of CP5B.

The optical transmission decreases in the crystal phase after applying greater polarizing electric fields; it decreases to zero as the sample passes to the isotropic phase.

IV. CONCLUSIONS

We studied the electro-optical properties when applying heating-cooling cycles corresponding to the Thermally Stimulated Depolarization Currents method.

The results of the field induced depolarization currents measurements on the CP5B and CP6B samples show a dipolar conduction mechanism. The values of the activation energy are typical for the nematic liquid crystal, indicating that it has a major part in the conduction of the device.

The optical transmission measured simultaneously with the depolarization currents depends on the pre-applied electric fields, decreasing when the electric field was greater and presenting a discontinuity at the phase transition. The temperatures of the nematic-isotropic phase transition thus found are in good agreement with the thermal analysis measurements.

REFERENCES

[1] Ivashenko, A. V., Titov, V. V., & Kovshev, E. I. (1976). *Molec. Cryst. Liq. Cryst.*, *33*, 195.

[2] Kelly, S. M. (1983). *J. Chem. Soc., Chem. Commun.*, 366.

[3] Morsy, M. A., Oweimreen, G. A., & Al-Tawfiq, A. M. (1998). *J. Phys. Chem. B*, *102*, 3684.

[4] Czarnecki, M. A., Okretic, S., & Siesler, H. W. (1997). *J. Phys. Chem. B*, *101*, 374.

[5] Stephens, C. E. & Sinnadurai, F. N. (1974). *Phys. E: Sci. Instrum.*, *7*, 641.

[6] Hendriks, P., de Kort, K., Horstman, R. E., Andre, J.-P., Foxon, C. T., & Wolter, J. (1988). *Semicond. Sci. Technol.*, *3*, 521.

[7] Frunza, S., Schönhals, A., Goering, H., Manaila-Maximean, D., Beica, T., Frunza, L., & Moldovan, R. (2008). *Mol. Cryst. Liq. Cryst.*, accepted.

[8] van Turnhout, J. (1975). *Thermally Stimulated Discharge of Polymer Electrets*, ed. Elsevier: Amsterdam.

[9] Rosu, C., Manaila-Maximean, D., Godinho, M. H., & Almeida, P. L. (2003). *Mol. Cryst. Liq. Cryst*, *391*, 1.

[10] Gray, G. W., Hird, M., Lacey, D., & Toyne, K. J. (1989). *Molec. Cryst. Liq. Cryst.*, *172*, 165.

[11] Lazareva, V. T., Titov, V. V., & Kovshev, E. I. (1975). *Zh. Obshch. Khim.*, *45*, 244.

[12] Karamysheva, L. A., Kovshev, E. I., & Barnik, M. I. (1976). *Mol. Cryst. Liq. Cryst.*, *37*, 29.

[13] Ivashchenko, A. V., Titov, V. V., & Kovshev, E. I. (1976). *Mol. Cryst. Liq. Cryst.*, *33*, 195.

[14] Dabrowski, R., Dziaduszek, J., Szczucinski, T., & Raszewski, Z. (1984). *Mol. Cryst. Liq. Cryst.*, *107*, 411.

[15] Hoffmann-La Roche : Product Information (1988).

[16] Boller, A., Cereghetti, M., Schadt, M., & Scherrer, H. (1977). *Mol. Cryst. Liq. Cryst.*, *42*, 215.

[17] Manaila- Maximean, D., Rosu, C., Yamamoto, T., & Yokoyama, H. (2004). *Mol. Cryst. Liq. Cryst.*, *417*, 215.

[18] Oweimreen, G. A. & Morsy, M. A. (1999). *Thermochim. Acta*, *325*, 111.