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## THERMALLY STIMULATED DEPOLARIZATION CURRENTS ON COLLOIDAL LIQUID CRYSTAL COMPOSITE SYSTEM

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*In this paper we examined the electrical and optical properties of the pure liquid crystal 8CB and in a composite system obtained by surface modified particles  $ZrO_2$  and the liquid crystal 8CB. Using the Thermally Stimulated Depolarisation Current (TSDC) method we obtained information regarding the conduction mechanism, the activation energy and the pre-exponential frequency factor in the Arrhenius diagrams. We study the dependence of phase transition temperatures on the magnitude of the polarizing d.c. electric field previously applied on the sample. The optical transmission is slightly dependent on the polarization field and the thermal switch behavior was obtained at the nematic–isotropic transition. The TSDC and optical results are compared with the ones obtained by rheology.*

**Keywords:** activation energy; liquid crystal colloidal composites; nematic liquid crystals; optical transmission; thermally stimulated depolarization currents

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## INTRODUCTION

In the recent years much attention has been paid to the particles/liquid crystals composites [1–4]. Dispersion of small silica particles in nematic LCs, called filled nematics [5] have been studied as a new class of light scattering materials for electro-optical switches. In dispersions, particles form internal interfaces with large specific surface, making possible to stabilize different director configurations. Small domains with different configurations and birefringence of host LCs have strong light scattering. By applying electric fields, the scattering state can be switched to transparent one due to reorientation of LC molecules. In all cases, surface properties of particles are of extreme importance to determine the scattering effects and colloidal properties of the systems.

We started the research on  $\text{ZrO}_2$ /8CB systems with the aim to construct ordered structures of the particle in LC host and the optical switching of their structural properties by means of cis-trans photoisomerization on the particle surface. We could actually control the viscosity of the systems by the photochemical manner. Potential applications for this ordered structure are optical memory devices, tunable photonic devices, and so on. The memory materials will be achieved by means of the local change of the refractive indices around the particles.

## Thermally Stimulated Depolarization Currents Method

Thermally stimulated depolarization is a low frequency technique that lends itself to determination of phase transitions that often present resolution difficulties with other techniques [6,7]. In the TSDC method, the sample is polarized by an electric field  $E_p$  at a temperature  $T_p$ . This polarization is subsequently frozen in by cooling the sample at a temperature  $T_o$  sufficiently low to prevent depolarization by thermal energy. Here the field is cut off and the sample is short-circuited for some time, to eliminate capacitive discharge. Finally the sample, short circuited through an electrometer, is heated with a constant heating rate. The TSDC spectra, registered as intensity of currents through the electrometer versus time or temperature, present several peaks indicating different processes occurred in the sample (depolarization of permanent dipoles, release of charges, polarization changes connected to phase transitions).

In this paper we examined the electrical and optical properties in the pure liquid crystal 8CB and in a composite system obtained by surface modified particles  $\text{ZrO}_2$  and the liquid crystal 8CB. The surface modification of particles ( $\text{ZrO}_2$ ) was performed with an azobenzene carboxylic acid in acetone.

Using the TSDC method we obtained information regarding the conduction mechanism. Optical transmission was simultaneously measured.

## EXPERIMENTAL

### Particles Modification

We used  $\text{ZrO}_2$  (monoclinic, Nippon Denko Co. LTD) and the liquid crystal 8CB, purchased from Aldrich (K-SmA: 21.5°C; SmA-N: 33.5°C; N-I: 40.5°C), as particles and host respectively. The particle size is 1.1  $\mu\text{m}$  and the surface area is 32  $\text{m}^2/\text{g}$ . Surface modification was performed according to the literature [8], with azobenzene carboxylic acid (4-octyl-4'-(5-carboxypentyloxy)azobenzene, 8AB5COOH). The surface coverage was calculated from a carbon content of the modified particle (8AB5COOH- $\text{ZrO}_2$ ), the surface area of  $\text{ZrO}_2$ , and a 0.47  $\text{nm}^2/\text{molecule}$  of the azobenzene derivative. After washing, particles showed light yellow color indicating the presence of the azobenzene moieties on the surface. The adsorption of 8AB5COOH on  $\text{ZrO}_2$  surface was confirmed by IR spectroscopy according to the literature [9]. Surface coverage was estimated to 56% in an average value.

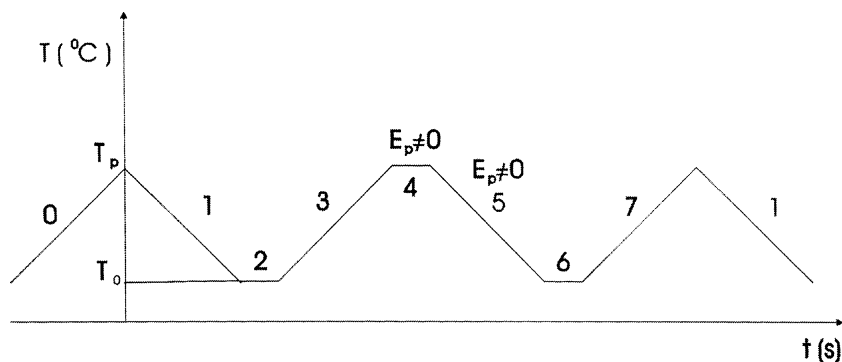
### Sample Preparation

The surface modified particles 8AB5COOH- $\text{ZrO}_2$  were mixed with the liquid crystal 8CB in a proportion of 5% b.w. The composite system was filled in a cell of conventional sandwich type, consisting of two ITO covered glass plates separated at a constant distance of 20  $\mu\text{m}$ .

### EXPERIMENTAL SET-UP

The experimental set-up has been described elsewhere [10]. 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, (where  $g$  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  $T_p = 95^\circ\text{C}$  and  $T_0 = 25^\circ\text{C}$ .



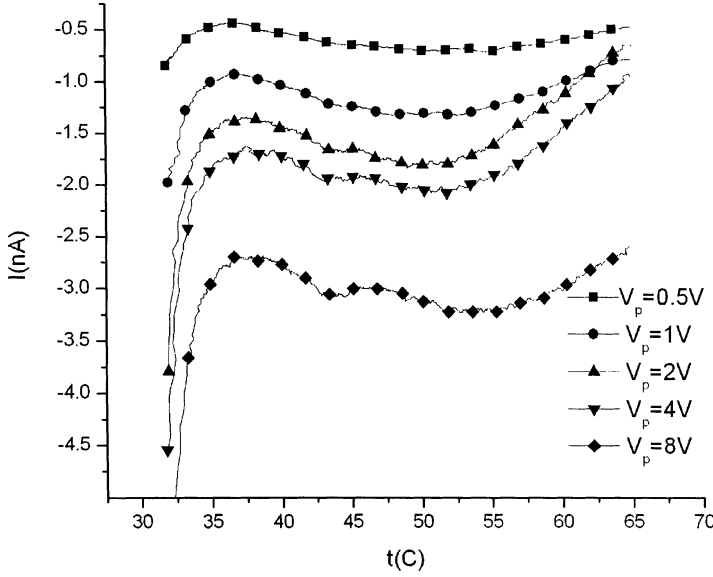
**FIGURE 1** Heating-cooling cycles applied to the samples.

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

## RESULTS AND DISCUSSIONS

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  $T_0$  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 2 and 3 we present the thermally stimulated depolarization



**FIGURE 2** TSDC spectra for pure liquid crystal 8CB.

currents versus temperature for the pure LC and for the composite system, respectively.

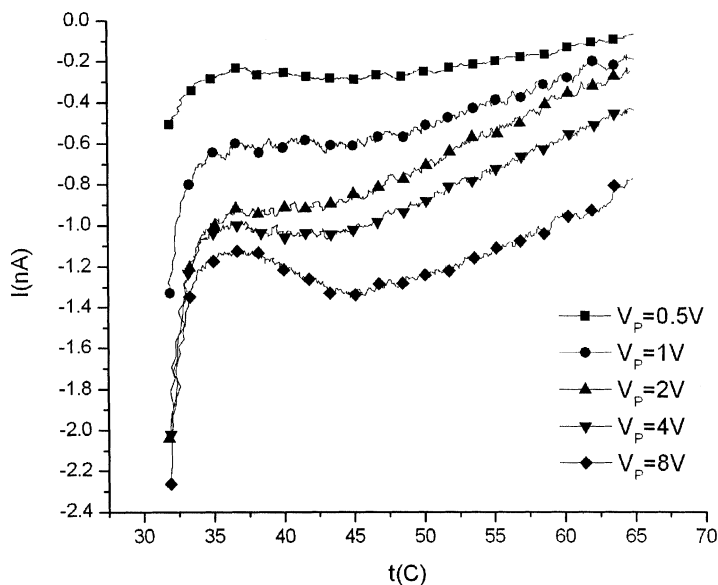
Considering the charge given by the Eq. (1) [10,11]:

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

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, respectively on the sign of variation of temperature  $\frac{dt}{dT}$ ; 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 spectra have shown negative currents, due to homocharges. At the increase of the temperature, the current values decrease in absolute value, towards zero and then towards positive values. The current will increase up to about 36.5°C both for the pure LC 8CB and



**FIGURE 3** TSDC spectra for composite liquid crystal 8CB/ZrO<sub>2</sub>, 5% b.w. (modified surface of particles).

for the composite system 8CB/ZrO<sub>2</sub> 5% b.w. This value can be correlated with the SmA-N transition of the pure LC, having a slightly higher value than the one given by the catalogue data. The rheological measurements have shown a value of about 35°C for the SmA-N transition. We mention that the rheological measurements [8] showed a temperature of the SmA-N transition of about 35°C, practically the same for the pure LC and the composite system. When increasing the temperature, the current will increase in absolute value. It will reach a maximum at about 42°C for pure LC and 45°C for the composite system and it will decrease again in absolute value. These temperatures can be associated to the N-I phase transition of 40.5°C. The value obtained by TSDC measurements can be correlated with the similar values obtained by rheological measurements: 42°C for the pure LC and about 45°C for the composite system.

The current values are of about two times smaller for the composite system as compared to the pure LC, for the same values of polarizing voltages. In the peak zone, the depolarization current curve present a region which is flatter for the composite system as compared to the pure LC. A similar result was obtained using the reological measurements and it leads to the conclusion that in the composite system appears a structure with different properties.



In the composite system a decrease of the magnitude of the electrical current can be noticed; this proves the presence of heterocharges, which compensate the initial homocharges and can explain the decrease of the current when comparing to the pure LC curve. The heterocharges can also be caused by the interfacial charges, specific to the heterogeneous materials, due to the electrical conductivity difference between the two phases of the system 8CB and  $\text{ZrO}_2$  (the Maxwell Wagner effect). The N-I phase transition temperature is higher for the composite system as compare to the pure LC; due to the surface treatment of the particles, more energy is needed to destroy the obtained ordered structures of the composite.

To study the conduction mechanism specific for the current, we represented in Figure 4 the peak value of this current versus the polarizing voltage for the pure LC and for the composite (surface modified particles).

We notice a quasilinear dependence of the peak current on the polarization voltage (Fig. 4a). As it is known [6], this is characteristic for the dipolar currents (for the currents limited by the space charge, this dependence is nonlinear). The dependency starts to have a nonlinear character for low voltages, in the composite.

The existence of a single peak in the TSDC spectra suggests, for small voltages, a single relaxation time. At higher polarization voltages  $U_p$ , this hypothesis should be amended with the influence of injection currents; an ulterior analysis will try to put into evidence the contribution of different conduction mechanisms in the magnitude of the total current.

By denoting by  $\tau$  this time, we may consider that the polarization of a material charged initially with the polarization  $P_e(T_p)$ , for which the applied field is interrupted (step 7), is given by the Eq. (2):

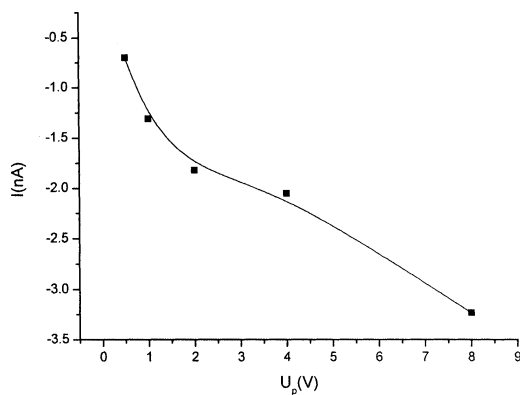
$$\frac{dP}{dt} = -\frac{(P - P_\infty)}{\tau} \quad (2)$$

This equation supposes a relaxation proportional with the difference between the instant polarization and the polarization  $P_\infty$  reached by the sample after a sufficiently long time.

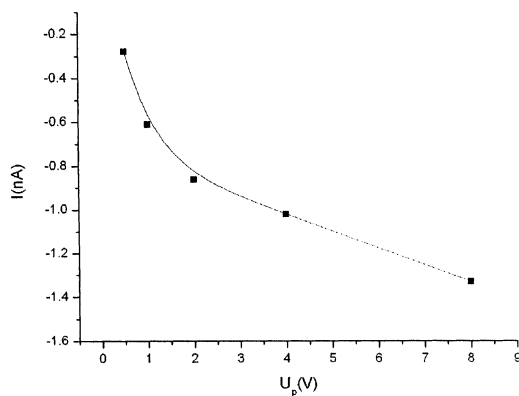
Suppose that step 7 is long enough so that at its end the polarization becomes zero,  $P_\infty = 0$ .

The proportionality factor  $\tau$  from Eq. (2) is the relaxation time, supposed constant at constant temperature. The temperature dependence of the relaxation time is given by an Arrhenius equation:

$$\tau = \tau_0 \cdot \exp\left(\frac{E}{k \cdot T}\right) = \frac{1}{s_0} \cdot \exp\left(\frac{E}{k \cdot T}\right) \quad (3)$$



(a)



(b)

**FIGURE 4** The peak value of depolarization currents obtained in step 7 versus the polarizing voltages; a) 8CB; b) 8CB + ZrO<sub>2</sub>, 5% b.w., surface modified particles.

where  $s_0$  is the frequency pre-exponential factor and  $E$  is the activation energy.

Considering that the temperature  $T$  changes according to the law:

$$T = T_0 + q \cdot t \quad (4)$$

where  $T_0$  is the temperature at the beginning of step 7 and  $q = \frac{dT}{dt}$  is the heating rate, the relaxation time will vary:  $\tau = \tau(T(t)) = \tau(t)$ .

Introducing Eq. (3) in Eq. (2), and integrating, we obtain:

$$\begin{aligned}
 P(t) &= P_e(T_p) \cdot \exp\left(-\int_0^t \frac{d\theta}{\tau(\theta)} \cdot d\theta\right) \\
 &= P_e(T_p) \cdot \exp\left(-\int_0^t s_0 \cdot \exp\left(-\frac{E}{k \cdot T(\theta)}\right) \cdot d\theta\right) \quad (5)
 \end{aligned}$$

Changing the variable  $T = T_0 + q \cdot t$ , we obtain:

$$P(t) = P_e(T_p) \cdot \exp\left(-\frac{s_0}{q} \cdot \int_{T_0}^T \exp\left(-\frac{E}{k \cdot \theta}\right) \cdot d\theta\right) \quad (6)$$

The dipolar depolarization current will be:

$$J = -\frac{\partial P}{\partial t} = P_e(T_p) \cdot s_0 \cdot \exp\left(-\frac{E}{k \cdot T} - \frac{s_0}{q} \cdot \int_{T_0}^T \exp\left(-\frac{E}{k \cdot \theta}\right) \cdot d\theta\right) \quad (7)$$

In order to calculate the coefficients  $E$  and  $s$ , we should estimate the integral in Eq. (7); to avoid calculus difficulties, we<sup>0</sup> have analyzed the dependence  $f(T) = J'(T)/J(T)$ , where  $J'(T) = dJ(T)/dT$ . This follows from:

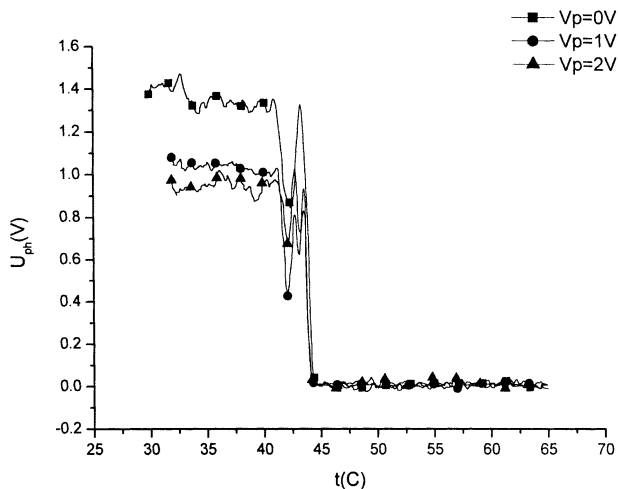
$$\begin{aligned}
 J'(T) &= P_e(T_p) \cdot s_0 \cdot \left(\frac{E}{k \cdot T^2} - \frac{s_0}{q} \cdot \exp\left(-\frac{E}{k \cdot T}\right)\right) \\
 &\times \exp\left(-\frac{E}{k \cdot T} - \frac{s_0}{q} \cdot \int_{T_0}^T \exp\left(-\frac{E}{k \cdot \theta}\right) \cdot d\theta\right)
 \end{aligned}$$

It results:

$$f = \frac{J'(T)}{J(T)} = \frac{E}{k \cdot T^2} - \frac{s_0}{q} \cdot \exp\left(-\frac{E}{k \cdot T}\right) \quad (8)$$

The numerical analysis of the experimental data obtained in step 7 allows the calculus of the activation energy and the frequency pre-exponential factor. We obtained the values  $E = 0.73$  eV;  $s = 3.24 \times 10_8 s_{-1}$  for pure 8CB and  $E = 0.84$  eV;  $s = 2.89 \cdot 10_{10} s_{-1}$  for the composite 8CB/ZrO<sub>2</sub>. Although small, the values of the pre-exponential factors are not uncommon<sup>2</sup> for these types of materials [7].

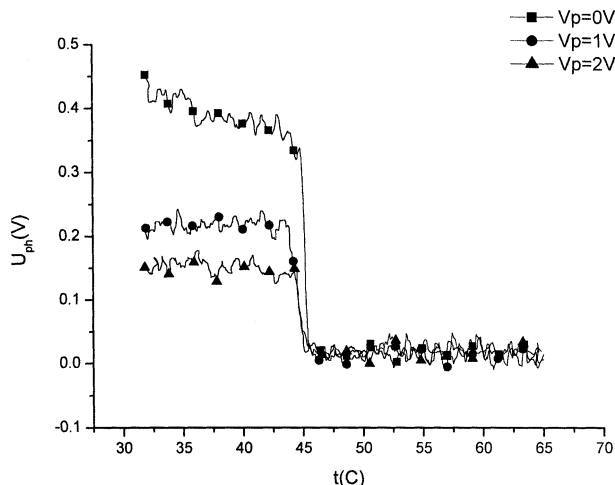
The optical transmission of the sample, measured in step 7, simultaneously with the depolarization currents is presented in Figure 5



**FIGURE 5** The optical signal measured by the photomultiplier in step 7 for the pure 8CB liquid crystal.

for the pure LC and in Figure 6 for the composite material. The optical transmission is practically constant till the N-I phase transition. At the SmA-N transition no modification was noticed, due to the too small birefringence difference between the of the smectic and nematic structures. For the pure LC, an important variation of the transmission is in the temperature range (41–44)°C. The optical transmission decreases abruptly to about 40% in an interval of 1°C, than it increases back to the maximum value in about 1°C, and finally it decreases to zero in the isotropic, nonbirefringent phase. This fluctuation in the optical signal are due to the unfavorable light scattering. The effect can not be put into evidence in the composite material, having the optical transmission of about three times smaller than the one of the LC, for similar polarizing voltages. This is due to the strong coupling between the LC molecules and the surface modified ZrO<sub>2</sub> particles.

In all studied cases, the optical transmission depends relatively strong on the polarizing voltage, because of its orientation effect upon the dipolar structure, proportional to the voltage value. The influence of the polarizing electric field on the optical transmission has a saturation effect, the modifications being smaller and smaller at the increase of the electric field. This result can also be correlated to the orientation effect of the dipolar structure; this structure, once it has been oriented, it becomes less sensitive to the applied external field.



**FIGURE 6** The optical signal measured by the photomultiplier in step 7 for the composite 8CB/ZrO<sub>2</sub>.

## CONCLUSIONS

The results of the field induced depolarization currents measurements on this composite device show a dipolar conduction mechanism. The values of the activation energy and the frequency pre-exponential factor 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 has a moderate dependence on the polarization field and has a discontinuity at the nematic-isotropic phase transition. To establish the influence of the particles surface modification on the phase transitions temperatures, more measurements are in progress.

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