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INFLUENCE OF POLARIZING ELECTRIC FIELD ON ELECTRICAL AND OPTICAL PROPERTIES OF PDLC FILMS

D. Manaila-Maximean [a b] & C. Rosu [a]

[a] Department of Physics, University "Politehnica Bucuresti", Splaiul Independentei 313, 77206 Bucharest, Romania

[b] CNRS, LPMC, UMR 6622, Universite de Nice-Sophia Antipolis, Parc Valrose, 06108 Nice Cedex 02, France

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D. Manaila-Maximean
Department of Physics – University "Politehnica Bucuresti", Splaiul Independentei 313, 77206 Bucharest, Romania
CNRS, LPMC, UMR 6622, Universite de Nice-Sophia Antipolis, Parc Valrose, 06108 Nice Cedex 02, France

C. Rosu
Department of Physics – University "Politehnica Bucuresti", Splaiul Independentei 313, 77206 Bucharest, Romania

We obtained polymer dispersed nematic liquid crystal films E7/PMMA. The thermally stimulated depolarization current (TSDC) measurements indicate a space charge limited current. Conduction of electronic type was proven and we measured the value of the activation energy, specific to the conduction process. Optical measurements have been performed simultaneously with TSDC measurements and the phase transition nematic – isotrop was detected by the switch of the optical transmission.

Keywords: conduction mechanism; polymer dispersed liquid crystal; thermally stimulated depolarization currents

INTRODUCTION

Polymer Dispersed Liquid Crystal (PDLC) composite materials consists of micrometer sized liquid crystal (LC) droplets embedded in a solid polymer matrix [1]. PDLC devices exhibit an electro-optical effect because of optical heterogeneity between the polymer and the LC domains. They can be switched from an "OFF" state to an "ON" state. For a LC with positive dielectric anisotropy, $\Delta\varepsilon > 0$, in the field "OFF" state, surface anchoring of the LC to the polymer causes a non-uniform director field in the

Address correspondence to D. Manaila-Maximean, Department of Physics – University 'Politehnica Bucuresti', Splaiul Independentei 313, 77206 Bucharest, Romania.

droplets. Thus the film scatters light due to the mismatch between the effective refractive index n_{eff} of the LC and the refractive index of the polymer n_p. In the field –ON state, the director is aligned along the field direction, $n_{eff} = n_{o(LC)}$, and for normal incidence light the film becomes transparent if the ordinary refractive index of the LC $n_{o(LC)}$ is equal to n_p [2].

The thermally stimulated depolarization current (TSDC) [3] method has been widely used to investigate the organic materials. Usually 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) [4]. The appearing conductivity effects are due to charge injection from the electrodes, charge transport through the liquid crystal, charge trapping and transport by alignment layers) [1,5]. The PDLC films are inhomogeneous and the ionic movement can set up depolarization fields opposed to the direction of the applied electric field, reducing the effective electric field across the droplet. The nature of the depolarization field depends on the relative conductivity of the polymer and liquid crystal. As the conductivity of the polymethyl methacrylate is three orders of magnitude smaller than the conductivity of the liquid crystal, charge will build up at the polymer/LC interface and tend to cancel the field across the droplet.

EXPERIMENTAL

We prepared PDLC films by the solvent induced phase separation method [5]. The polymer and the liquid crystal were mixed in the ratio of 50% LC by weight. Chlorophorm was added in a 6:1 weight ratio. After stirring well, the mixture was placed on ITO coated glass plates, and the chlorophorm was evaporated. Then another ITO coated glass plate was used to sandwich the PDLC film. The thickness of the samples was of 110 μm.

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), lower than the glass transition of the polymer matrix, initial depolarization of the sample takes place. The steps 1, 2, and 3 are performed to eliminate the eventually existing charges in the sample, due to

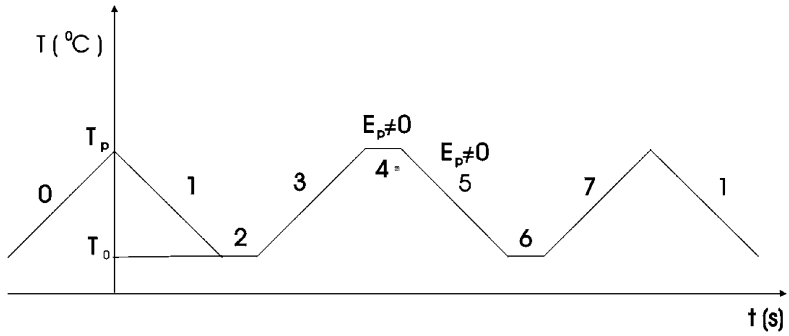

FIGURE 1 Heating-cooling cycles applied to the samples.

previously treatments applied on the sample. During step 4, at T_p, the polarizing field E_p is applied, and it is maintained during the cooling down to T_0 (step 5). 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. The experimental setup was described elsewhere [5].

RESULTS AND DISCUSSIONS

In Figure 2 are presented the depolarization currents during step 7 of the experiment, for several values of E_p.

We notice that the TSDC spectra have a maximum in absolute value, which corresponds to the nematic-isotropic phase transition of the LC. This peak shifts towards higher temperatures at the increase of the polarization electric field. The value of the depolarizing currents increases proportional to the polarizing field. We shall examine this phenomenon. Let us consider that the charge is given by:

$$Q = -\int_{t_1}^{t_2} i(t) \cdot dt = -\frac{dt}{dT} \cdot \int_{T_1}^{T_2} i(T) \cdot dT \tag{1.1}$$

where t denotes the time and T denotes the temperature. We notice that the sign of the charge depends on the sign of the current, 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. The negative sign of the registered currents in step 7

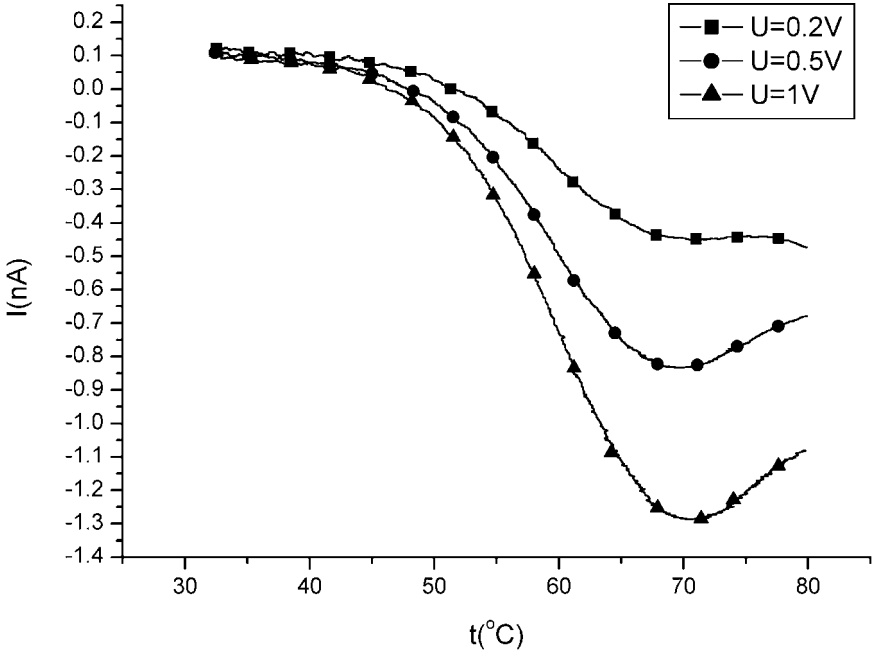

FIGURE 2 TSDC spectra for different applied polarizing electric fields for the 50% E7/PMMA sample.

is specific to homocharges. To study the conduction mechanism specific for the homocharge current, we represented in Figure 3 the peak value of this current versus the polarizing voltage.

As it is known [6], this nonlinear shape is characteristic for the currents limited by the spatial charge (for dipolar currents, the dependence of the peak amplitude on the polarization voltage is linear). In order to obtain information on the conduction mechanism, we examined the dynamics of the depolarization currents generated by the spatial charge. We start from the general law of magnetic circuit:

$$\nabla \times \vec{H} = \vec{J} + \frac{\partial \vec{D}}{\partial t} + \rho_V \cdot \vec{v} + \nabla \times (\vec{P} \times \vec{v}) \tag{1.2}$$

where ρ_V is the volumic density of the electric charge, $\vec{v}$ is the local velocity and $\vec{P}$ is the electric polarization of the medium.

The significance of the right hand terms are: $\vec{J}_1 = \sigma\vec{E}$ is the conduction current density, $\vec{J}_2 = (\partial\vec{D}/\partial t) = \varepsilon(\partial\vec{E}/\partial t)$ is the displacement current density, $\vec{J}_3 = \rho_V\vec{v}$ is the convection current density and $\vec{J}_4 = \nabla \times (\vec{P} \times \vec{v})$ is the experimental Röntgen current density [7].

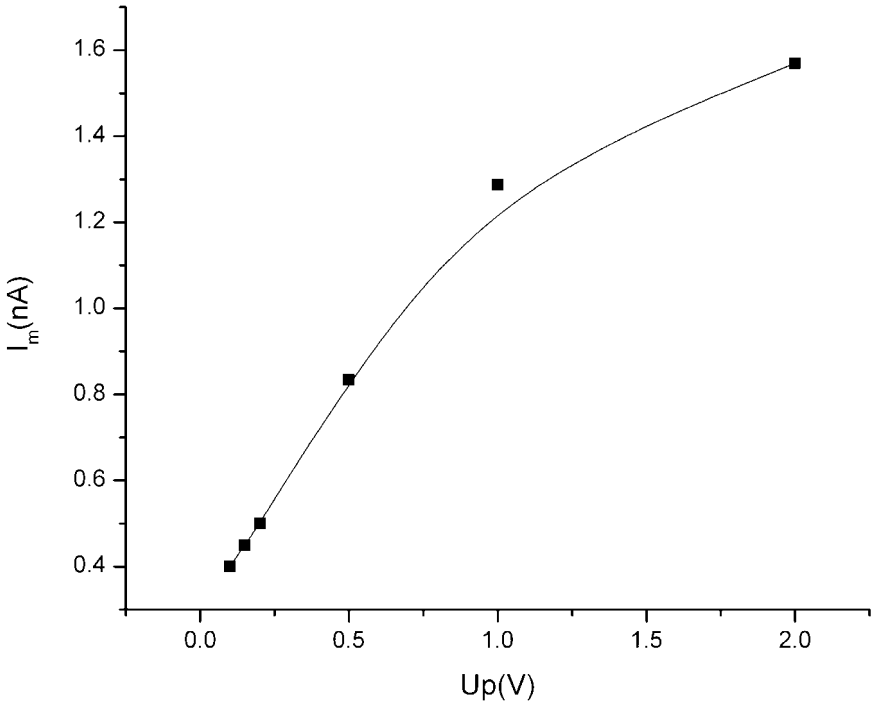

FIGURE 3 The peak value of depolarization currents obtained in step 7 versus the polarizing voltages for the 50% E7/PMMA sample.

The volume charge density satisfies the Poisson equation:

$$\nabla \vec{D} = \rho_V \tag{1.3}$$

The local velocity depends on the electric field according to the relation: $\vec{v} = \mu \cdot \vec{E}$, where μ is the charge mobility.

We consider that the mobility and the electric conductivity of the charge are constant in the volume of the sample, depending only on the temperature: $\sigma = \sigma(T)$; $\mu = \mu(T)$.

Depending on the collision type suffered by the charge carriers in the medium, the temperature dependencies of the mobilities can have different forms. In the case of the ionic conduction, it is [8]:

$$\mu = \mu_0 \cdot \exp\left(-\frac{E_1}{kT}\right) \tag{1.4}$$

where μ_0 and the activation energy E_1 are material constants.

In the case of electronic conduction, the mobility can be correlated with the mean time between two collisions $\bar{\tau}$, suffered by the carriers, according to the relation:

$$\mu = \frac{e \cdot \bar{\tau}}{m} \tag{1.5}$$

where e and m are respectively the charge and the mass of the carriers.

Frequently, the temperature dependence of the time $\bar{\tau}$ is given by an Arrhenius-type equation [9]:

$$\tau = \tau_0 \cdot \exp\left[\frac{E_2}{k \cdot T}\right] \tag{1.6}$$

where E_2 represents the activation energy and $s_0 = 1/\tau_0$ is the pre-exponential frequency factor. In this case the mobility (Eq. 1.5) becomes:

$$\mu = \mu_0 \cdot \exp\left[\frac{E_2}{k \cdot T}\right] \tag{1.7}$$

By applying the operator divergence to the relation 1.1, and considering the relations (1.2, 1.3), we obtain the continuity equation for the charge carriers:

$$\frac{\partial \rho_V}{\partial t} = -\nabla\left(\sigma\vec{E} + \rho_V \cdot \mu \cdot \vec{E}\right) \tag{1.8}$$

In the case of our samples, the electrodes are of rectangular shape of area S, placed at a distance g from one-another, and the electric filed is perpendicular to the electrode surface; thus we can simplify the above equations, considering an uni-dimensional geometry. Considering the Ox axis perpendicular to the electrodes, we obtain from (1.3) and (1.8), the partial derivative equations describing the evolution of the volumic charge and the electric field.

$$\begin{aligned} &\frac{\partial \rho(x,t)}{\partial t} = -\frac{\partial}{\partial x}[\sigma(T) \cdot E(x,t) + \mu(T) \cdot \rho_V(x,t) \cdot E(x,t)] \quad (a) \\ &\frac{\partial E(x,t)}{\partial x} = \frac{\rho_V}{\varepsilon} \qquad (b) \end{aligned} \tag{1.9}$$

These equations can be solved using the initial and limit conditions specific for the system. One of these conditions is the value U of the voltage applied on the sample, which was maintained constant in time during steps 4 and 5 of the experiments, but different from one experiment to the other.

$$\int_0^g E(x,t) \cdot dx = U \tag{1.10}$$

The total current density is given by the right hand side term in Eq. (1.2), where we considered for the nematic liquid crystal used $P = 0$.

$$\vec{J}_t = \vec{J}_1 + \frac{\partial \vec{D}}{\partial t} + \rho_V \cdot \vec{v} = (\sigma(T) + \rho_V(x,t) \cdot \mu(T)) \cdot \vec{E}(x,t) + \varepsilon \cdot \frac{\partial \vec{E}(x,t)}{\partial t} \tag{1.11}$$

By integrating the equation on the x variable, along the whole thickness of the cell, taking into account the relations (1.9) and (1.10), and the time-constant of the applied voltage, we obtain:

$$\begin{aligned} J_t &= \frac{\sigma(T) \cdot U + \mu(T) \cdot \int_0^g \rho_V(x,t) \cdot E(x,t) dx}{g} \\ &= \frac{\sigma(T) \cdot U + \mu(T) \cdot \varepsilon \cdot [E^2(g,t) - E^2(0,t)]}{2 \cdot g} \end{aligned} \tag{1.12}$$

$E(g,t)$, $E(0,t)$ represent the values of the electric field on the surface of the electrodes.

The integration of the equations in the general case is extremely difficult. Thus we shall suppose a sample with zero conductibility. In the first stage of the redistribution of the charges, in step 7, the front of the charge has not yet reached the opposed electrode, and thus $\rho_V(g,t) = 0$; Eq. (1.11) becomes:

$$J_t = \varepsilon \cdot \frac{\partial E(g,t)}{\partial t} \tag{1.13}$$

By integrating the Eq. (1.9.b) on the x variable, throughout the whole thickness of the sample, we obtain the total charge Q_V accumulated in the sample:

$$Q_V = \int_0^g \rho(x,t) \cdot S \cdot dx = \varepsilon \cdot S \cdot [E(g,t) - E(0,t)] \tag{1.14}$$

The relations (1.12), (1.13) and (1.14) form a system of ordinary differential equations with the functions $J(t)$, $E(g,t)$, $E(0,t)$. By solving the system we obtain the time dependency of the electric field $E(g,t)$:

$$E(g,t) = \frac{1}{2} \cdot \left\{ \frac{Q_V}{\varepsilon \cdot S} + \left[2 \cdot E(g,0) - \frac{Q_V}{\varepsilon \cdot S} \right] \cdot \exp\left[\frac{Q_V}{\varepsilon \cdot g \cdot S} \cdot \int_0^t \mu(\tau) \cdot d\tau \right] \right\} \tag{1.15}$$

Let us consider the linear time dependence of the temperature in phase 7:

$$T = T_0 + q \cdot t \tag{1.16}$$

where T_0 is the initial temperature at the beginning of step 7 and $q = dT/dt$ is the heating rate. Using the variable change (1.16), the relation (1.15) will be:

$$E(g,T) = \frac{1}{2} \cdot \left\{ \frac{Q_V}{\varepsilon \cdot S} + \left[2 \cdot E(g,0) - \frac{Q_V}{\varepsilon \cdot S} \right] \cdot \exp\left[\frac{Q_V}{\varepsilon \cdot g \cdot S \cdot q} \cdot \int_{T_0}^{T} \mu(\tau) \cdot d\tau \right] \right\} \tag{1.17}$$

Introducing (1.17) in (1.13) we obtain the current density in the sample, in the first phase of the redistribution process of the spatial charge

$$J(T) = \frac{Q_V \cdot \mu(T)}{2 \cdot g \cdot S} \cdot \left[2 \cdot E(g,0) - \frac{Q_V}{\varepsilon \cdot S} \right] \cdot \exp\left[\frac{Q_V}{\varepsilon \cdot S \cdot g \cdot q} \cdot \int_{T_0}^{T} \mu(T) \cdot dT \right] \tag{1.18}$$

The maximum current throughout the sample correspond to a temperature T_m given by the equation $dJ/dT = 0$; from Eq. (1.18) we obtain:

$$\frac{d\mu(T)}{dT} + \frac{Q_V}{\varepsilon \cdot S \cdot g \cdot q} \cdot \mu^2(T) = 0 \tag{1.19}$$

The total charge Q_V will be proportional to the polarizing voltage $U_p = E_p \cdot g$ applied in steps 5 and 6 of the measurement process. It is difficult to establish the exact form of the dependency, because of the very complicated equations. For the sake of simplicity, we shall consider that this is obtained in the beginning of step 5, for a time interval t_p, and is of the form:

$$Q_V = I \cdot t_p = \sigma(T_p) \cdot S \cdot t_p \cdot U/g \tag{1.20}$$

The condition (1.19) to obtain the maximum of the current dependence on temperature is:

$$\frac{d\mu(T)}{dT} + \frac{\mu^2(T) \cdot \sigma(T_p) \cdot t_p \cdot U}{\varepsilon \cdot g^2 \cdot q} = 0 \tag{1.21}$$

If we suppose that the conduction has an ionic origin, by introducing the mobility (1.4) in the relation (1.21), we obtain an equation giving the temperature T_m corresponding to the maximum of the current:

$$\frac{\sigma(T_p) \cdot t_p \cdot \mu_0 \cdot U}{\varepsilon \cdot g^2 \cdot q} \cdot \exp\left(-\frac{E_1}{k \cdot T} \right) = -\frac{E_1}{k \cdot T^2} \tag{1.22}$$

As we have shown, the injected charge is positive $\sigma(T_p) > 0$, and in step 7 (heating) $q > 0$. It results that Eq. (1.22) will not be satisfied, since the two terms have opposite signs. It follows that the conduction can not be ionic.

Because of the electronic nature of the conduction we shall use the expression (1.7) of the mobility; the Eq. (1.21) becomes:

$$\frac{\sigma(T_p) \cdot t_p \cdot \mu_0 \cdot U}{\varepsilon \cdot g^2 \cdot q} \cdot \exp\left(\frac{E_2}{k \cdot T}\right) = \frac{E_2}{k \cdot T^2} \tag{1.23}$$

Using the notation $\lambda = \dfrac{\sigma(T_p) \cdot t_p \cdot \mu_0}{\varepsilon \cdot g^2 \cdot q}$, the above relation becomes:

$$\lambda \cdot U \cdot \exp\left(\frac{E_2}{k \cdot T}\right) = \frac{E_2}{k \cdot T^2} \tag{1.24}$$

By fitting the relation (1.24) in the parameters λ, E_2, we have obtained the energy $E_2 = 4.58\,\text{eV}$; in Figure 4 we have represented with a continuous line the fitting curve and by dots the experimental values (U_p, T_m):

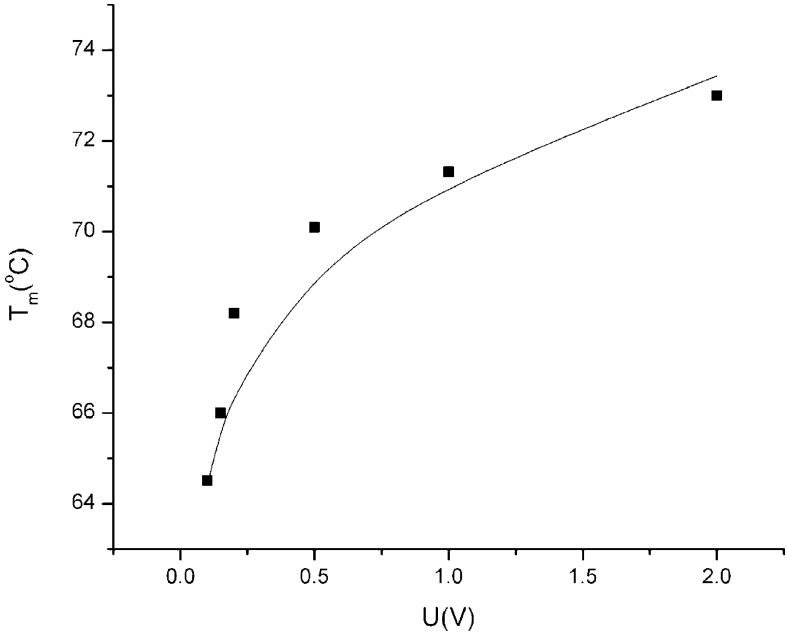

FIGURE 4 The dependence of the temperature corresponding to the maximum current in step 7, on the pre-polarization voltage U_p; the dots corresponds to the experimental data and the continuous line to the fitting curve.

A development of the present method can be the determination of the mobility and distribution of the charges. Collins [10] has measured the modifications of the surface potential in time, when heating with a short laser pulse; thus he determined the average position of the charges and the main characteristics of the charge distribution. By using pressure pulses, instead of light pulses, Lewiner [11] obtained similar results.

The optical transmission has been measured simultaneously during the experiment. In Figure 5 is shown the optical signal during step 7, for several previously applied polarizing fields. The transmission increases at the N-I phase transition because of the match between the refractive index of the LC in the isotropic phase $n_{(LC)iso}$ and the refractive index of the polymer n_p. Thus the PDLC film can also act as a temperature switch. We notice from Figure 5 that at low temperatures, when the LC is in the N phase, the transmission increases at the increase of the electric field. This can be explained considering the order parameter, which increases at higher electric fields. At higher temperatures, the difference between $n_{(LC)iso}$ and n_p increases with the electric field because of the shielding effect generated by the spatial charge.

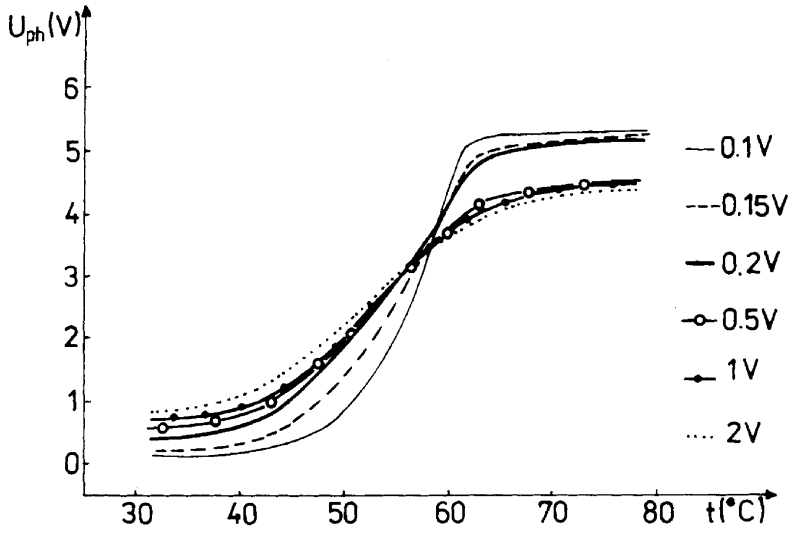

FIGURE 5 Optical signal versus temperature in step 7 for the 50% E7/PMMA sample.

CONCLUSIONS

We obtained polymer dispersed nematic liquid crystal films E7/PMMA. We have registered the TSDC spectra for the N-I transition of the LC. The obtained peak shifts towards higher temperatures at the increase of the polarization electric field and the value of the depolarizing currents increases as well with the polarizing field. By examining this phenomenon we have reached the conclusion that the process is due to a space charge limited current. Conduction of electronic type was proven and we measured the value of the activation energy, specific to the conduction process.

Regarding the optical transmission, a steep slope is obtained when no electric field was previously applied on the sample; the slope decreases when increasing the polarizing field and the temperature interval corresponding to the ON-OFF optical states increases with the increase of the polarizing field. The ratio between the ON and OFF optical signals decreases with the increase of the E_p.

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