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Influence of Polarizing Electric Field on Phase Transition Temperatures and Optical Transmission of PDLC Films

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Influence of Polarizing Electric Field on Phase Transition Temperatures and Optical Transmission of PDLC Films

DOINA MANAILA-MAXIMEAN[a], RODICA BENA[a], CONSTANTIN ROSU[a] and MAURIZIO FURLANI[b]

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We obtained polymer dispersed nematic liquid crystal films E7/PMMA. Using the thermally stimulated depolarization currents method and registering the optical signal simultaneously we studied the dependence of the phase transitions temperatures on the polarizing electric field. Thermal switch behavior and its dependence on polarizing electric field is obtained.

Keywords: thermally stimulated depolarization currents; liquid crystals; polymers; PDLC; thermophysical properties

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. One achieves switching between an opaque field-"off" and a transparent field-"on" state by matching the ordinary refractive index of the LC to the refractive index of the polymer matrix.

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In this paper we study the phase transitions in PDLC films by the thermally stimulated depolarisation currents (TSDC) [2] method and by differential scanning calorimetry (DSC) [3]. The optical signal has been simultaneously measured. The hysteresis observed in the optical signal is discussed in connection with the magnitude of the polarizing electric fields.

The thermally stimulated depolarization current (TSDC) 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)[3].

Even in the absence of an initial external polarization electric field [3], applying the same cooling and heating cycle as described above, high discharge currents can be registered. In some dielectrics as well as in LC, some phase transitions are accompanied by charge separation at the dielectric-electrode interface giving raise consequently to a short circuit current in the external measuring circuit. This effect is reversible and is known as the Costa Ribeiro effect [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]. 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, as shown in Figure 1. As the dielectric constants of the polymer and LC differ, bound depolarization charges will enhance the field across one phase at the expense of the field across the other phase. The schematic presentation of the

depolarization fields in Figure 1 applies to bound depolarization charges as well as to mobile ions.

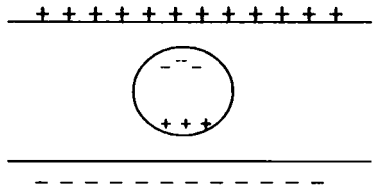

FIGURE 1. Depolarization across LC droplet, with decrease in the electric field across the droplet.

EXPERIMENTAL

We prepared PDLC films by the solvent induced phase separation method [5]. The polymer and the liquid crystal were mixed in three ratios of 30%, 50%, 70% 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.

For the DSC experiments, the films have been solvent-casted and sealed in aluminium pans.

In Figure 2 is presented the schematic experimental set-up. The analyzed sample (CL) was introduced in a oven (F) having the heating-cooling rate computer controlled. The computer also controls the value of the voltage source (U), using a digital/analog converter. The switches K_1 and K_2 , computer controlled, perform the steps succession of the experiment. When K_1=a and K_2=b, the voltage of the U source is applied on the sample; when K_1=b and K_2=b, the sample is short-circuited and the picoammeter (pA), also computer controlled, measures the current through the sample. Finally, if K_1=b and K_2=a, the sample is short-circuited and the stored charges will be eliminated.

Figure 3 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 sample polarization with the electric field E_p is preceded by steps 1, 2, and 3, for erasing the

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"memory" of the sample. During step 4, at T_p, the polarizing field 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 1K/min and steps 2, 4 and 6 were of 15 minutes.

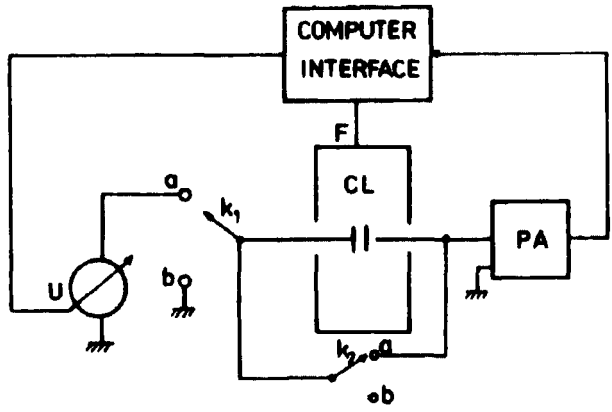

FIGURE 2. Schematic set-up for TSDC and optical measurements.

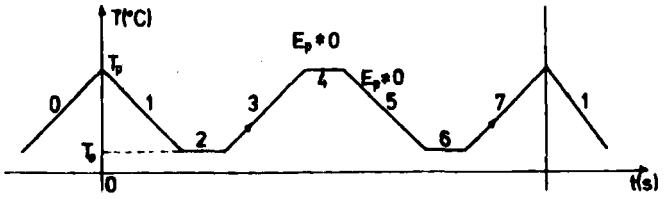

FIGURE 3. Heating-cooling cycles applied on the samples.

RESULTS AND DISCUSSIONS

To obtain the dependence of phase transition temperatures on the magnitude of the polarizing d.c. electric field previously applied on the sample, we registered the depolarizing electric currents during step 7 of the experiment for several values of E_p, presented in figure 4. The 0V

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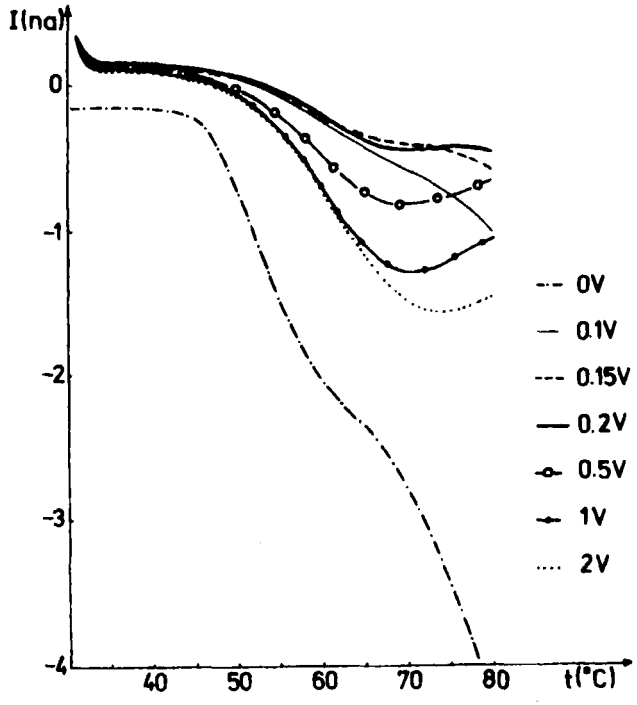

FIGURE 4. TSDC spectra for different applied polarizing electric fields for the 50% E7/PMMA sample.

curve (step 0), corresponds to initial depolarization currents; its changes in the values of the slope are connected to the domains of the LC melting, 45-60 ^{0}C and to the on-set of the PMMA glass transition.
Increasing the polarization field the aspect of the TSDC spectra changes, presenting a maximum in connection with the "off-set" of the N-I transition temperature. The temperature corresponding to the maximum (in modulus) shifts towards higher values when increasing the electric field. The value of the depolarizing currents increase as well with the polarizing field.
The temperature interval of the N-I transition increases with the applied polarizing field. This can be explained as follows: when a polarizing

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electric field is applied at higher temperatures, the dipoles are oriented. Keeping the field applied during cooling, the dipoles are "frozen in". At the increase of the temperature, thermally stimulated depolarization currents are registered. If the polarizing field is stronger, more dipoles are oriented, and more energy, that is a broader temperature interval will be needed to disorient them and to pass in the isotropic state.

The optical transmission has been measured simultaneously during the experiment. The results are shown in Figures 5 and 6. Two distinct transmission states, "off" and "on" are noticed. Thus the temperature switch function of the PDLC is demonstrated. Analyzing the curves in Figure 5, we observe a great hysteresis area between the "0" and "1" steps. Between two successive heating curves (0,3), sample "memory" also appears, although no electric field has been applied. This is due to the thermal reset of the droplets dimension. The heating steps 3 and 7 and the cooling steps 1 and 5 are almost superposed.

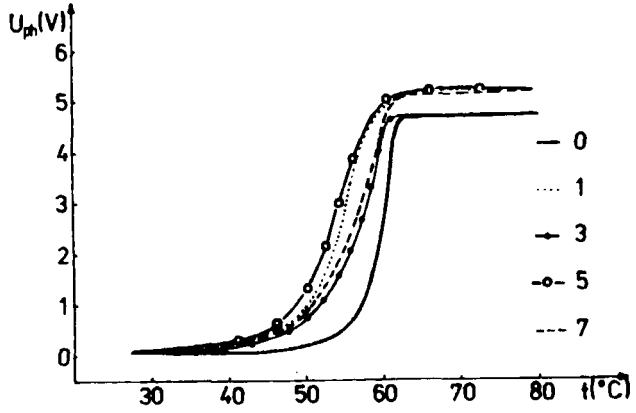

FIGURE 5. Optical transmission versus temperature for the E7/PMMA 50% sample. Curves 0, 3, 7 heating; curves 1, 5, cooling. Step 7- after polarizing the sample with 0.1V.

In Figure 6 is shown the optical signal during step 7, for several previously applied polarizing fields. We notice that the slopes of the curves decrease when increasing the previously applied polarizing electric field. Correspondingly, the temperature interval of the N-I transition increases, in full agreement with the results obtained from the TSDC analysis.

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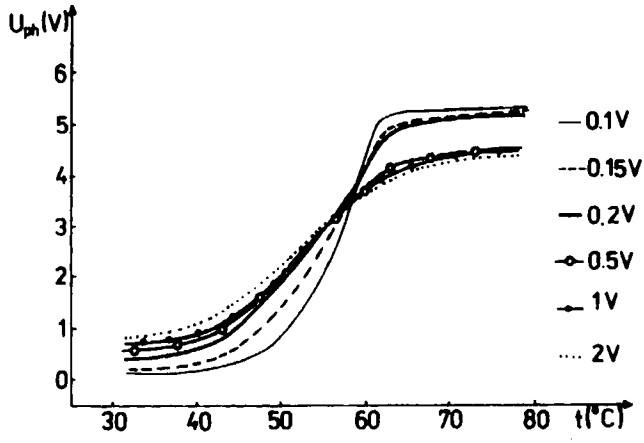

FIGURE 6. Optical signal versus temperature in step 7 for the 50% E7/PMMA sample.

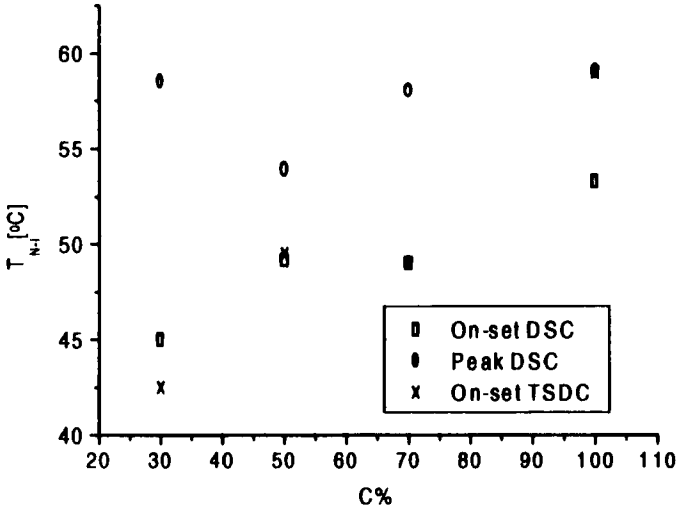

FIGURE 7. N-I phase transition temperature versus LC content b.w.

Similar measurements have been performed on the 30% and 70% E7/PMMA samples and the same behavior of the TSDC spectra and the optical signal was obtained.

In order to check the obtained by TSDC results, we run also DSC experiments for non-polarized samples of different concentrations. In Figure 7 we summarized the results of the DSC experiments, and for the TSDC. A good agreement between the two methods is observed.

CONCLUSIONS

Using the thermally stimulated depolarization currents method and registering the optical signal simultaneously we studied the dependence of the phase transitions temperatures on the polarizing electric field.

From the TSDC spectra results an increase of the phase transition N-I temperature interval when increasing the polarizing field. The depolarization current increases also with the polarizing field.

The optical signal measurements demonstrate the temperature switch behavior of the sample. 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 . The conclusions drawn from the TSDC spectra, the DSC experiments and the ones from the optical measurements are in good agreement, which recommends the TSDC method for the study of the thermophysical properties of PDLC.

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