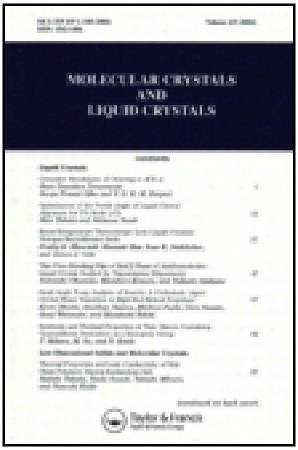

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Synthesis and Electro-Optical Studies on Composite Material: Functionalized Copolymer Particles/Nematic Liquid Crystal

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Synthesis and Electro-Optical Studies on Composite Material: Functionalized Copolymer Particles/Nematic Liquid Crystal

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We have synthesized new functionalized copolymers of the type divinyl benzene – maleic anhydride (DVB-MA) in order to ensure a better compatibility with the penthyl-phenol group of the liquid crystal. These particles have been mixed by stirring and ultrasound with nematic liquid crystals ZLI 1221 (Merck), concentration 5% b.w. (copolymer/LC). We applied cycles of temperature and electric field, corresponding to the TSDC method. We measured the depolarization currents and simultaneously the optical transmission as a function of the electric field and temperature. We obtained information regarding the conduction mechanism, the distribution of the activation energy and the influence of the polarizing voltage on the optical transmission.

Keywords: functionalized copolymers; liquid crystal colloidal composites; optical transmission; TSDC

INTRODUCTION

Colloidal dispersions of small particles in nematic liquid crystal are a novel type of soft matter [1–6]. Understanding of surface treatments that would induce special particles self-assembly in NLC, influence

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of electric and magnetic field on such systems, particle manipulation could lead to future application of such materials.

In this paper we examined the electrical and optical properties of pure liquid crystal ZLI 1221 (Merck) and in a composite system obtained by introducing new synthesized functionalized copolymer particles, “hairy” type, that can determine a better compatibility with the LC.

Using the Thermally Stimulated Depolarization Currents (TSDC) [7,8] method we obtained information regarding the conduction mechanism. Optical transmission was simultaneously measured.

TSDC is a low frequency technique that helps determination of phase transitions that often present resolution difficulties with other techniques. 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).

EXPERIMENTAL

Synthesis of Functionalized Copolymer Particles

We have synthesized new copolymers of the type divinyl benzene – maleic anhydride (DVB-MA) by radical polymerization in solvents (heptane-methyl ethyl ketone) (code name D24). To ensure a better compatibility between the liquid crystal and the colloidal particles, these copolymers have been functionalized by ternary copolymerization in presence of 1% nonyl phenol ethoxylated maleic monoesther with 4 moles ethylene oxide ($MEMNPEO_4$) (code name D23) formula given in (1)

$$C_9H_{19} - C_6H_4 - (OCH_2CH_2)_4 - O - CO - HC = CH - COOH \qquad (1)$$

The synthesis was performed [9], starting from the mixtures presented in Table 1, mixing for 4 hours, at 70°C. The maleic monoester (1) offer the opportunity the presence of alkyl phenyl group (1) after the copolymerization of DVB-MA. Thus we insured the attachment

TABLE 1 Composition of Starting Mixtures: Ma-Maleic Anhydride, Dvb-Divinylbenzen, Initiator: Aibn-Azoisobutyro Nitrile

Code name	Monomers (g) MA/DVB	Surfactant (g)	Solvent (ml)	Initiator (g)	Conversion (%)
D23	4/4	1.0	100	0.2	96
D24	4/4	–	100	0.2	99

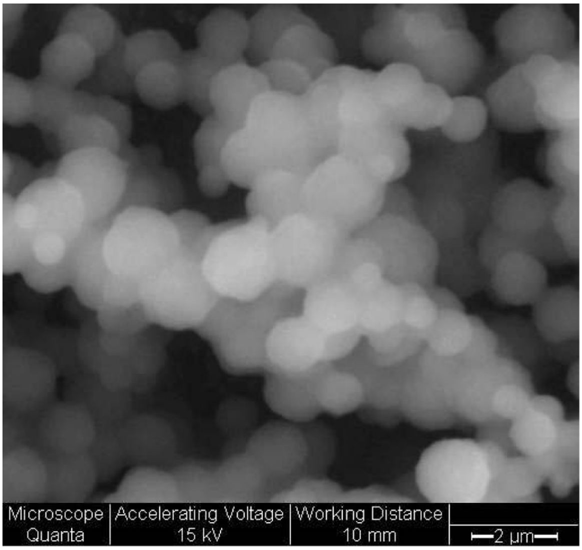
of some chains with nonyl-phenyl group on the D23 polymer particle, compatible with the penthyl-phenyl group from the liquid crystal.

These lateral groups determine a better compatibility between the polymer particle and the LC and an increased stability of the system.

In Figure 1 are presented the electron microscopy images of the copolymer particles. The dimensions of the particles are D23 = 823 nm; D24 = 995 nm.

Sample Preparation

We made samples of composite material containing the obtained copolymer particles and nematic liquid crystal ZLI 1221 (K-N: −11°C, N-I: 90°C) provided by Merck. The particles have been mixed by



D23

FIGURE 1 Electron microscopy picture of copolymer particles.

TABLE 2 The Obtained Copolymer Particles/Liquid Crystal Mixtures

Nr	Particle nature	Code	Liquid crystal	Composite material, concentration 5% b.w. particle/LC
1	Copolimer DVB-MA functionalized	D23	ZLI 1221- nematic	D23/ZLI 1221
2	Copolimer DVB-MA	D24	ZLI 1221- nematic	D24/ZLI 1221

stirring and ultrasound with nematic liquid crystal, in a concentration of 5% b.w. The copolymer particles/NLC mixtures are presented in Table 2. 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 μm.

EXPERIMENTAL SET-UP

The experimental set-up has been described elsewhere [10]. Figure 2 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

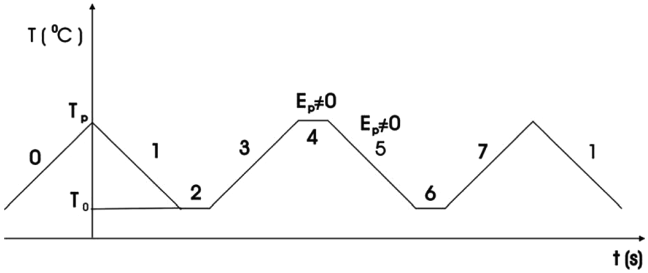


FIGURE 2 Heating-cooling cycles applied to the samples.

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 $T_p = 130°C$ and $T_0 = 25°C$.

The light is transmitted through the sample and measured by the photomultiplier; crossed polarizers have been used.

RESULTS AND DISCUSSIONS

According to the heating–cooling cycles presented in Figure 2, 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 3 and 4 we present the thermally stimulated depolarization currents versus temperature for the pure LC and for the composite system, D23/ZLI 1221 respectively.

Considering the charge given by the Eq. (2) [8]:

$$Q = -\int_{t_1}^{t_2} i(t) \cdot dt = -\frac{dt}{dt} \cdot \int_{T_1}^{T_2} i(T) \cdot dt \qquad (2)$$

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,

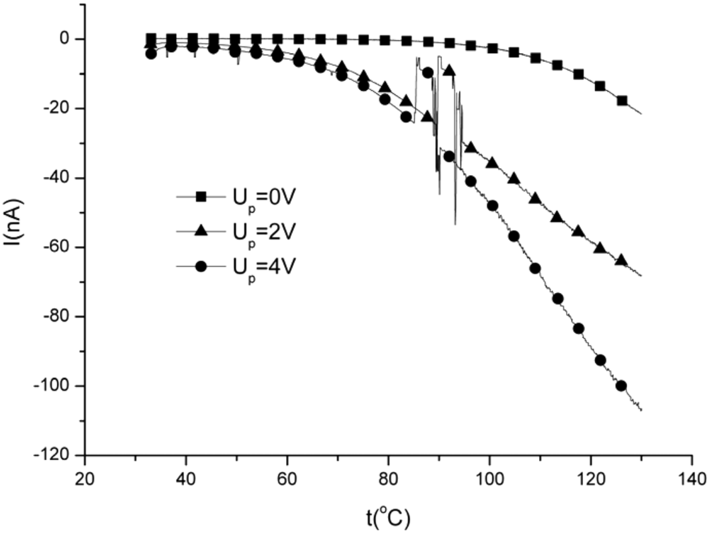


FIGURE 3 TSDC spectra for the pure liquid crystal ZLI 1221, measured in step 7.

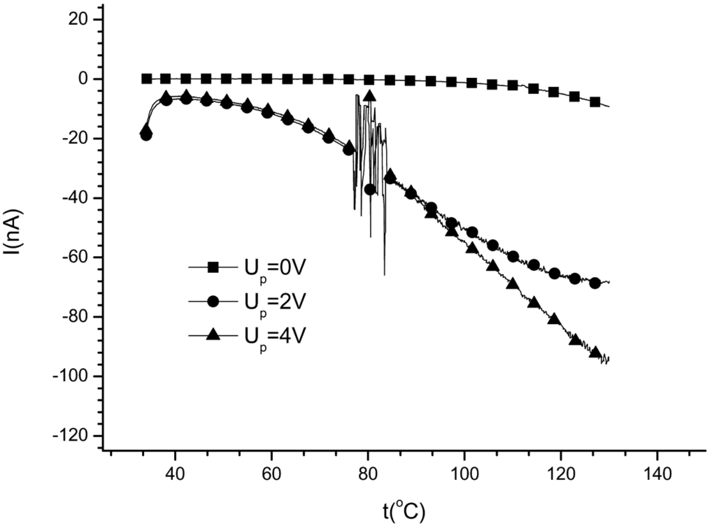


FIGURE 4 TSDC spectra for the composite sample functionalized copolymer particles/liquid crystal: D23/ZLI 1221 (5% b.w.), measured in step 7.

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 spectra have shown negative currents, due to homocharges.

We notice from Figure 3, that for the pure LC, the depolarization current increases at the increase of the polarizing voltage. The nematic-isotropic phase transition is marked by a peak (fluctuations) of the current and the phase transition temperature is lower for smaller polarizing voltage values. The form of the TSDC spectra suggest a dipolar conduction mechanism. The wide shape indicates that the dipolar conduction is characterized by several values of the activation energy of the dipoles. This situation is generated by the dispersion of the polar groups of the LC molecule (at low temperatures) or by the dispersion of the inertia momenta of the dipoles at high temperatures. A proof of this is represented by the Arrhenius diagram ln(I) = f(1/T) plotted in step 5 (see Fig. 5).

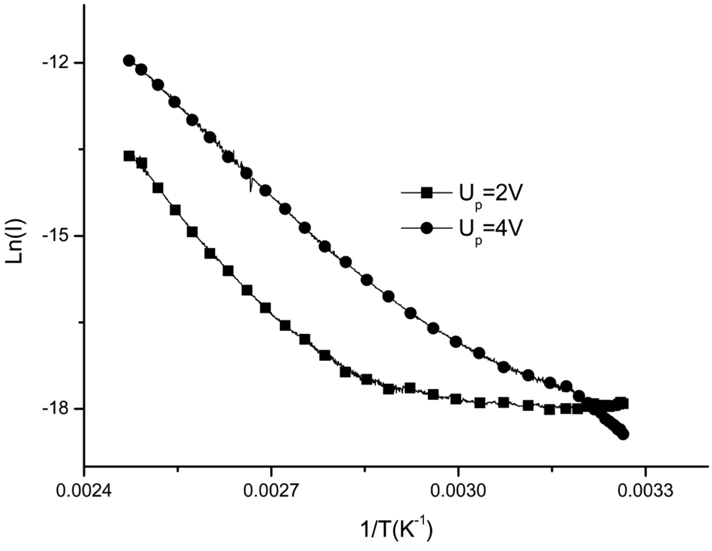


FIGURE 5 The Arrhenius diagram for the pure ZLI 1221 sample, step 5 of the TSDC: ■ $U_p = 2V$, ● $U_p = 4\,V$.

One notice that for high temperatures the activation energies computed from the slope of the graph are practically constant: $\Delta E = 1.046\,eV$ for $U_p = 2\,V$, and $\Delta E = 0.667\,eV$ for $U_p = 4\,V$ respectively. The lower value of the activation energy obtained for high polarization voltages, indicate an ordering effect of the field, effect that leads at a easiness of the dipolar dynamics.

At low temperatures, (under about 70°C) starts a strong dispersion of the activation energies, which is put into evidence by the nonlinear Arrhenius plot from Figure 5.

The activation energies can vary between about 1 eV and some tenths of eV, that generate flatter TSDC spectra at lower temperatures, as compared to higher temperatures.

We observe (Fig. 4) that for the composite sample D23/ZLI 1221 due to complex interactions between the particles and the LC, the peak of the depolarization current curve shifts towards higher temperatures when increasing the polarizing voltages.

The presence of a high degree of disorder (positional and compositional) in the D23/ZLI 1221 sample, leads to the apparition of a high number of localized states in the band gap. Thus, a higher dispersion of the activation energy appears, as compared to the pure LC. This is also put into evidence by the Arrhenius diagram (see Fig. 6), that

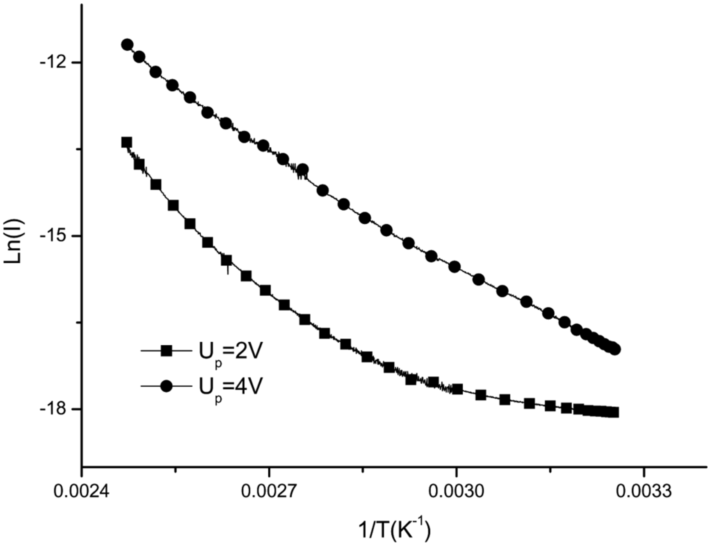


FIGURE 6 The Arrhenius diagram for the composite sample D23/ZLI 1221, step 5 for different applied voltages.

shows a higher degree of nonlinearity (even for high temperatures), as compared to the corresponding diagram for the pure LC (Fig. 5). At the increase of the polarizing voltage, the behavior is similar to that of the pure LC, showing that the polar groups in the LC plays a more important role that the LC-polymer interactions.

In Figures 7 and 8 are presented the optical transmission for the pure LC (ZLI 1221) and composite material, respectively, measured in step 7, simultaneously with the depolarization currents.

The curves have one common characteristic: high optical transmittance until approximate 90°C, and a low transmittance afterwards, when the LC is in isotropic state.

As expected, if no polarizing field has been previously applied, the optical transmission is smaller for the composite sample, as compared to the pure LC (in the nematic state). In the case of the composite sample, it increases after the application of polarizing fields, 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

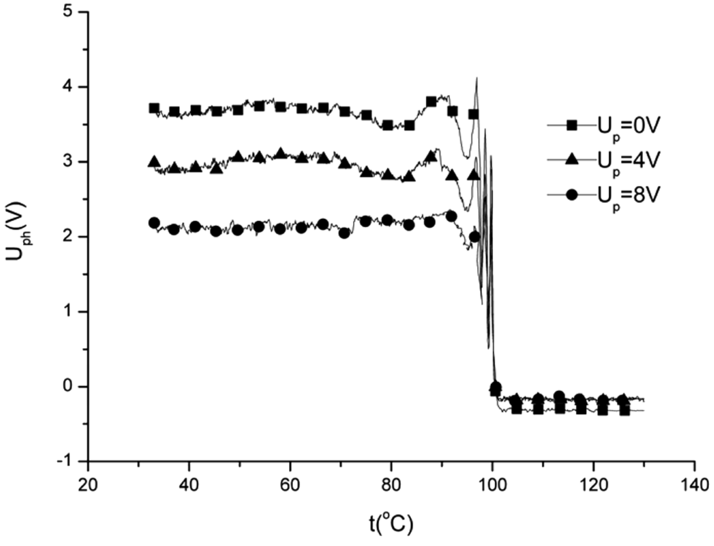


FIGURE 7 Optical signal measured in step 7 for the pure liquid crystal ZLI 1221, after applying different polarizing electric fields in steps 4 and 5.

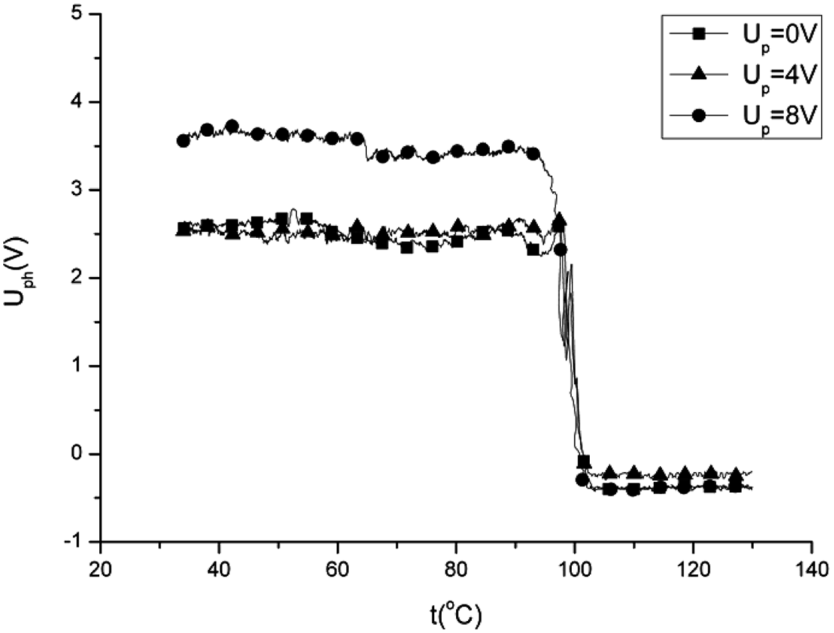


FIGURE 8 Optical signal measured in step 7 for the composite functionalized copolymer particles/liquid crystal: D23/ZLI 1221 (5% b.w.), after applying different polarizing electric fields in steps 4 and 5.

dipolar structure; the structure, once oriented, becomes less sensitive to the applied external field.

CONCLUSIONS

We have synthesized a new composite material of the type: functionalized copolymer particles/NLC. Thus we obtained a "hairy" particle that is more compatible with the liquid crystal.

We have studied the electro-optical properties when applying heating-cooling cycles corresponding to the TSDC method.

The results of the field induced depolarization currents measurements on this composite sample show a dipolar conduction mechanism. For the composite system, the optical transmission measured simultaneously with the depolarization currents increases when the pre-applied polarizing field increases. To establish the influence of the particles surface modification on the phase transitions temperatures, more studies are in progress, especially for lower polarizing voltages.

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