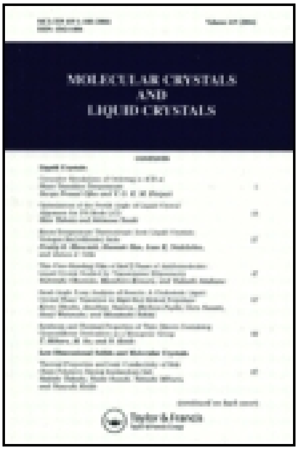


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Synthesis and Electro-Optical Studies on Composite Materials Polymer Particles/Nematic Liquid Crystal

D. Manaila-Maximean [a] , C. Rosu [a] , D. Donescu [b] , S. Frunza [c] & T. Beica [c]

[a] Department of Physics II-University “Politehnica Bucuresti”, Bucharest, Romania
[b] ICECHIM, Bucharest, Romania
[c] INCDFM, National Institute of Material Physics, Bucharest, Romania

To cite this article: D. Manaila-Maximean, C. Rosu, D. Donescu, S. Frunza & T. Beica (2007): Synthesis and Electro-Optical Studies on Composite Materials Polymer Particles/Nematic Liquid Crystal, Molecular Crystals and Liquid Crystals, 475:1, 209-219

To link to this article: http://dx.doi.org/10.1080/15421400701735699

Mol. Cryst. Liq. Cryst., Vol. 475, pp. 209–219, 2007
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400701735699

Synthesis and Electro-Optical Studies on Composite Materials Polymer Particles/Nematic Liquid Crystal

D. Manaila- Maximean
C. Rosu
Department of Physics II – University "Politehnica Bucuresti",
Bucharest, Romania

D. Donescu
ICECHIM, Bucharest, Romania

S. Frunza
T. Beica
INCDFM, National Institute of Material Physics, Bucharest, Romania

We have synthesized polymer particles of the type alternated copolymers DVB-maleic anhydride. The dimensions of the obtained particles have been determined by electron microscopy and are in the range 1–2 μm. These particles have been mixed by stirring and ultrasound with nematic liquid crystals ZLI 1221 (Merck), in a concentration of 5% b.w.(polymer/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 activation energy and the pre-exponential frequency factor in the Arrhenius diagrams. The dipolar current obtained is consequent to a superposition of a dipolar distribution with a wide spectrum of relaxation times.

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

The author acknowledges the Romanian Ministry of Education and Research for financial support under the CEEX program, Project CEX-05-D11-76, and the Merck Company for providing the liquid crystal.

Address correspondence to D. Manaila- Maximen, Department of Physics II – University "Politehnica Bucuresti", Splaiul Independence 313, Bucharest 060042, Romania. E-mail: doinamanaila@hotmail.com

INTRODUCTION

In the recent years much attention has been paid to the particles/liquid crystals composites [1–4]. 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.

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 [5,6]. 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 article we examined the electrical and optical properties in the pure liquid crystal ZLI 1221 (Merck) and in a composite system obtained by introducing synthesized polymer particles.

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

EXPERIMENTAL

Synthesis of Polymer Particles

The synthesis was performed as in [7], starting from the mixtures presented in Table 1. The mixtures have been stirred for 4 hours, at 70°C. NPO_4 is a surfactant with a terminal functional group hydroxyl (OH) that can react with maleic anhydride in the polymer. Thus we insured the attachment of some chains with phenyl group on the polymer particle. These lateral groups insure a better compatibility between the polymer particle and the LC and an increased stability.

TABLE 1 Compositions of Starting Mixtures: MA-Maleic Anhydride, DVB-Divinylbenzene, MEK-Methylethyl Ketone, AIBN-Azobisisobutyronitrile $NPEO_4$ -Nonyl Phenol Ethoxylated with 4 Moles Ethylene Oxide.

Code name	Monomers (g)	Surfactant (g)	Solvent (ml)	Initiator (g)	Conversion (%)
D10	MA/4.0 DVB/4.0	–	MEK/4.0 Heptane/60	AIBN/0.15	90
D12	MA/4.0 DVB/4.0	$NPEO_4$/0.2	MEK/4.0 Heptane/60	AIBN/0.2	90
D14	MA/4.0 DVB/4.0	$NPEO_4$/0.2	MEK/4.0 Heptane/60	AIBN/0.4	95

In Figure 1 are presented the electron microscopy images of the obtained polymer particles.

Sample Preparation

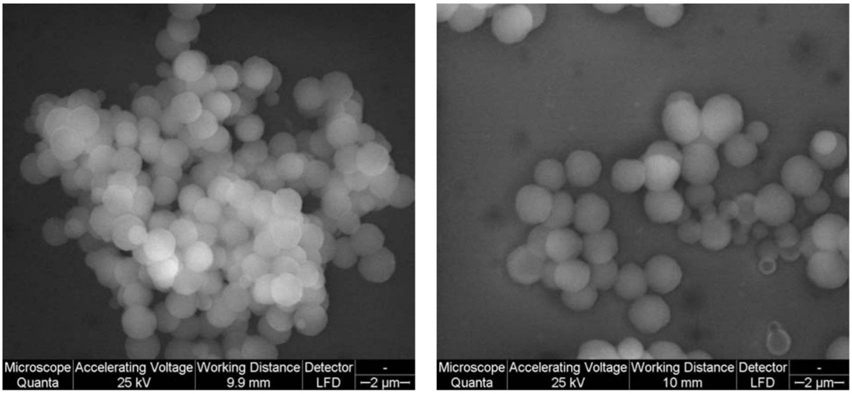
The polymer particles have been mixed with the liquid crystal ZLI 1221 (Merck) in a proportion of 5% b.w. The composite system was filled in a cell of conventional sandwich type, consisting of two ITO covered glass plates separated at a constant distance of 20 μm.

EXPERIMENTAL SET-UP

The experimental set-up has been described elsewhere [6]. 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).

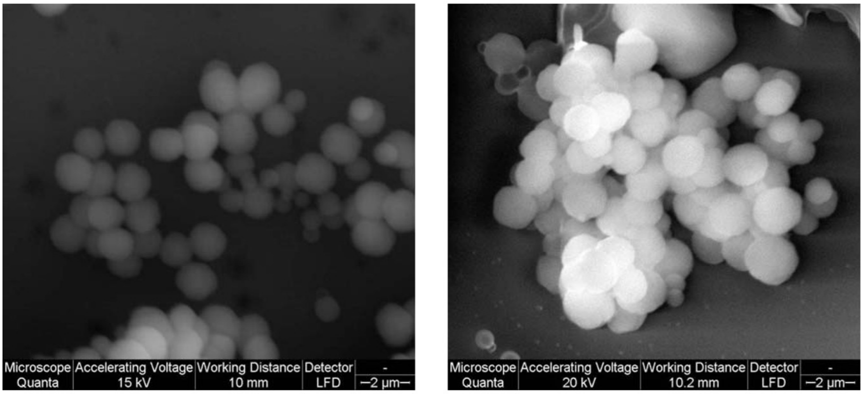
During step 4, at $T_{p,}$ the polarizing field $E_p = V_p/g$ is applied, (where g is the thickness of the sample) and it is maintained during the cooling down to T_o (step 5). During the phase 6, the field E_p is cut-off and the sample is short-circuited to eliminate capacitive discharge. The depolarizing currents are registered during step 7. The heating – cooling rates were of 1 K/min and steps 2, 4, and 6 were of 15 min. In this experiment, the polarization temperature is $T_p = 120°C$ and $T_0 = 25°C$.

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



particles of type D10
(a)

particles of type D12 (25 kV accelerating voltage)
(b)



articles of type D12 (15 kV accelerating voltage)
(c)

D14 particles
(d)

FIGURE 1 Electron microscopy picture of polymer particles.

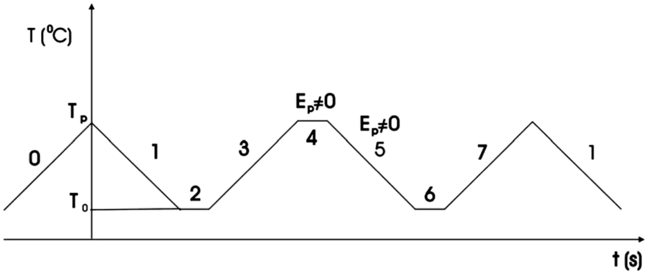


FIGURE 2 Heating – cooling cycles applied to the samples.

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_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 pure LC and for the composite system, respectively.

Considering the charge given by the Eq. (1) [6]:

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

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 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.

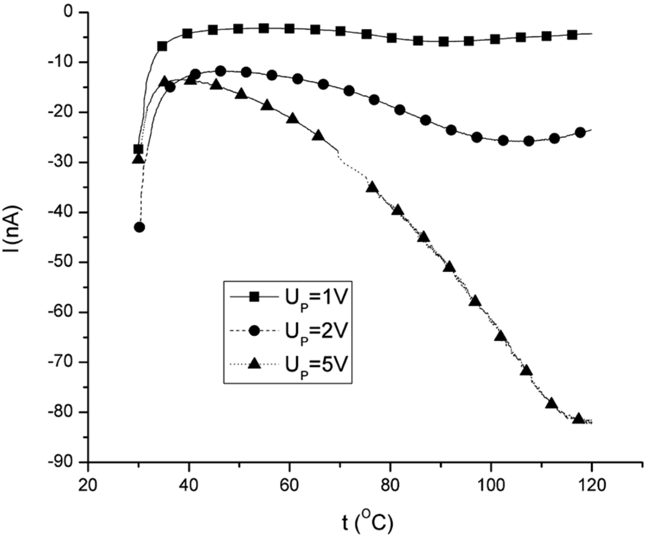


FIGURE 3 TSDC spectra for pure liquid crystal ZLI 1221.

To study the conduction mechanism specific for the current, we represented in Figure 5 the peak value of this current versus the polarizing voltage for the pure LC and for the composite.

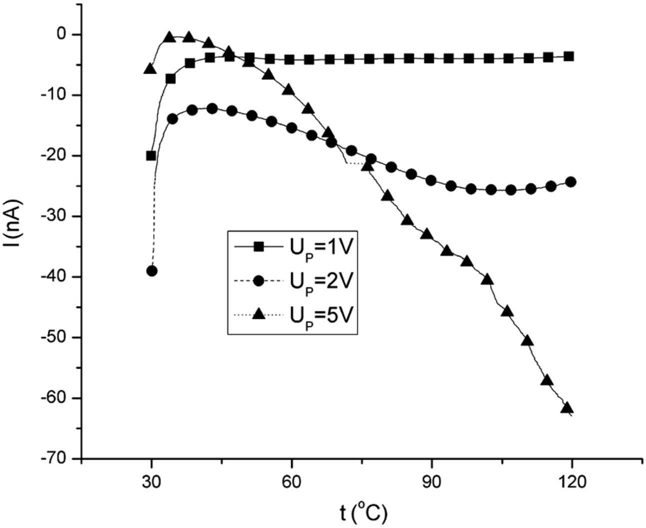


FIGURE 4 TSDC spectra for the composite system D12/ZLI 1221, 5% b.w.

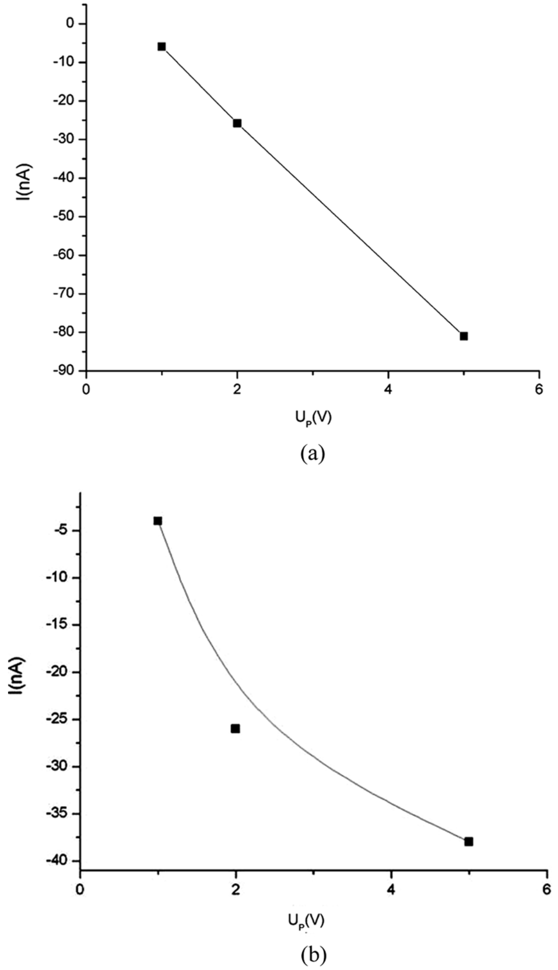


FIGURE 5 The peak value of depolarization currents obtained in step 7 versus the polarizing voltages; a) ZLI 1221; b) D12/ZLI 1221, 5% b.w.

We notice a quasilinear dependence of the peak current on the polarization voltage (Fig. 5a). As it is known [5], 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 τ this time, we may consider that the polarization of a material charged initially with the polarization $P_e(T_p)$, for which the applied filed is interrupted (step 7), is given by the Eq. (2):

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

This equation supposes a relaxation proportional with the difference between the instant polarization and the polarization P_∞ 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 τ 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:

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

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:

$$T = T_0 + q \cdot t \tag{4}$$

where T_0 is the temperature at the beginning of step 7 and $q = dT/dt$ 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:

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

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

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

The dipolar depolarization current will be:

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

In order to calculate the coefficients E and s_0, we should estimate the integral in Eq. (7); to avoid calculus difficulties, we have analyzed the dependence $f(T) = J'(T)/J(T)'$,

where $J'(T) = dJ(T)/dT$. This follows from:

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

It results:

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

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 $\mathrm{E} = 0.52\,\mathrm{eV}$; $\mathrm{s}_0 = 2.24\,10^8\,\mathrm{s}^{-1}$ for pure ZLI 1221 and $\mathrm{E} = 0.587\,\mathrm{eV}$; $\mathrm{s}_0 = 4.89\,10^{10}\,\mathrm{s}^{-1}$ for the composite ZLI D12 5%. Although small, the values of the pre-exponential factors are not uncommon for these types of materials [8].

In Figure 6 is presented the optical transmission for the composite material D12/1221, measured in step 7, simultaneously with the

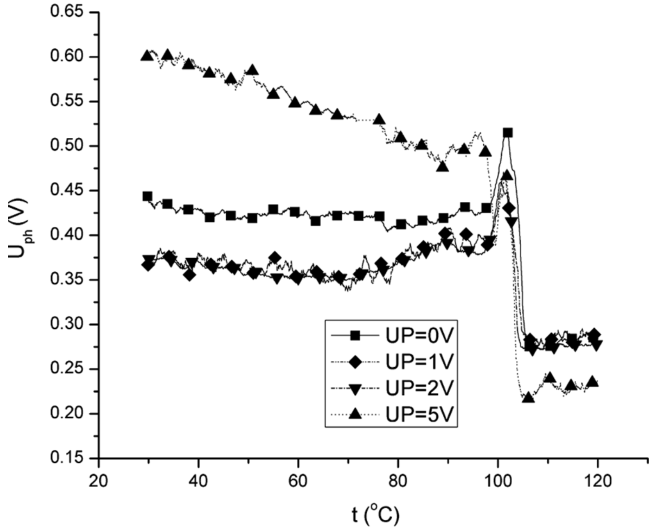


FIGURE 6 The optical signal measured by the photomultiplier in step 7 for the composite D12/ZLI1221 (5% b.w.), after applying different polarizing electric fields in steps 4 and 5.

depolarization currents. The optical transmission decreases slowly when the temperature approaches the nematic – isotrop transition T = 89°C, then it decreases abruptly in the isotropic phase. The optical transmission is smaller in the composite material, due to the strong coupling between the LC and the 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.

CONCLUSIONS

We have obtained a composite material of the type: polymer particles/NLC. We have 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 this composite sample 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 studies are in progress.

REFERENCES

[1] Stark, H. (2001). Physics of colloidal dispersions in nematic liquid crystals. *Physics Reports*, *351*, 387–474.

[2] Loudet, J. C., Barois, P., & Poulin, P. (2000). Colloidal ordering from phase separation in a liquid-crystalline continuous phase. *Nature*, *407*, 611–613.

[3] Kuksenok, O. V., Ruhwandl, R. W., Shiyanovskii, S. V., & Terentjev, E. M. (1996). Director structure around a colloid particle suspended in a nematic liquid crystal. *Phys. Rev. E*, *54*, 5198–5203.

[4] Kreutzer, M. & Eidenschink, R. (1996). Filled nematics, In: *Liquid Crystals in Complex Geometries*, Crawford, G. P. & Zumer, S. (Eds.), Taylor and Francis: London, 307–324.

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

[6] Rosu, C., Manaila-Maximean, D., Godinho, M. H., & Almeida, P. L. (2003). Thermally stimulated depolarization currents and optical transmission on liquid crystal/cellulose derivative composite devices. *Mol. Cryst. Liq. Cryst.*, *391*, 1–11.

[7] Frank, R. S., Doweney, J. S., & Stőver, H. D. H. (1998). Synthesis of divinylbenzene – maleic anhydride microspheres using precipitation polymerization. *J. Polym. Sci. Part A: Polymer Chemistry*, *36*, 2223.

[8] Manaila- Maximean, D., Rosu, C., Yamamoto, T., & Yokoyama, H. (2004). Thermally stimulated depolarization currents on colloidal liquid crystal composite system. *Mol. Cryst. Liq. Cryst.*, *417*, 215–226.