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ELECTRO-OPTICS OF SUSPENSIONS OF MONODISPERSED INORGANIC NANOPARTICLES IN LIQUID CRYSTALS

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Monodispersed spherelike nanoparticles (MNP) of Sb_2O_5 with sizes of 7–11 nm are used as filler for the nematic liquid crystal (LC) E7. The insertion of Sb_2O_5 particles in the LC leads to a drastic increase of light scattering, which can be controlled by an external electric field. The electrooptic properties of both undoped and polymer stabilized “E7- Sb_2O_5 ” composites are studied. While the “ Sb_2O_5 -E7” suspensions suffer from phase separation, the corresponding polymer stabilized samples are stable and operable. On the other hand, compared with “E7-Polymer” compounds, the “E7- Sb_2O_5 -Polymer” composites possess substantially improved electro-optic performance, for instance, enhanced contrast and faster operation times. Owing to this, “LC-MNP-Polymer” composites are suggested as advanced materials for LC devices operating in light scattering mode. The morphology and light scattering mechanisms of “LC-MNP-Polymer” samples are discussed.

Keywords: antimony pentoxide particles; electro-optics; light scattering; liquid crystals; monodispersed nanoparticles

1. INTRODUCTION

Liquid crystals (LC) are attractive for a number of electro-optic applications because of two principle effects – electrically controlled birefringence and electrically controlled light scattering. The first effect is utilized in monodomain LC samples and nearly all commercial display technologies, whereas the second is used in polydomain samples with enhanced light scattering properties and is being considered for a number of new applications. Most known liquid crystal devices fall into one of the two above

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mentioned areas. The advantages of the devices from the first class are high contrast, low voltage and low power consumption. In contrast, the devices from the second class are distinguished by high brightness, simple construction and wide viewing angle. There are many techniques to enhance light scattering in polydomain LCs. Among them LC doping is most frequently used. In this case either LC can be dispersed in a new phase (LCs in porous matrices [1], polymer dispersed LCs (PDLC) [2]) or, vice versa, the new phase is dispersed into the LC (polymer network LCs (PNLC) [3], LC emulsions [4], and filled LCs [5–12]).

The latter sort of heterogeneous LCs, filled LCs, is rapidly developing now due to the recent achievements of modern nano-technologies. One of the most intriguing classes of new materials is obtained from monodispersed nanoparticles (MNP). The use of these particles as LC fillers may create novel properties in comparison with the properties of “LC-aerosil” suspensions [5–8]. The electro-optical properties of suspensions of some *organic* monodispersed spheres in liquid crystals has been studied by Boxel and co-workers [11–12].

Our general goal is to study properties of LC suspensions based on *inorganic* monodispersed nanoparticles. The choice of the inorganic MNP is motivated by their specific optical, electrical and surface properties, which may result in the development of qualitatively new “LC-MNP” composites. As the first step, we study electro-optic performance of these sorts of suspensions. We employed MNP of antimony pentoxide having refractive index distinctly different from that of other fillers commonly used, such as aerosil, polystyrene, *etc.* This allowed to enhance scattering of filled LC due to refractive index mismatch between LC and MNP aggregates. Both pure “MNP-LC” composites and “MNP-LC” composites stabilized by polymers are investigated. In the latter series of samples the concentration of the polymer is varied so that various polymer morphologies are obtained. This allows us to study the influence of MNP on the electrooptics of well known “LC-Polymer” composites, such as PNLCs and PDLCs. Three-component composites “LC-MNP-Polymer” are suggested as advanced materials for LCDs operated in light scattering mode.

2. EXPERIMENTAL PART

2.1. Samples

As MNP filler we used antimony pentoxide (Sb_2O_5) spheres with sizes of 7–11 nm. The colloidal dispersion of these particles in methanol (with the particle content of 30 weight%) was supplied by Nissan Chemical America Corp. The nematic mixture E7 was purchased from Merck. As photopolymerizing material we employed UV curable adhesive No. 65 from Norland

Inc. (USA), widely used earlier to prepare LC-Polymer composites [13,14]. At first the LCs were thoroughly mixed with methanol dispersion of Sb_2O_5 particles. The intensive mixing caused evaporation of methanol and, hence, substitution of methanol with LC in the suspension. The complete removing of alcohol was obtained by applying a vacuum to the suspension at 10^{-2} Torr over 0.5 h. The concentration of MNP c_{mnp} ($c_{\text{mnp}} = m_{\text{mnp}} / (m_{\text{mnp}} + m_{\text{lc}})$, m_{mnp} and m_{lc} are the weights of monodispersed particles and LC, respectively) was varied within 5 and 25 weight%. For preparation of the polymer containing composites the prepolymer was added to the “E7- Sb_2O_5 ” suspension. The components were mixed in red light to avoid polymerization. The concentration of prepolymer c_p ($c_p = m_p / (m_p + m_m)$, m_p and m_m are the weights of polymer and LC + MNP components, respectively) was varied within 0 and 50 weight%.

A small amount of spacer ($d = 25 \mu\text{m}$) was introduced into the mixtures to fix the thickness of the tested layers. The suspension was placed between two glass substrates covered with ITO layers on the inner side. The substrates were pressed and glued with an epoxy glue. The samples containing pre-polymer were irradiated with the mercury lamp ($100 \text{ mW}/\text{cm}^2$, 20 min) in order to provide photopolymerization and corresponding structuring of polymer phase.

2.2. Methods

The electro-optic characteristics were measured using a setup previously described in reference [8]. The setup allows measurement of the sample transmittance T as a function of applied voltage U at fixed frequency f of the field. To detect memory effect, the T - U curves were measured twice – as the voltage increase to the saturation of T , and as the voltage decreases to 0. The T vs. f dependencies ($U = \text{const}$) were estimated using the oscilloscope program. In addition the switch on and switch off characteristics $T(t)$ were measured by step-wise switching the applied voltage ($f = 2 \text{ kHz}$) between 0 and 200 V.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1. Electro-optic Characteristics: General Consideration

The T - U , T - f and T - t curves measured for different concentrations of components demonstrated similar behavior. The curves are considered below.

T-U Curves

Typical T - U curves are presented in Figure 1. Curve 1 corresponds to the first step-up voltage scan, whereas curve 2 corresponds to the step-down voltage scan. From the curve 1 one can obtain the initial zero-field sample

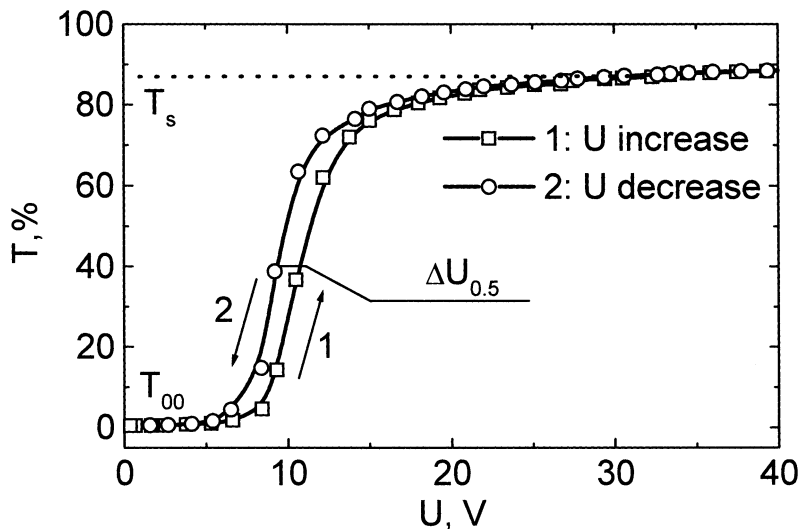


FIGURE 1 Transmittance vs. voltage curves for the “E7-Sb₂O₅-Polymer” composite ($c_{\text{mnp}} = 15 \text{ wt\%}$ and $c_p = 15 \text{ wt\%}$).

transmittance, T_{00} (the transmittance before the first voltage increase); from the curve 2 – zero-field transmittance after the voltage application (memory transmittance), T_0 ; from the curves 1 and 2- the hysteresis value, $U_{0.5}$ measured as the width of hysteresis loop at $T = 0.5T_s$; from the curve 1 – the saturation transmittance, T_s , the controlling voltage, $U_{0.9}$ (corresponding to $T = 0.9 T_s$), and the switching contrast $CR = T_s/T_0$.

T-f Curve

The transmittance variation under the applied sinusoidal voltage consists of an alternative T_a , and a current T_c component. The typical T_a - f , T_c - f and $T = (T_a + T_c) - f$ curves are represented in Figure 2. The $T_a(f)$ curve monotonously decreases, whereas the $T_c(f)$ curve monotonously grows with the field frequency. In contrast, the total transmittance is practically constant. Similar results were earlier obtained for “LC-Aerosil” and “LC-Aerosil-Polymer” composites [8,14]. The T_a component was assigned to the LC domains capable of reorienting in time with the change of electric field. In turn, the T_c component was attributed to large domains, which can not respond in time with the electric field alternation. The constant value of T can be explained assuming fixed amount of LC aggregates. In frame of this model the observed decrease of T_a and simultaneous increase of T_c with the field frequency f can be interpreted as diminution of the part of LC domains reorienting in time with the changes of electric field.

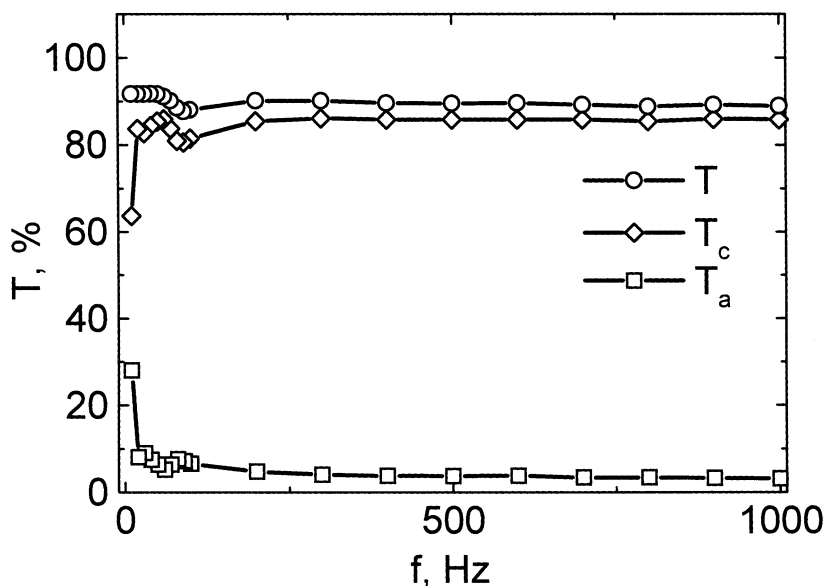


FIGURE 2 Frequency dependencies $T(f)$, $T_a(f)$ and $T_c(f)$ for the “E7-Sb₂O₅-Polymer” composite ($c_{\text{mnp}} = 15 \text{ wt\%}$ and $c_p = 15 \text{ wt\%}$).

The relaxation frequency f_r was estimated as the frequency corresponding to 0.9 decay of the T_a . The f_r value was used to estimate switching on time as $\tau_{\text{on}} = 1/f_r$.

T(t) Curves

The typical kinetic curves corresponding to step-wise switching on and switching off the applied voltage are shown in Figure 3. The decay curve $T(t)$ was used to estimate the decay time, τ_{off} . The rise time, τ_{on} , can be estimated from the $T(t)$ rise curve only roughly. It is shown to be less than 40 ms. This estimate is in good agreement with that derived from the relaxation frequency.

The introduced electro-optic parameters were estimated for all samples we prepared. These data are described in the following section subdivided in three parts according to content of the composites.

3.2. Concentration Dependencies

“LC-MNP” Composites

Figure 4a shows $T_{00}(c_{\text{mnp}})$, $T_s(c_{\text{mnp}})$ and $CR(c_{\text{mnp}})$ curves for “LC-MNP” composites. As can be seen, the increase of the MNP concentration results

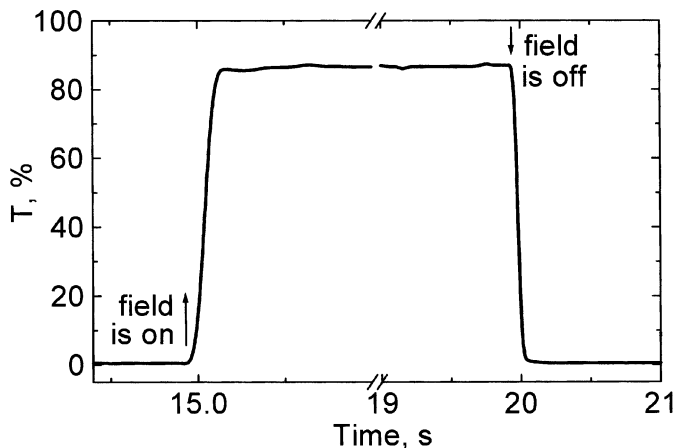


FIGURE 3 Rise and decay kinetic of the “E7-Sb₂O₅-Polymer” composite ($c_{\text{mnp}} = 15 \text{ wt\%}$ and $c_p = 15 \text{ wt\%}$) at the step-wise switching on and switching off the applied voltage ($U = U_{0.9} = 17 \text{ V}$, $f = 2 \text{ kHz}$).

in a monotonous reduction of the sample transmittance in the field-off state, T_{00} . This is in good agreement with the results earlier obtained for other fillers [5–12]. However, in contrast to previous results, the increase of the concentration of MNP leads to considerable reduction of the field-on transmittance T_s . As well as for other filled LCs, intensive scattering in the field-off state is mainly caused by LC orientational defects generated by MNP aggregates. At the same time, the essential scattering in the field-on state seems to be caused by refractive index mismatch between coexisting phases. It is known that MNP aggregate in LC matrix [6,7]. The aggregates with sizes comparable to the wavelength of visible light and the refractive index different from the LC may cause additional scattering in “LC-MNP” suspensions. In the field-on state, ordinary refractive index of LC, n_{lc}^o , and n_{mnp} should be compared, since $n_{\text{lc}} = n_{\text{lc}}^o$ (for the normal incidence of testing light). In case of LC E7 and MNP Sb₂O₅, $n_{\text{lc}}^o = 1.52$ and $n_{\text{mnp}} = 1.7$. This substantial difference demonstrates that the refractive index mismatch is an important factor of light scattering in “E7-Sb₂O₅” suspensions. In case of LC E7 and aerosil, $n_{\text{lc}}^o = 1.52$ and $n_{\text{mnp}} = 1.46$ which shows why the field-on scattering is low [7–8].

In spite of the essential decrease of the $T_s(c_{\text{mnp}})$ curve, the $\text{CR}(c_{\text{mnp}})$ curve grows quasi-linearly in practically all the range of MNP concentrations we studied. The maximal value of CR 16:1 is reached at $c_{\text{mnp}} = 25 \text{ weight\%}$. Since $T_0 \approx T_{00}$, the “E7-Sb₂O₅” composites are memory free, in contrast to “LC-Aerosil” compounds [5–8].

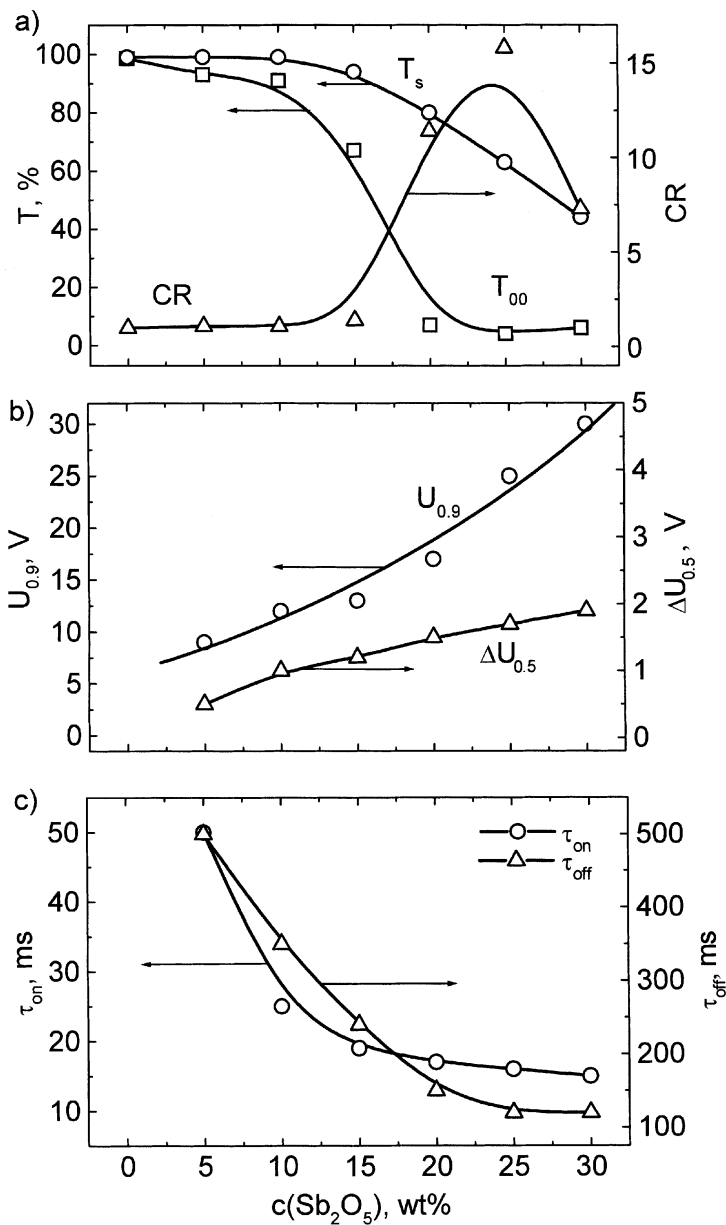


FIGURE 4 T_{00} , T_s and CR (a); $U_{0.9}$ and $\Delta U_{0.5}$ (b); τ_{on} and τ_{off} (c) vs. c_{mnp} curves for “E7- Sb_2O_5 ” composites.

As can be seen from the Figure 4b, the increase of CR is accompanied with the increase of the controlling voltage $U_{0.9}$. However, while the CR grows by factor of 16, the $U_{0.9}$ increases only by a factor of 2. The Figure 4b also shows that the hysteresis value, $\Delta U_{0.5}$, is small and slightly changes with the increase of c_{mnp} .

The plots for τ_{on} and τ_{off} are presented in Figure 4c. The τ_{off} varies in the range of hundreds of milliseconds, whereas the τ_{on} in the range of tens of milliseconds. Both $\tau_{\text{on}}(c_{\text{mnp}})$ and $\tau_{\text{off}}(c_{\text{mnp}})$ curves monotonously decrease.

The principle drawback of “E7-Sb₂O₅” composites is phase separation, which is especially strong under the applied low frequency field. For this reason we decided to fix the MNP structure with a rigid polymer network formed by a photo-polymerization of the pre-polymer composition dissolved in LC. By changing the concentration of the pre-polymer we obtained series of “LC-Polymer” composites described in the following subsection.

“LC-Polymer” Composites

Figure 5a shows T_{00} , T_s and CR as functions of polymer concentration. One can see that an increase of c_p leads to a non-monotonous change of T_{00} and to only slight alteration of T_s . This results in a non-monotonous behavior of the $\text{CR}(c_p)$ curve going through a maximum at $c_p = 35\text{--}40$ weight%. As is earlier known [13], at this concentration of pre-polymer the composites “E7-Norland-65” have PDLC morphology.

The change of c_p from 5 to 50 weight% results in the increase of the controlling voltage $U_{0.9}$ almost by factor of 3 and hysteresis $\Delta U_{0.5}$ by a factor of 6 (Figure 5b). The $\tau_{\text{off}}(c_{\text{mnp}})$ curve monotonously decreases (Figure 5c).

The obtained concentration dependencies may be explained based on light scattering mechanisms and morphological peculiarities of “LC-Polymer” composites. As is known, UV irradiation of the “LC-Polymer” mixtures containing a small amount of pre-polymer (1–10 weight%) leads to the formation of a polymer network (PNLC morphology). By contrast, the photopolymerization reaction in the mixtures enriched with pre-polymer (30–50 weight%) results in a permanent polymer phase with encapsulated LC drops (PDLC morphology) [2,3]. Since in our experiments the concentration of polymer is widely varied, various morphologies should be realized.

The main factor of light scattering in PDLCs is the refractive index mismatch between the LC and polymer [2,3] domains. The value of the refractive index of polymer is unknown. However, since $T_s \approx 100\%$, it is close to n_{lc}^0 . The scattering maximum at $c_p = 35\text{--}40$ weight% is caused by maximal concentration of scattering centers (LC drops). The poor contrast at $c_p < 25$ weight% suggests that the PDLC morphology is still not formed

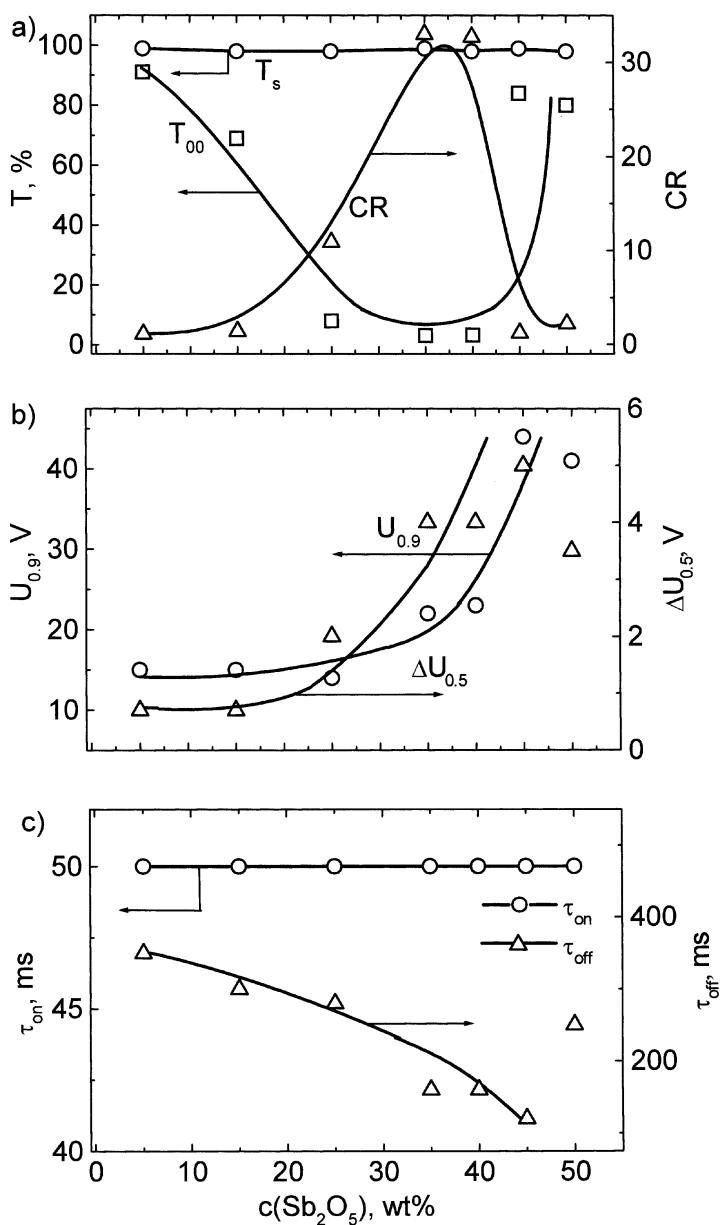


FIGURE 5 T_0 , T_s and CR (a); $U_{0.9}$ and $\Delta U_{0.5}$ (b); τ_{on} and τ_{off} (c) vs. c_p curves for “E7-Polymer” composites.

and the morphology of polymer network prevails. On the other hand, the decrease of $CR(c_p)$ curve at $c_p > 45$ weight% may be caused by diminution of the number of scattering sources, reduction of LC birefringence because of large amounts of pre-polymer impurities, *etc.*

Thus, the change of the scattering intensity of “LC-Polymer” samples with the increase of the polymer concentration can be explained by morphological changes. A smooth change of $U_{0.9}$, $\Delta U_{0.5}$, and τ_{off} with the increase of c_p suggests that the morphology of composites changes permanently.

“LC-MNP-Polymer” Composites

The plots related to these samples are presented in Figure 6. The first thing that can be concluded is that insertion of Sb_2O_5 MNP in the “LC-Polymer” composites increases switching contrast (Fig. 6a). The increase of CR can be observed for different polymer concentrations that is for samples with PNLC and PDLC morphology. The maximal contrast 62:1 is observed for the composites with $c_p = 30\text{--}35$ weight% and $c_{mnp} = 15$ weight%, i.e., for the samples with PDLC morphology. This CR is 2.1 times higher than the maximal contrast of “LC-Polymer” samples. That is important to mark that the increase of the CR by a factor of 2.1 is accompanied by the increase of the controlling voltage by only a factor of 1.3 (Fig. 6b). This makes “LC-Polymer-MNP” composites promising for LC devices working in light scattering mode.

The addition of MNP considerably reduces τ_{off} value; τ_{off} gradually decreases with the increase of MNP concentration (Fig. 6c). Note that τ_{off} is mainly modified for the samples with $c_p < 30$ weight%. In turn, τ_{off} for the samples with $c_p > 35$ weight% (i.e. for the samples with PDLC morphology) is practically unmodified. Similar regularity, but less clear, can be also observed for $U_{0.9}$ (Fig. 6b). This may imply that MNP does not disturb essentially the director configuration inside the LC drops.

Because three-component composites have only been recently suggested [8,14], their morphology and light scattering mechanisms are not known or understood. We believe that polymer morphology is only slightly distorted by MNP and, hence, “LC-MNP-Polymer” compounds can be divided in two groups depending on polymer morphology; MNP doped PNLC and MNP doped PDLC. The first group comprises polymer network stabilized filled LCs. The main scattering mechanism in these samples seems to be same as in the non-stabilized analogues. This mechanism is light scattering on orientational defects generated by MNP. The scattering caused by the polymer network is quite weak as can be seen from Figure 5a.

In contrast to the first group, there is a challenge to determine the major scattering mechanism for the samples with high concentration of polymer, i.e., presumably, samples of PDLC morphology. The first assumption that can be made is that the scattering factors of “LC-Polymer” and

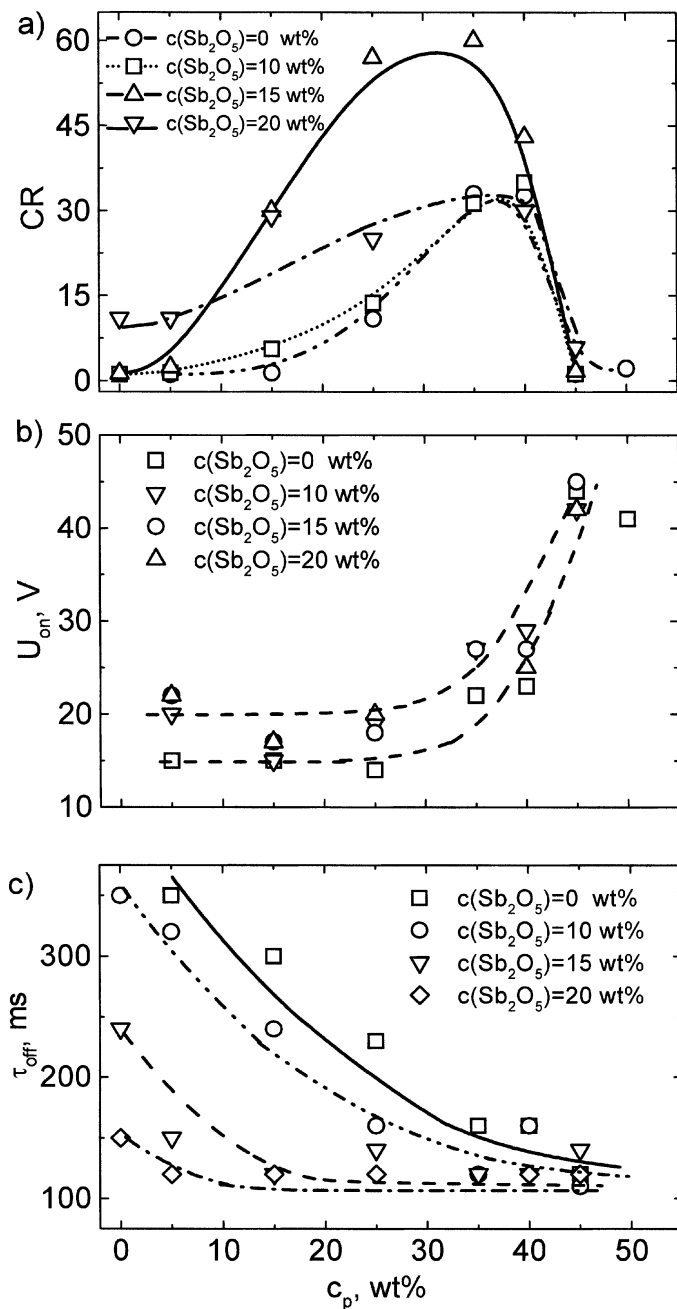


FIGURE 6 CR (a); $U_{0.9}$ (b); τ_{off} (c) vs. c_p characteristics for "E7-Sb₂O₅-Polymer" composites. The curves are presented for various values of c_{mnp} .

“LC-MNP” composites superpose. However, comparing Figure 4 and Figure 6 one can conclude that insertion of MNP strengthens scattering of the LCs much more effectively than the scattering of “LC-Polymer” composites. In turn, in the case of “LC-Polymer” composites, the effect of MNP is stronger for the samples of PNLC morphology. Several reasons of this difference can be discussed. The first of them can be connected with a specificity of the phase separation in “LC-MNP-Polymer” compounds. One can assume that MNP dispersed in the mixture of LC and pre-polymer are the germs of the polymer phase formed under UV irradiation. In this process, a polymer skeleton will involve large amounts of MNP. The part of MNP remaining in the LC seems to be small, especially in case of composites with a high polymer content (PDLC samples). As we believe, these MNP located in LC drops do not change essentially the drop’s configuration and so scattering by disorientation mechanism. They can, however, slightly enhance scattering by the refractive index mismatch between LC and MNP, as well as between LC and MNP modified polymer. Further studies involving modern methods of a research of morphology (SEM, AFM, *etc.*) are needed to clarify mechanisms of phase separation and morphological peculiarities of the studied composites.

CONCLUSIONS

LC filled with inorganic MNP and corresponding polymer stabilized composites are suggested as new classes of composites exhibiting electrically controlled light scattering effect. The latter systems, which can be also considered as MNP modified “LC-Polymer” composites, are the most promising from the practical point of view. Comprising all advantages of PDLC, these composites exhibit improved contrast and operation times. In addition, modification of “LC-Polymer” systems with MNP leads to only slight increase of the controlling voltage. The following optimization is needed to obtain samples for practical uses. In parallel with practical aspect, present research opens interesting problems related to phase separation in the composites “LC-MNP-Polymer”, MNP structuring in LC and polymer matrices, modification of LC and polymer phases with MNP etc. The morphology of “LC-MNP-Polymer” composites is under study and will be elucidated in our forthcoming paper.

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