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Dispersions of Diamond Nanoparticles in Nematic Liquid Crystal/Polymer Materials

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Diamond nanoparticles (DNP) were added in small quantities to low molecular weight liquid crystals (LC). These particles were also combined with monomers and cured monomer/LC mixtures to elaborate polymer-LC-NP dispersions. The influence of sample composition and irradiation conditions was studied by several experimental techniques and especially by the analysis of the electro-optical response, polarizing optical microscopy, and differential scanning calorimetry. Electro-optical characteristics of polymer-LC-NP dispersions exhibit lower transmittance values in the ON state and higher switching voltages compared to polymer/LC systems.

Keywords Diamond nanoparticles; electro-optical properties; liquid crystal; phase separation; polymer; ultraviolet irradiation

1. Introduction

Polymer dispersed liquid crystal (PDLC) systems represent one of the latest and interesting organic materials for applications in the fields of electro-optical devices and information displays [1–3]. These heterogeneous PDLC films scatter visible light because of the refractive index mismatch between LC and polymer, two adjacent phase separated LC domains, and within the LC domains [4]. The strong decrease of the light scattering in the field ON state is caused by the unidirectional alignment of LC within the domains, influencing the refractive index matching of LC and polymer. In contrast, the intense light scattering in filled LC is mainly caused by the particles of filler in LC media. In the field ON state, these defects practically

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disappear, which results in a strong increase of sample transmittance. The advantages and disadvantages of PDLC and filled LC from the viewpoint of applications have been widely discussed [5,6].

Nanoparticles (NP) have attracted great interest in recent years because of unique mechanical, optical and magnetical properties [7]. Recently, the merging of nanomaterials and nanotechnology into electro-optical (EO) device technology such as LCDs may attract researchers who are interested in inaugurating a new kind of combination of different fields [8–12]. Among the rest, metal NP have received much attention from the viewpoint of optical, magnetic, and biological properties which depend not only on size and structure, but also on covering materials that play the role of stabilizers as well [9,13].

Ouskova *et al.* doped a nematic LC with ferroelectric NP ($Sn_2P_2S_6$), and observed that the dielectric properties were strongly affected [14]. The introduction of the same NP into a cholesteric matrix has been shown as a promising method of improvement of electro-optical characteristics of different LC cells by a non-chemical way [15]. An unique electro-optical response, that is sensitive to frequency modulation of applied voltage, was found by doping polymer/LC films with silver (Ag) as NP [16].

Ferroelectric NP such as ($Sn_2P_2S_6$) and ($BaTiO_3$) were employed [17,18] to modify properties of nematic, smectic, and cholesteric LCs. NP doped PDLC systems were studied by O. Yaroshchuk *et al.* [19,20], by modifying the polymer refractive index with inorganic NP such as SiO_2, Sb_2O_5, and TiO_2.

Diamond NP (DNP) is an attractive material, for scientific and technological applications. Its high chemical and mechanical resilience, high surface stability, high thermal conductivity make diamond a promising candidate in the field of electrochemistry.

In the present work two and three component systems consisting of LC, polymer (P) and DNP were considered. Our particular interest concerns the preparation and characterization of DNP-PDLC systems, since NP - doping may substantially improve electro-optical properties of PDLC films so that DNP-PDLC samples can be regarded as valuable materials for LC applications.

2. Experimental Part

2.1. *Materials*

A commercially available thiol-ene blend and E7 (Merck) were used as prepolymer and nematic LC mixture, respectively. The thiol-ene blend consists of a mixture of 2,4,6-Triallyloxy-1,3,5-Triazine (3-AE) (TT) (Fig. 1a) and Pentaerythritol tetrakis (3-mercaptopropionate) 4-SH monomers (PT) (Fig. 1b). Exposure to UV light promotes the photoinitiator Darocur 1173, from Ciba-Geigy, to an excited state, initiating polymerization through hydrogen abstraction of the thiol monomer, thus generation of thiyl radicals.

The LC is an eutectic mixture of nematic LCs, commercially known as E7, consisting of 4-pentyl-4′-cyanobiphenyl (5CB), 4-heptyl-4′-cyanobiphenyl (7CB), 4-octyloxy-4′-cyanobiphenyl (8OCB), and 4-pentyl-4′-cyanobiphenyl (5CT) [21]. The chemical structure of the LC components are shown in Figure 1c.

The Diamond - NP was obtained from Sigma-Aldrich and used as received. DNP exhibit sizes <10 nm with spherical shape, and a bulk density of 0.17 g/ml.

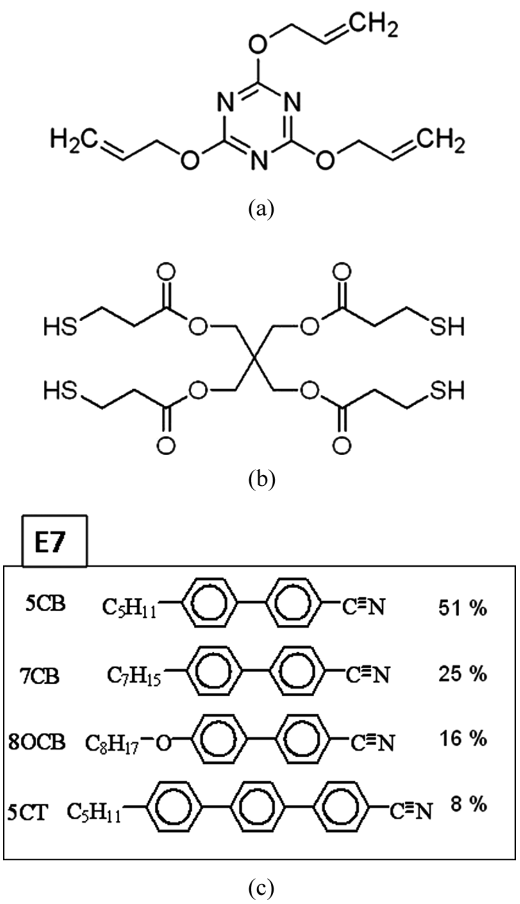

Figure 1. Chemical structures of monomers used in the preparation of polymer/LC systems: (a) 2,4,6-Triallyloxy-1,3,5-Triazine (TT), (b) Pentaerythritol tetrakis (3-mercaptopropionate) (PT), (c) Chemical structure of LC E7.

2.2. *Sample Preparation*

A mixture composed of 40 wt% of prepolymer and 60 wt% of LC was mixed at room temperature for several hours. One drop of the initial mixture was placed between two glass slides having transparent ITO electrodes from the inner side. Two series of UV-cured samples were prepared from the same mixture containing 0.5 and 1 wt% of DNP. These blends were submitted to a standard ultrasonic treatment during 30 min and then exposed at room temperature to a static UV lamp (Hamamatsu LC 3), equipped with an optical fiber. The exposure time was fixed to 1 min yielding a dose value of 430 mJ/cm^2, which is sufficient to achieve complete conversion of the monomers in the precursor system.

2.3. *Electro-Optical Measurements*

The cell thickness of samples used for electro-optical measurements was set between 10 and 35 μm using appropriate spacers. The electro-optical characteristics were measured by the measuring system described earlier in reference [22]. A linearly collimated beam from He-Ne laser light ($\lambda = 632.8\,\text{nm}$) passes through the sample with normal incidence, and the light transmission intensity is detected by a silicon photodiode. The output of the photodiode is linear with light intensity over the range used. An electric field of known intensity and duration is provided by application of a linear increasing voltage ramp followed by a decreasing voltage ramp passing through a desired maximum value V_{max} from a pulse generator and amplifier to transparent conductive electrodes. The frequency of the applied sinusoidal voltage was fixed at 1 KHz.

2.4. *Differential Scanning Calorimetry*

DSC measurements were performed on a Perkin Elmer Pyris Diamond calorimeter equipped with an Intracooler 2P system allowing cooling experiments. Samples for calorimetric measurements were prepared by introducing approximately 8 mg of the film into aluminium DSC pans, which have been sealed to avoid evaporation effects during the temperature treatment. A rate of 10°C/min (heating and cooling) was used in the temperature range -70 to $+100$°C. The program consists first in cooling the sample followed by three heating and cooling cycles to take into account eventual thermal events related to the sample preparation history. The thermograms presented in this work were obtained from the first heating ramps. In each case, at least five duplicate samples having the same composition and prepared independently were used to check the reproducibility of results. The nematic-isotropic transition temperatures were determined from the maximum of the transition range of the thermograms.

2.5. *Polarizing Optical Microscopy*

Polarizing optical microscopy (POM) is a common technique that gives information on the morphology of materials. This technique is often used in literature to study the morphology and phase transitions (e.g., transition from the nematic state to isotropic state) for polymer composites and LC.

The apparatus used in this study was a polarizing optical microscope Olympus BX-41 connected to a digital camera and a computer that can record images with high resolution.

3. Results and Discussion

Significant changes in the electro-optical response curves of polymer/LC systems can be observed in both cases with and without DNP. Figure 2 displays the transmittance versus voltage curves of polymer/LC (TT+PT/E7) and polymer/LC/NP (TT+PT/E7/DNP) films with (40/60 wt.%) and (39.5/60/0.5 wt.%), respectively, as function of the applied voltage. Both samples shown here exhibit the same film thickness (17.7 μm). The continuous lines in Figure 2 correspond to the scan up cycle by increasing the electrical field whereas dashed and dotted lines represent the scan down cycle by decreasing the voltage, following the application shown in [22].

The transmission values in the OFF state (T_{OFF}) remain nearly the same before and after applying an electrical field meaning that there were no or only weak optical memory effects. It can be noticed that the film without DNP shows a higher

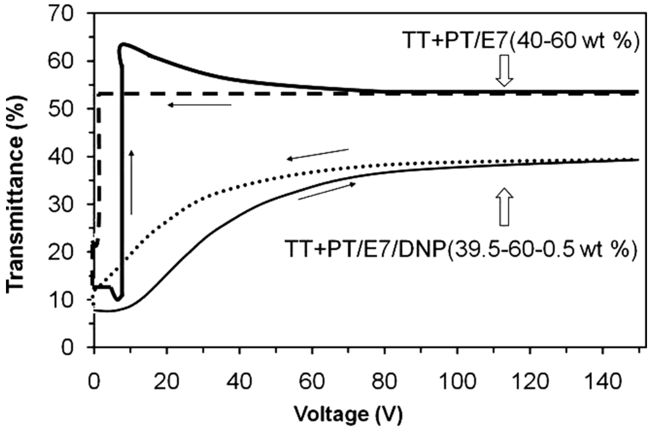

Figure 2. Electro-optical response of UV-irradiated polymer/LC/NP and E7/polymer films prepared using initial composition 39.5 wt.% "TT+PT"/60 wt.% E7/0.5 wt.% DNP and 40 wt.% "TT+PT"/60 wt.% E7, respectively. Continuous and dashed (dotted) lines correspond to increasing and decreasing voltage cycles, respectively. The PDLC films presented here exhibit the same thicknesses (17.7 μm).

transmittance in the ON state ($T_{ON} = 55\%$) compared to the film with DNP ($T_{ON} = 35\%$). A plateau value was easily reached in the case of the mixture without DNP while constant transmission values were not obtained for the DNP mixture.

The electro-optical response curves of the system without DNP reveal unusual features which have already been discussed in literature [23]. In particular, increasing voltage leads first to a decrease of the transmittance value followed by a sharp uptake and then some kind of overshoot was found at high transmittance values before reaching a plateau value in the ON state. On the other hand, adding DNP to the TT+PT-E7 blend yields to a well known classical electro-optical response [4], whereby the switching from OFF to ON state occurs on a much larger voltage range than in the DNP-free case.

Since strong differences were found from EO analysis of DNP-TT+PT-E7 films compared to the TT+PT-E7 system, it would be interesting to investigate their phase behavior by calorimetry measurements.

Figure 3 shows DSC thermograms corresponding to pure E7 (lower part), a mixture composed of 99.5 wt.% of LC and 0.5 wt.% of DNP (upper part) and the cured system composed of 39.5 wt.% TT+PT, 60 wt.% of LC, and 0.5 wt.% of DNP (middle part). The low molecular weight LC E7 shows two transition temperatures, a glass transition at T_g (LC) = −61°C followed by a nematic-isotropic transition at T_{NI} (LC) = 63.3°C. In the presence of 0.5 wt.% DNP, the glass transition temperature of E7 significantly lowers down from $T_g = -61.3$°C (pure E7) to $T_g = -66.5$°C. The nematic-isotropic transition temperature also experiences a pronounced shift from $T_{NI} = 63.3$°C to $T_{NI} = 57.7$°C together with a broadening of the peak and the appearance of a shoulder on the high temperature-side of the peak. These results show clearly the strong influence of the presence of DNP on LC properties. Moreover, a broad nematic-isotropic transition was found around $T_{NI} = 50.3$°C for the cured TT+PT/E7/DNP (39.5-60-0.5 wt.%) system.

It can be easily understood that application of an electrical field on DNP containing phase separated E7 domains will lead to variations of the EO response curves. In

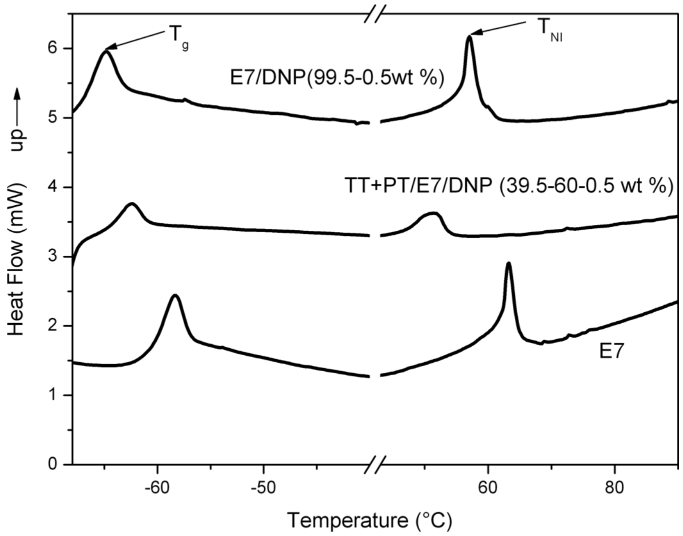

Figure 3. Thermograms obtained from DSC measurements of the pure LC E7, a mixture composed of "TT+PT"/E7/DNP (39.5 wt.% /60 wt.% /0.5wt %) and E7-DNP (99.5 wt.%/ 0.5 wt.%) systems. T_g represents the glass transition temperature of E7, and T_{NI} is the nematic-isotropic transition temperature of E7.

order to get a deeper understanding of the obtained sample morphologies in relationship with the EO response, all systems were analyzed by polarizing optical microscopy.

Figure 4 shows POM micrographs of a) (TT+PT/E7), b) LC/NP (E7/DNP), c) TT+PT not polymerized/DNP, d) TT+PT polymerized/DNP and e) polymer/LC/ NP (TT+PT/E7/DNP). The pictures were taken in the nematic phase of the LC, at $T = 25°C$. Figure 4a presents the morphology of the polymerized (TT+PT)/E7 (40/ 60 wt.%) system in the absence of DNP. LC domains are shown in blue color and LC domains are of lengthened spherical shape. They have a diameter of about 1 μm close to the limit of resolution of the POM, and seem to be scattered randomly in the polymer matrix without forming aggregates.

The micrograph of DNP dissolved in pure E7 is presented in Figure 4b. This photo shows the presence of DNP aggregates with diameters between 2 and 10 μm, which appear opaque and possess lengthened forms. It should be mentioned that these aggregates were also formed using lower DNP concentration, i.e., 0.5 wt.%. Some small aggregates seem to group together to form big ones, and it was found that these aggregates are randomly scattered in the entire sample.

In the case of the prepolymer mixture with a concentration of 1 wt% of DNP; presented in Figure 4c, phase separation phenomena were also observed and the aggregates were of lengthened forms with diameters greater than 10 μm. A more important number of aggregates was found compared to the E7/DNP mixture shown in Figure 4b. It can be concluded that DNP is more soluble in the LC than in the monomer mixture. Furthermore, phase separation occurs even more intensively if the monomer is transformed into polymer thus decreasing again the DNP solubility (Fig. 4d). As a consequence, an increasing number of growing aggregates was found in the polymer matrix and it can be noticed that these aggregates generally possess a circular shape.

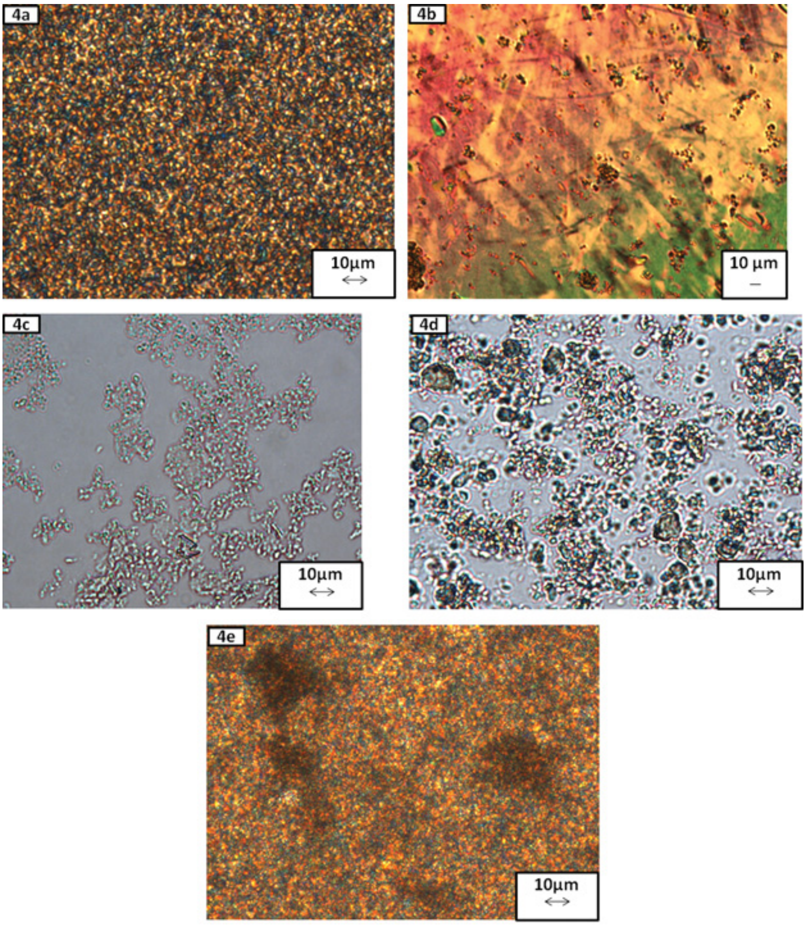

Figure 4. Film morphology obtained by the POM technique, (a) polymerized "TT+PT"/E7 (40 wt.%/60 wt.%), (b) E7/DNP (99 wt.%/1 wt.%), (c) prepolymer mixture "TT+PT"/DNP (99 wt.%/1 wt.%), (d) polymerized "TT+PT"/DNP (99 wt.%/1 wt.%), (e) polymerized "TT+PT"/E7 /DNP (39 wt.%/60 wt.%/1 wt.%). (Figure appears in color online.)

The PDLC containing DNP (Fig. 4e) also presents a certain number of aggregates and cause a darkening of the sample. It is evident that such triple phase separated structures (DNP-LC, DNP-polymer, and LC-polymer) strongly scatter light and that the refractive index mismatch condition between LC and polymer matrix will not be fulfilled. Furthermore it can be easily understood that transmittance values of the investigated PDLC-DNP films in the ON state can never reach maximum values.

4. Conclusions

In summary, substantial morphological changes have been observed in LC and PDLC systems when they are doped with NPs. In particular, the presence of DNP leads to a shift of the glass transition temperature T_g and the nematic-isotropic transition temperature T_{NI}. The electro-optical response of PDLC films with and without DNP revealed striking differences and in particular, DNP doped PDLC systems present higher switching voltages as well as lower transmission plateau in the ON state, compared to the film without DNP.

Undoubtedly, these observations offer new and promising routes for practical applications of polymer/LC/DNP systems.

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