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The Effect of Diamond Nanoparticles on Electro-Optical Properties of Polymer Dispersed Liquid Crystals

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Polymer dispersed liquid crystal films were elaborated by the polymerization induced phase separation technique. In particular, the influence of the incorporation of diamond nanoparticles was investigated by measuring optical and electro-optical properties of the corresponding films. The presence of a small amount of diamond nanoparticles leads to a strong increase of the optical transmittance under an applied electrical field. This effect was attributed to a phase separation phenomenon by the formation of micron-sized aggregates of diamond nanoparticles, which was confirmed by observations carried out by optical microscopy.

Keywords Diamond; electro-optical properties; liquid crystal; nanoparticles; morphology; polymer

1. Introduction

Polymer dispersed liquid crystal (PDLC) materials have been intensively studied in the past few decades, consisting of thin films exhibiting micro-sized domains of liquid crystal (LC) domains dispersed in polymer matrices [1–4], usually formed by phase separation of the initially homogeneous LC/polymer mixtures. PDLCs have some advantages over conventional twisted nematic displays in that one can make large size and flexible displays since no polarizer is required and it is much easier to fabricate them. PDLC films are potentially useful as electro-optical devices which can be switched electrically from a light-scattering "off-state" to a highly transparent "on state" [5–7], and therefore, they have attracted much attention for their large-area display applications [8–10].

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A challenging direction in the modern physical chemistry of polymers concerns the development of advanced approaches for the preparation of a new class of mesomorphic polymer nanocomposites, which combine the properties of LCs, polymers and specific characteristics of nanoscale objects [11–13]. The incorporation of nanoparticles into a polymer matrix can lead to a simultaneous improvement of different material properties. Especially toughness and stiffness of the nanocomposite can be enhanced at the same time, which is not possible for conventional composites with micro- or even macro-scale fillers to the same degree and for the same low filler contents [14, 15]. Nanoparticles have attracted great interest in recent years because of their unique mechanical, electrical, optical [16–18] and magnetic properties [19–21]. All the properties of nanoparticles are strongly related to the three-dimensional confinement of electrons and holes in a small volume.

Recently, nano-diamond powder has become a new engineering material with possible applications in many fields [22–24]. Nano-diamond crystallites possess not only important properties of bulk crystalline diamond but also other properties such as optical properties and high magnetoresistivity [25].

Only a few reports are known dealing with electro-optical properties of PDLC systems, doped with diamond nanoparticles [26]. In this investigation, experimental results will be presented on electro-optical properties of PDLC samples prepared in our laboratories, using the PIPS method. This method consists in mixing a blend of monomer/initiator/nematic LC and DNP, followed by exposure of the sample to UV-light. The effect of the presence of the diamond nanoparticles on the phase behavior of the LC/polymer system will be investigated.

2. Experimental Part

2.1. Materials and Sample Preparation

The nematic LC used in this work was the eutectic mixture E7, which was purchased from Merck, containing four cyanoparaphenylene derivatives [26]. It exhibits a nematic-isotropic transition temperature at $T_{NI} = 61^{\circ}C$ and a positive dielectric anisotropy. The monomer was Tripropyleneglycoldiacrylate (TPGDA) (UCB, Belgium) shown in Fig. 1a. PDLC films composed of TPGDA/E7 (30–70 wt.%) and TPGDA/E7/DNP (29-70-1 wt.%) were used for UV curing. 2wt-% (of the acrylate mixture) of a conventional photoinitiator, 2-hydroxy-2-methyl-1-phenyl-propane-1-one (Darocur 1173, Fig. 1b), was added to both mixtures. Diamond nanoparticles, representing overall diameters smaller than 10 nm, were obtained from Sigma-Aldrich. These blends were mixed together at room temperature for several hours until they became homogeneous, using an ultrasonic bath and a mechanical stirrer.

Samples for electro-optical studies were prepared by sandwiching the initial reactive mixture between two glasses coated with a thin transparent layer of conducting indium/tin

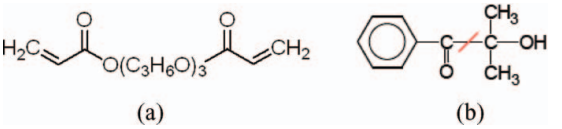


Figure 1. Chemical structures of a) the monomer Tripropyleneglycoldiacrylate (TPGDA) and b) the photoinitiator 2-hydroxy-2-methyl-1-phenyl-propane-1-one (Darocur 1173).

oxide (ITO). In that way, the reactive mixtures were in contact with both transparent conducting ITO-layers. The film thickness was measured by a micrometer caliper (Mitutoyo; uncertainty: ± 1 μm).

2.2. *Ultraviolet Curing*

Samples for UV-curing were placed at room temperature under a static UV lamp (Hamamatsu LC3) and exposed during 1min via an optical fiber. A dose value of 430 mJ/cm^2 was obtained, which was sufficient to achieve complete conversion of the monomers in the precursor system.

2.3. *Electro-Optical Measurements*

Electro-optical experiments were performed at room temperature by measuring the transmission of an unpolarized HeNe laser light at a wavelength of $\lambda = 632.8$ nm orienting the films normal to the incident laser beam. The experimental set-up is displayed in Fig. 2a. The

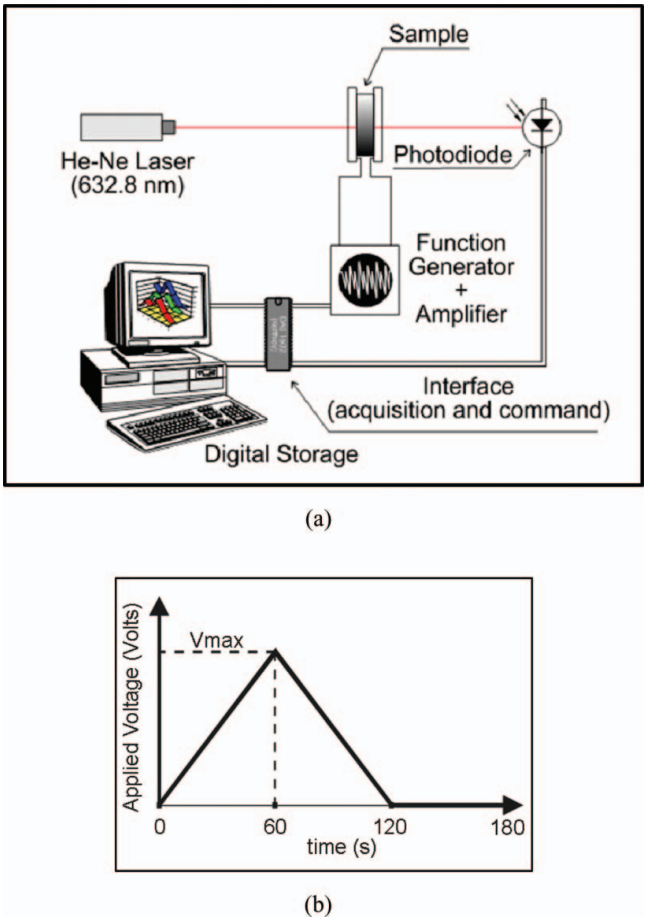


Figure 2. (a) Experimental set-up used to measure the electro-optical properties of PDLC films. (b) Sinusoidal voltage cycle of 1kHz applied as a function of time.

distance between the sample cell and the detector (silicon photodiode) was approximately 30 cm. The collection angle of the transmitted intensity was about $\pm 2^{\circ}$. The intensity of transmitted light was recorded on a micro-computer using an interface card (DAS 1600-2) [28].

For electro-optical measurements, an external electric field was applied across the PDLC film. The output of a frequency generator was amplified and used to drive the shutter device. Starting from the electrical off-state, the applied sinusoidal voltage of frequency 1 kHz was increased continuously up to a desired maximum value V_{max}. It was subsequently decreased in the same way. The whole scan up and down ramp took 120 s with an additional measuring time of 60s allowing to follow the relaxation behavior of the transmittance in the off-state. The same procedure was repeated several times using the appropriate maximum voltage. Fig. 2b displays the voltage cycle as a function of time. It should be emphasized that a further increase of the actual voltage application time (i.e. 120s) did not considerably change the observed electro-optical curves, since the time dependant voltage cycle was applied in order to take into account the different relaxation processes of the sample. The absence of an optical memory effect represents a further indication that the time period of the application of the voltage cycle was sufficiently large to obtain representative and reproducible results in terms of the electro-optical responses.

2.4. Polarized Optical Microscopy

Polarized optical microscopy (POM) is a common technique that gives information on the morphology of materials. This technique is often used in literature to study morphology and phase transitions (e.g. transition from the nematic to the isotropic state) for polymer composites and LC. The apparatus used in this study was a polarized optical microscope Olympus BX-41 connected to a digital camera and a computer that can record images with high resolution.

3 Results and Discussion

Figure 3 shows the electro-optical response of PDLC films in the absence and presence of 1 wt.% of diamond nanoparticles as a function of the applied voltage. The samples exhibited the same thicknesses. The closed symbols correspond to the scan up cycle by increasing the electric field whereas the open symbols represent the scan down cycle by decreasing the voltage.

Obviously such a small addition of DNP caused a large change of transmittance of PDLC films. Transmittance of samples without DNP was higher than in the presence of DNP not only in the OFF state, but also in the ON state, as shown in Fig. 3 and particularly in Figs 4a and 4b. The ON-state transmittance of the samples containing DNP decreases dramatically from 70% to 45%.

Figures 4a and b illustrate the film thickness dependence of the transmission values in the initial OFF-state T_{OFF}, and in the ON-state T_{ON}, respectively. The latter quantity is represented on a logarithmic scale. The voltage-dependent optical transmission of a PDLC film is generally affected by several parameters, such as LC domain shape and size, and LC concentration. The films with diamond nanoparticles showed enhanced light scattering effects in both OFF and ON states.

Figure 5a shows a comparative plot of the transmission as a function of applied voltage, at fixed frequency, for three different representative films of the TPGDA-E7 (30-70 wt.%) system. The transmission values of all samples investigated increase with increasing voltage

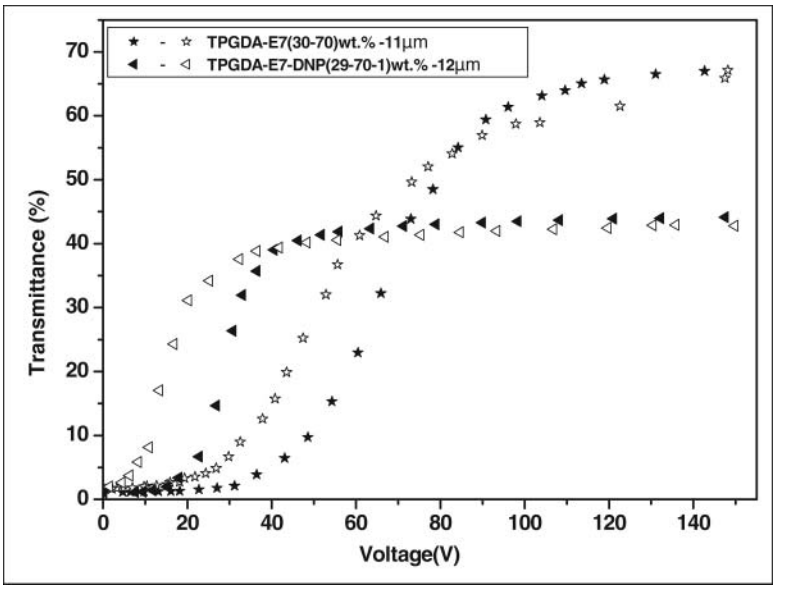


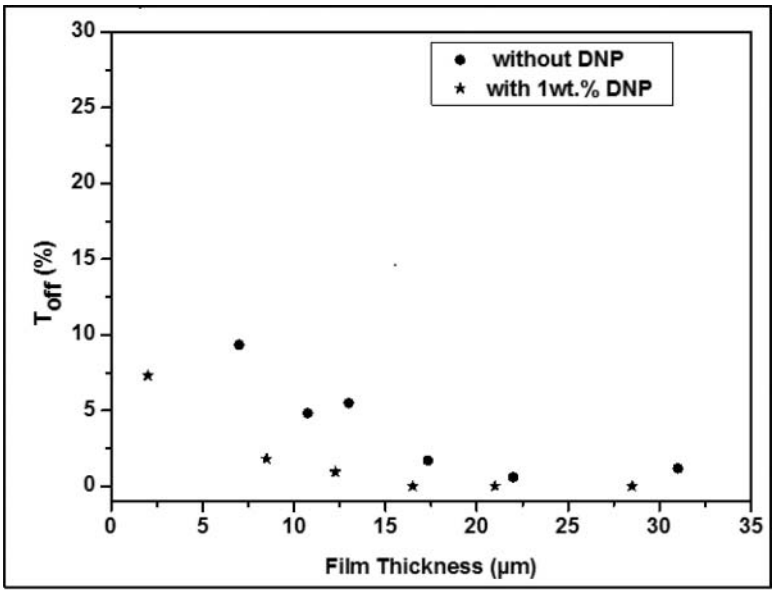
Figure 3. Electro-optical response curves of PDLC films in the presence and absence of DNP. The transmission values represent uncorrected values with respect to the absorption of the glass supports of the PDLC devices.

until a horizontal plateau was reached. Note that when the film thickness increases, the plateau values in the ON-state decrease. When the voltage was removed, the transmittance returned to the initial level of the cycle for the film with 23 μm. In this case no memory effect was observed. For both other films (e = 7 μm and e = 11 μm), a small memory effect was found.

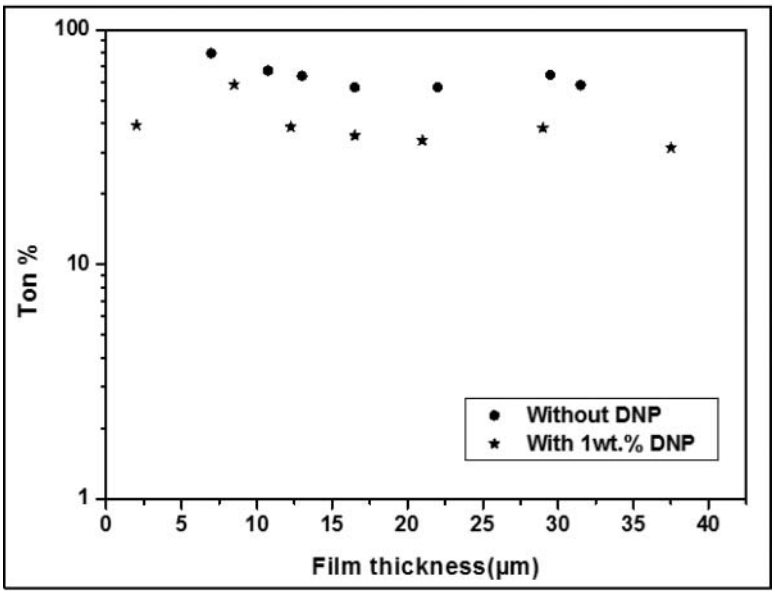
Figure 5b displays the effect of the introduction of 1 wt.% of DNP in the TPGDA-E7 (30–70 wt.%) system, as function of the film thickness. Compared with the previous system, a strong decrease of the plateau values of the transmittance was observed, and the films with 17 μm and 29 μm thickness did not exhibit constant values for the ON-state. Interestingly, a downwards shift of the maximum transmittance occurred for these films at the maxima of voltage applied, and the curves of the voltage ramps down cross the curves of the increasing voltage cycles. A strong decrease of the maximum transmission was found with increasing film thickness. Threshold and saturation voltages exceed largely the values obtained for the undoped system, without exhibiting a memory effect.

Based on these observations made on the two systems, it can be concluded that the addition of DNP has a significant influence on the optical properties of undoped PDLC films. The presence of DNP in a TPGDA-E7 mixture might create DNP-aggregates that prevent the passage of light and thus causes the decrease of the transmittance. This decrease is even more visible as the concentration of nanoparticles is important, that may be due to the increased volume of aggregates and/or their density. The DNPs affect also the memory effect that decreases or disappears when it is introduced to the monomer/LC mixture.

In order to confirm the assumption of the presence of DNP aggregates, the morphology of the two systems was investigated as shown in Fig. 6. Figure 6a shows the morphology of the TPGDA-E7 (30-70 wt.%) system without DNP, in the nematic phase. The LC domains



(a)

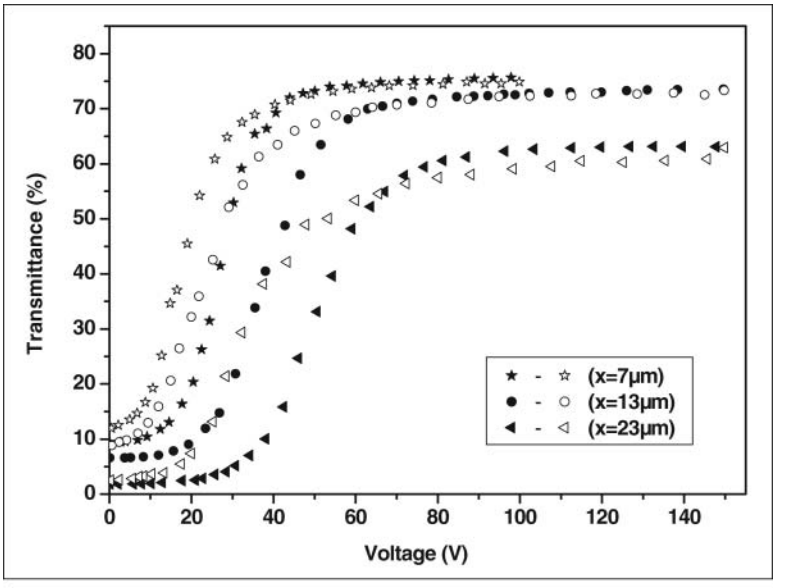


(b)

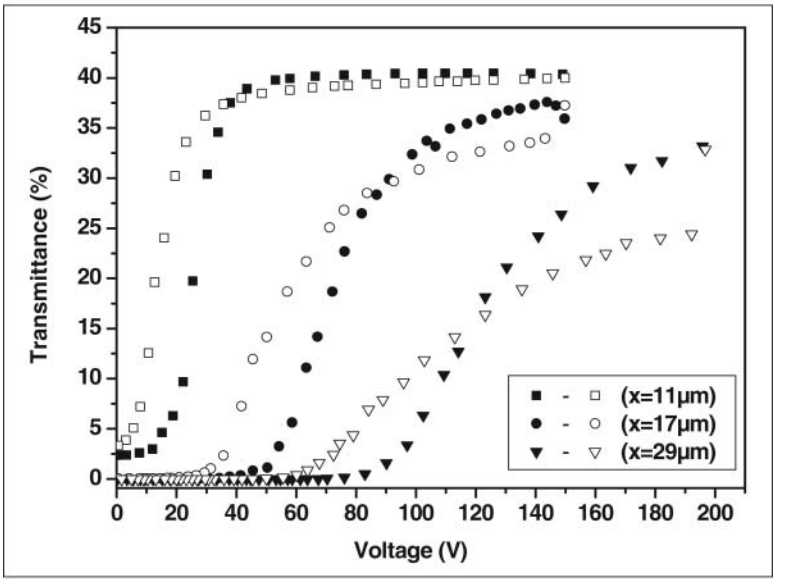
Figure 4. Optical transmission a) in the initial off-state (T_{off}) and b) in the on-state (T_{on}), of PDLC films with and without DNP, as function of the film thickness.

are of spherical shape; they have an average diameter of 1μm, and seem to be randomly dispersed in the polymer matrix. The films were heated up into the isotropic state (Fig. 6b), showing a homogeneous transparent simple phase.

An example of a PDLC film containing DNPs is shown in Fig. 6c. Indeed, an additional darkening was observed randomly on the morphology of the film, indicating the presence



(a)



(b)

Figure 5. Experimentally obtained electro-optical response curves of: a) (30wt.% TPGDA/70wt.% E7) and b) (29 wt.% TPGDA/70 wt.% E7/1 wt.% DNP) PDLC films with different thicknesses as indicated on the figures. Closed and open symbols correspond to increasing and decreasing voltage cycles, respectively.

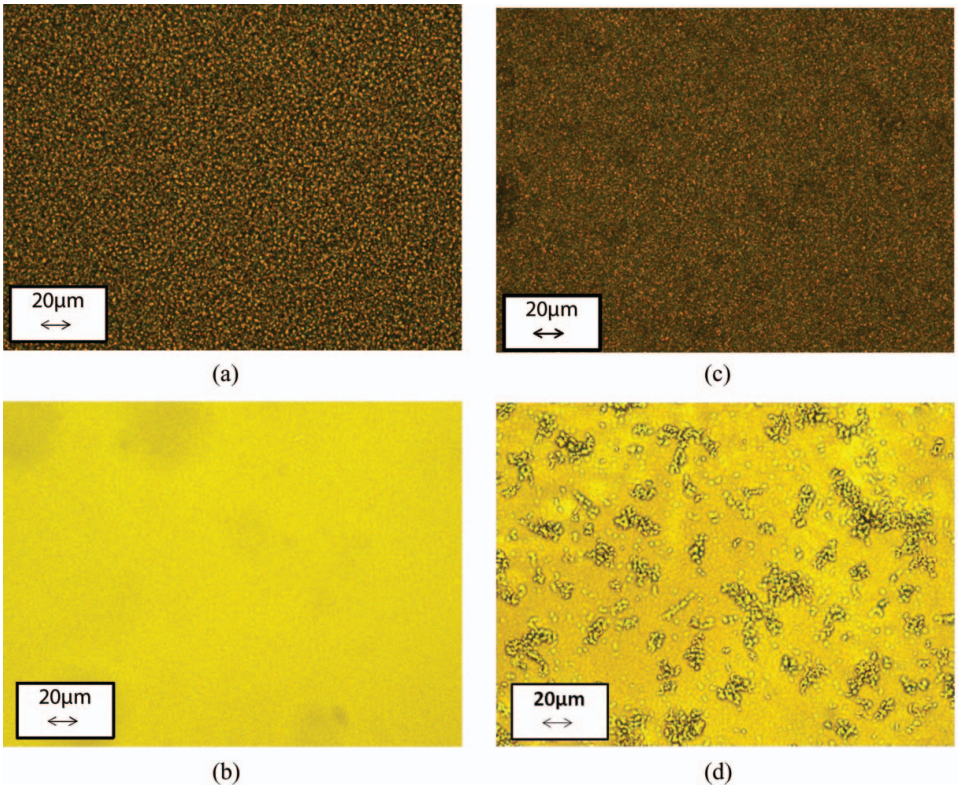


Figure 6. Micrographs obtained from optical microscopy studies of PDLC films; a) without DNP at T = 30°C; b) without DNP at T = 57.5°C, c) with 1wt.% of DNP at T = 30.4°C; d) with 1wt.% of DNP at T = 57°C.

of DNP aggregates. Figure 6d displays the morphology of the TPGDA-E7-DNP (29-70-1 wt.%) system, in the isotropic phase. The effect of the presence of DNPs on the morphology of the PDLC film was clearly observed in comparison with Fig. 6b. Aggregates of DNPs with diameters between 5 and 100 μm, were found in the isotropic state, confirming thus the assumption made before.

4. Conclusions

The presence of DNPs has a significant influence on the optical and electro-optical properties of PDLC films. Using a low DNP concentration of 1wt.%, aggregation of DNPs took place, thus reducing the optical transmittance under applied electrical field.

Indeed the micrographs of the corresponding PDLC films revealed dispersed DNP-aggregate structures with rather reproducible dimensions, which change with DNP concentration. It would be interesting to evaluate, if the addition of DNP could present an effective method to control transmission properties of PDLC films.

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