DOI: 10.1002/masy.201150515

Optical and Calorimetrical Studies of Liquid Crystalline Materials Doped with Nanoparticles

Malika Elouali,[1,2] *Christophe Beyens,*[1] *Fatima Zohra Elouali,*[1,3] *Oleg Yaroshchuk,*[4] *Boucif Abbar,*[2] *Ulrich Maschke**[1]

Summary: Electro-optical properties of Polymer Dispersed Liquid Crystal (PDLC) films doped with different nanoparticles (NPs), as well as optical and morphological properties of liquid crystal/NP mixtures have been investigated. PDLC films were prepared by UV irradiation of thiol-ene monomers and liquid crystal E7 in the presence of a small amount (0.5 and 1 wt.%) of nanoparticles. The presence of NP strongly influence the properties of liquid crystal/NP mixtures. In particular, adding nanoparticles results in a decrease of the glass and nematic-isotropic transition temperatures of the LC, suggesting that strong interactions occur between LC and nanoparticles.

Keywords: differential scanning calorimetry (DSC); glass transition; morphology; nanoparticles; photopolymerization

Introduction

Due to their numerous and important properties, liquid crystal (LC)/polymer blends and composites are studied for a wide variety of optical applications, the most popular being displays and shutters.[1–4] The electro-optical properties of LC/polymer systems depend both on LC and polymer phase. Polymer Dispersed LCs (PDLCs) are generally elaborated by the exposure of a photo-reactive monomer/LC mixture sandwiched between two conductive glass plates to a broad-band UV light source.[4–7] The conversion of monomer to a chemically crosslinked polymer of the initially homogeneous mixture results in a phase separated random dispersion of micron-sized LC domains surrounded by solid polymer. Early studies of such PDLC materials were focused on maximal improvement of their electro-optic performance based on optimization of curing conditions (UV exposure, curing temperature, polymer concentration, etc.).[4–7] The fractions of LC in separated LC domains and polymer matrix were established for different curing conditions and concentrations in the initial LC–prepolymer mixture.

Thiol–ene free-radical polymerization processes have been well-known for about fifty years. Progress in this area is well documented by reports from Jacobine et al.[8], Bowman and Cramer et al.[9] and Hoyle et al.[10]. The free-radical chain reaction between a thiol and an ene proceeds by a step-growth process; a free radical addition followed by a chain-transfer reaction. It was shown that PDLC samples prepared from thiol–ene systems exhibit improvements in uniformity of LC domain size and shape, switching speeds, contrast ratios and high transmission in the on-state.[11,12] Recently, White et al.[13] considered effect of functionality of thiol- and ene-monomers on

---

[1] Unité Matériaux et Transformations (UMET), UMR 8207–CNRS, Bâtiment C6, Université Lille 1-Sciences et Technologies, 59655 Villeneuve d'Ascq Cedex, France
Fax: (+33)-(0) 3 20 43 43 45;
E-mail: ulrich.maschke@univ-lille1.fr

[2] Département de Physique, Université Djillali Liabès, 22000 Sidi Bel Abbès, Algeria

[3] Laboratoire de Recherche sur les Systèmes Biologiques et la Géomatique, Université de Mascara, Route de Mamounia, 29000 Mascara, Algeria

[4] Institute of Physics, NASU, prospect Nauki 46, 03680 Kyiv, Ukraine

polymerization kinetics and morphology of PDLC composites. It was found that increasing monomer functionality (both thiol and ene) accelerates achievement of gelation point of thiol–ene pre-polymer and thus reduces size of LC droplets in PDLC samples. This gives additional way for optimization of thiol–ene based PDLCs.

Recently, metal nanoparticles have received much attention from the viewpoint of optical[14–16] magnetic[17,18] and biological properties[19] in addition to the catalysis.[20,21] These properties of metal nanoparticles depend not only on the size and structure of metal nanoparticles, but also on covering materials that play the role of stabilizers as well.[22–24]

In this work interest was focussed on composite materials combining unique properties of polymer/LC systems and nanomaterials. To our knowledge, only few authors reported on the influence of the presence of nanoparticles on the formation and electro-optical behaviour of the obtained PDLC films.[25] The present work consider morphological and calorimetrical investigations of LC/nanoparticles. Furthermore, electro-optical properties of some thiol-ene–E7 based polymer/LC were studied as function of the type of nanoparticles and curing conditions.

Experimental Part

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 stoichiometric mixture of 2,4,6-Triallyloxy-1,3,5-Triazine (3-AE) (TT) (Figure 1a) and Pentaerythritoltetrakis (3-mercaptopropionate) 4-SH monomers (PT) (Figure 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).[26] The chemical structures of the LC components are shown in Figure 1c. E7 has a nematic to isotropic transition temperature (T_{NI}) at 63.3°C and is characterized by a positive dielectric constant. A series of NP, diamond nanoparticles (D-NP), titanium dioxide nanoparticles (TiO_2-NP), cesium carbonate nanoparticles (Cs_2CO_3-NP) and silver nanoparticles (Ag-NP) were used in this study. These nanoparticles represent overal dimensions smaller than 100 nm and are obtained from Sigma-Aldrich. All materials were used as received.

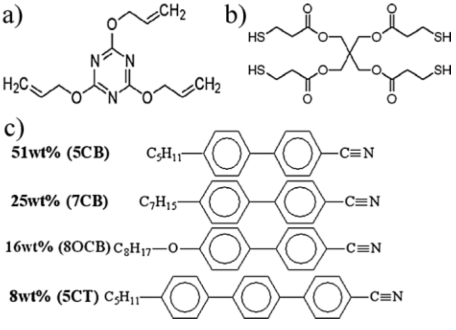

Figure 1.
Chemical structures of monomers and liquid crystals: (a) 2,4,6-Triallyloxy-1,3,5-Triazine (TT), (b) Pentaerythritol tetrakis (3-mercaptopropionate) (PT), (c) multicomponent nematic mixture E7.

Sample Preparation

A stoichiometric mixture composed of 40 wt.% of prepolymer (TT + PT) and 60 wt.% of LC was stirred mechanically at room temperature for several hours. One drop of the initial mixture was trapped between two glass slides having transparent ITO electrodes on the inner side.

The amount of this mixture between the two glass slides determines the thickness of the sample, if no appropriate spacer is used. Samples for UV-curing were placed at room temperature under a static UV lamp (Hamamatsu LC3) and exposed during 1 min 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.

Electro-Optical Measurements

The cell thickness of samples used for electro-optical measurements was set between 10 and 35 μm using appropriate spacers. Electro-optical properties were analyzed by using the set up described earlier in reference.[27] A linearly collimated beam from He-Ne laser light ($\lambda = 632.8$ nm) passes through the sample with normal incidence, and the light transmission intensity was measured by a silicon photodiode. For electro-optical measurements, an external electric field is applied across the PDLC film. The output of a frequency generator is 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 Vmax. It is subsequently decreased in the same way. The whole scan up and down ramp takes 120 s with an additional measuring time of 60 s allowing to follow the relaxation behaviour of the transmittance in the off-state. The same procedure was repeated several times using the appropriate maximum voltage.

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) measurements were performed on a Perkin Elmer Pyris Diamond calorimeter equipped with an Intracooler 2P system allowing cooling experiments. 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. The thermograms presented in this work were obtained from the first heating ramps.

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 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 polarized optical microscope Olympus BX-41 connected to a digital camera and a computer that can record images with high resolution.

Results and discussion

Figure 2 represent electro-optical response curves (transmittance versus applied voltage) of PDLC films based on UV- cured TT + PT/E7/D-NP (39.5/60/0.5 wt.%) and TT + PT/E7/Ag-NP (39.5/60/0.5 wt.%). Generally a decrease of the transmittance in the on-state is observed in comparison with curves without NP.

The dashed and dotted lines in Figure 2 represent the scan up and down cycle of the TT + PT/E7/D-NP (39.5/60/0.5 wt.%) system which show an usual electro-optical response. The addition of 0.5 wt.% D-NP led to a maximum transmittance of not more than 35% by application of 150 V; the increase/decrease of the voltage is accompanied by a hysteresis and the transmittance returns to its initial state after the end of the voltage application.

The continuous lines in Figure 2 correspond to the scan up and down cycle of the TT + PT/E7/D-NP (39.5/60/0.5 wt.%) film which exhibit a quite unusual electro-optical response. The transmission values changed only from approximately 12% to 18% upon application of 120 V. A further

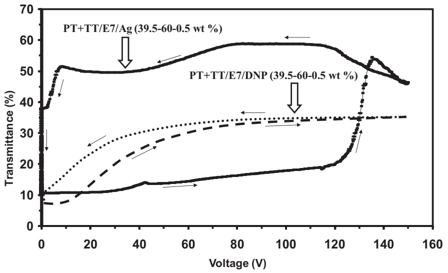

Figure 2.
Electro-optical response of UV-irradiated polymer/LC/NP films prepared using initial composition 39.5 wt.% "TT + PT"/60 wt.% E7/0.5 wt.% D-NP, and 39.5 wt.% "TT + PT"/60 wt.% E7/0.5 wt.% Ag-NP, respectively.

increase of the voltage leads first to a drastical increase of transmission up to a maximum of 55% at 135 V, then the transmitted intensity decreases with voltage up to 45% at 150 V. Another unusual behaviour has been observed in the decreasing electrical field. The transmission increases with decreasing electrical field until a nearly horizontal plateau is reached. The transmitted intensity decreases from 52 to 38% if the voltage is further reduced from 10 V to 0 V. An important memory effect was observed which vanished after a relaxation time of 60 s since the system has recovered the transmission value corresponding to the initial off-state.

A POM analysis was carried out in order to get a better understanding of the phenomena observed during electro-optical analysis. Morphological observations of four LC/NP systems were conducted by polarized optical microscopy in the isotropic phase, using a concentration of 1wt.% of each NP. A comparison between the dispersion of different NPs in E7 is shown in Figure 3, a) E7 + Ag-NP, b) E7 + D-NP, c) E7 + TiO_2-NP, d) E7 + CC-NP.

Figure 3a presents the morphology of the Ag-containing LC sample which form clusters with size and shape similar to those of TiO_2–NP (Figure 3c). The dispersion containing D-NP shows different objects (Figure 3b). They are transparent to light, only the contours distinguish them, exhibiting a difference of refractive indices. Their shape is circular or rod-shaped and their size varies between 1 and 5 micrometers. Agglomerates larger than 20 microns can be clearly revealed and correspond to an assembly of smaller aggregates. The micrograph of CC-NP dissolved in pure E7 is presented in Figure 3d. This case is very interesting because CC-NP is completely dissolved in the LC and there are no aggregates formed.

In order to correlate these results with thermophysical data, DSC analysis was

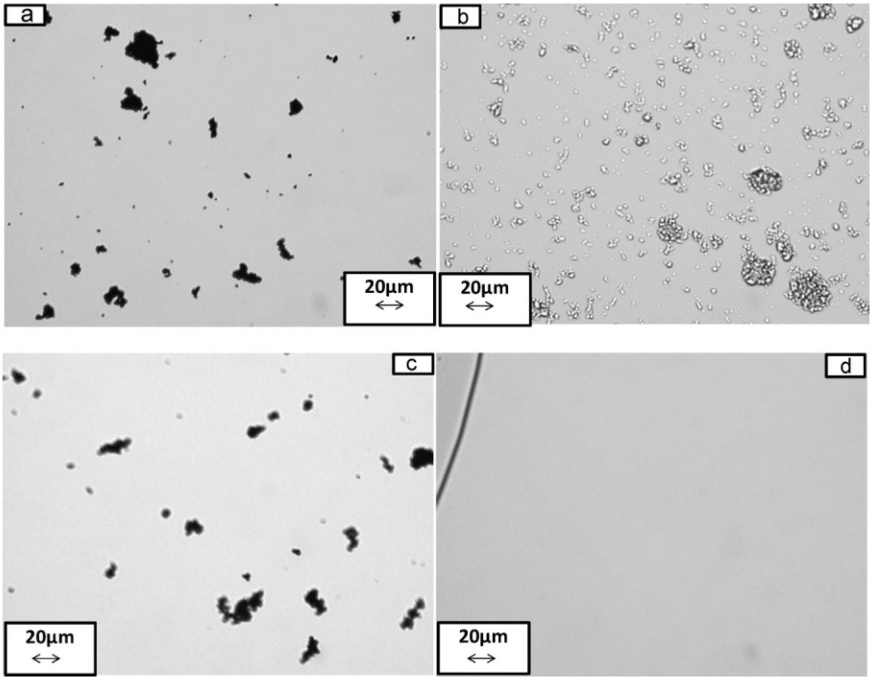

Figure 3.
Film morphology obtained by the POM technique, of LC/NP (99 wt.% / 1 wt.%) systems (a) E7/Ag-NP, (b) E7/D-NP, (c) E7/TiO_2-NP, (d) E7/CC-NP respectively, in the isotropic phase.

carried out for all systems studied earlier by POM. The thermograms are presented in Figure 4 and 5, corresponding to E7, E7 + 0.5 wt.% Ag-NP, E7 + 0.5 wt.% D-NP, E7 + 0.5 wt.% TiO_2-NP and E7 + 0.5 wt.% CC-NP. Figure 4 presents the LC glass transition while Figure 5 shows the nematic-isotropic transition. Indeed, the low molecular weight LC E7 shows two transition temperatures, a glass transition T_g at -61.3°C (on the lower part of Figure 4) followed by a nematic-isotropic transition T_{NI} at 63.3°C (on the lower Part of Figure 5).

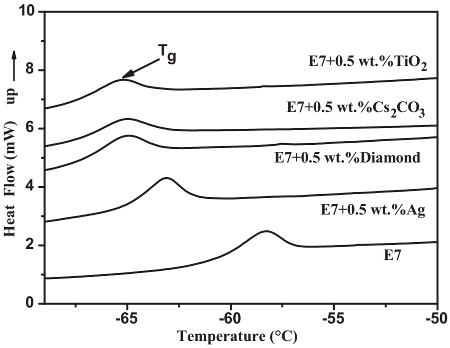

Figure 4.
Thermograms showing the glass transition temperature (T_g) obtained from DSC measurements of the pure LC E7, as well as of mixtures of E7 with nanoparticles: Ag, Diamond "D", Cesium Carbonate "CC", and Titanium Oxide "TiO_2", respectively (99.5 wt.% / 0.5 wt. %) systems.

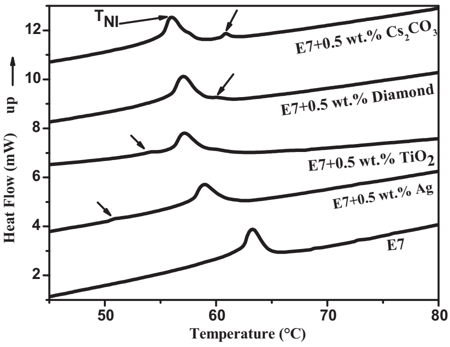

Figure 5.
Thermograms showing the nematic-isotropic transition temperature (T_{NI}) obtained from DSC measurements of pure LC E7, and mixtures of E7 with several nanoparticles: Ag-NP, Diamond "D-NP", Cesium Carbonate "CC-NP", and Titanium Oxide "TiO_2-NP", respectively (99.5 wt.% /0.5wt %).

In the presence of 0.5 wt.% Ag-NP, the glass transition temperature of E7 significantly lowers down from T_g = -61.3°C (pure E7) to T_g = -65.4°C. When 0.5 wt.% D-NP was added, the glass transition shifted to T_g = -66.5°C. Even lower values were obtained in the case of 0.5 wt.% CC-NP (T_g = -66.7 °C) and 0.5 wt.% TiO_2-NP (T_g = -66.9 °C). These results can be explained by the strong plasticizing effect of the NP.

Figure 5 exhibits clearly a decrease of the nematic-isotropic transition temperature T_{NI} with addition of different NPs. By addition of 0.5 wt.% of Ag-NP T_{NI} decreases from T_{NI} = 63.3°C (pure E7) to T_{NI} = 59.7°C. If Ag-NP was replaced by TiO_2-NP or D-NP, T_{NI} continued to decrease and reached 57.9°C and 57.7 °C, respectively. The lowest value was reached by adding 0.5 wt.% CC-NP, T_{NI} = 56.7 °C. Note that the thermograms of E7 including NP reveal the presence of small transitions at temperatures below or beyond the T_{NI} – value of pure E7 indicating that the latter LC mixture lost its eutectic properties. These results show clearly the strong influence of the presence of NP on LC properties. It can be easily understood that application of an electrical field on nanoparticles containing E7 droplets will lead to variations of the EO response curves.

Conclusion

In this work we report that properties of nematic LCs change drastically when they were doped with a small amount of NPs. Indeed doping a nematic LC with a small amount of NP strongly affects the glass transition temperature T_g and the nematic-isotropic transition temperature T_{NI}. T_g was significantly decreased by 4.1°C, 5.2°C, 5.4°C and 5.6°C when the LC was doped with Ag-NP, D-NP, Cs_2CO_3-NP, and TiO_2-NP, respectively. A decrease of T_{NI} between 3.6°C and 6.6°C was also noticed but in another order of NP: Ag, TiO_2, D, Cs_2CO_3. Substantiel microstructural and morphological changes have been observed in these nematic LC/NP systems. The electro-optical response of UV–cured E7/TT + PT/NPs films was investigated experimentally as function of applied voltage. The curves giving the transmission in terms of the applied electrical field show considerable differences between films with Ag-NP and D-NP.

[1] D. Coates, *J. Mater. Chem.* **1995**, *5*, 2063.

[2] D. A. Higgins, *Adv. Mater.* **2000**, *12*, 251.

[3] M. Mucha, *Progr. Polym. Sci* **2003**, *28*, 837.

[4] N. A. Vaz, G. W. Smith, G. P. Montgomery, *Mol. Cryst. Liq. Cryst.* **1987**, *146*, 1.

[5] A. M. Lackner, J. D. Margerum, E. Ramos, K.-C. Lim, *SPIE.* **1989**, *53*, 1080.

[6] G. W. Smith, *Mol. Cryst. Liq. Cryst.* **1991**, *89*, 196.

[7] J. H. Erman, A. M. Lackner, E. Sherman, J. D. Margerum, *J. SID.* **1993**, *57*, 1.

[8] A. F. Jacobine, In: J. D Fouassier, J. F. Rabek, Eds, Radiation curing in polymer science and technology 3, London *Elsevier Applied Science*, **1993**, 219.

[9] N. B. Cramer, C. N. Bowman, *J. Polym. Chem A.* **2001**, *39*, 3311.

[10] C. E. Hoyle, T. Y. Lee, T. Roper, *J. Polym. Sci, Part A.* **2004**, *42*, 5301.

[11] L. V. Natarajan, C. K. Shepherd, D. M. Brandelik, R. L. Sutherland, S. Chandra, V. P. Tondiglia, et al, *Chem. Mater.* **2003**, *15*, 2477.

[12] L. V. Natarajan, V. P. Tondiglia, R. L. Sutherland, D. Tomlin, T. J. Bunning, *Polym Mater. Sci. Eng.* **2003**, *89*, 48.

[13] J. W. Timothy, V. N. Lalgudi, P. T. Vincent, J. B. Timothy, C. A. Guymon, *Macromolecules* **2007**, *40*, 1112.

[14] K. Fukumi, A. Chayahara, K. Kadono, T. Sakaguchi, Y. Horino, M. Miya, K. Fujii, J. Hayakawa, M. Satou, *J. Appl. Phys.* **1994**, *75*, 3075.

[15] P. Lu, J. Dong, N. Toshima, *Langmuir.* **1999**, *15*, 7980.

[16] S. Link, Z. L. Wang, M. A. El-Sayed, *J. Phys. Chem. B.* **1999**, *103*, 3529.

[17] S. Sun, C. B. Murray, D. Weller, L. Folks, A. Moser, *Science.* **2000**, *287*, 1989.

[18] T. Teranishi, M. Miyake, *Chem. Mater.* **1999**, *11*, 3414.

[19] W. D. Geoghegan, J. J. Scillian, G. A. Ackerman, *Immunol. Commun.* **1978**, *7*, 1.

[20] J. S. Bradley, *Clusters and Colloids: From ''Theory and Application''* (Ed, G. Schmid, VCH, Weinheim 456, **1994**.

[21] N. Toshima, T. Yonezawa, *New. J. Chem.* **1998**, *22*, 1179.

[22] N. Toshima, T. Takahashi, H. Hirai, *Chem. Lett.* **1986**, 35.

[23] N. Toshima, Y. Shiraishi, T. Teranishi, M. Miyake, T. Tominaga, H. Watanabe, W. Brijoux, H. Bonnemann, G. Schmid, *Appl. Organomet. Chem.* **2001**, *15*, 178.

[24] N. Toshima, Y. Shiraishi, T. Teranishi, *J. Mol. Catal. A: Chem.* **2001**, *177*, 139.

[25] O. V. Yaroshchuk, L. O. Dolgov, A. D. Kiselev, *Phys. Rev.* **2005**, *E72*, 051715–1.

[26] P. Nolan, D. Coates, *Electro-optical liquid crystal system. US Patent.* **1995**, *5*, 476.

[27] L. Méchernène, L. Benkhaled, D. Benaissa, U. Maschke, *Optical Materials.* **2009**, *31*, 632.