Journal of Molecular Liquids 209 (2015) 336–345

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

The ferroelectricity effect of nanoparticles on thermodynamics and electro-optics of novel cyanobiphenyl eutectic binary mixture liquid crystals

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ARTICLE INFO

Article history:
Received 17 March 2015
Received in revised form 5 May 2015
Accepted 8 May 2015
Available online xxxx

Keywords:
Liquid crystal
Nanoparticle
Texture
Phase transition
Electro optics
Diffusion coefficient

ABSTRACT

The phase transition of pentylcyanobiphenyl (5CB) 55% and heptylcyanobipheny (7CB) 45% (E_{5CN7}) doped with TiO_2 and Fe_3O_4 was investigated using differential scanning calorimetry (DSC) and polarized optical microscopy (POM) techniques. Based on the obtained results, noticeable differences were indicated in nematic–isotropic phase transition temperature and thermodynamic properties including enthalpy and entropy changes between the pure and doped compounds. The mentioned phenomena were attributed to the spherical structure of nanoparticles while the LC texture showed completely different results which were attributed to the formation of Schlieren textures by TiO_2. Furthermore, electronic properties of LCs doped with TiO_2 and Fe_3O_4 were monitored using impedance spectroscopy. The impedance results showed that Fe_3O_4 NP effect on LC semiconducting properties is stronger compared to TiO_2. Doping of LCs with NPs forms the colloidal LCs with negative anisotropic properties and nanoparticles change the local ordering of liquid crystals. The diffusion coefficient calculations showed that the insertion of NPs reduces the diffusion of LCs toward the electrode surface. The dielectric constant of mentioned systems was studied as well.

1. Introduction

The nanomaterial colloidal suspensions based on liquid crystal (LC) have spawned a considerable interest from both technological and scientific aspects during recent years because of the capacity of the LC media acting as a platform for nanomaterial self-assembly [1,2]. Many colloidal particles in nematic LCs having complex self-assembled structures, resulted from nematic–mediated anisotropic interaction between the particles, have been widely studied [3,4]. Nematic LCs are particularly interesting because of their coupling ability with external electric and magnetic fields. A variety of nanomaterials including zero-, one-, and two-dimensional shapes have been dispersed into LC media in order to form composites having improved physical properties, to monitor the liquid crystalline phase behavior of nanomaterials, and to synthesize novel nanomaterials using LCs as "templates" [5,6].

Recently, the optical, electronic, and magnetic properties of metal nanoparticles have been widely investigated [7,8]. The mentioned properties depend not only on the size and structure of metal nanoparticles themselves but also on the covering materials acting as stabilizer. The metal nanoparticles covered by organic materials can be highly dispersed in organic media. Organic media formed of metal nanoparticle-dispersed system may have new properties which are considerably different compared to those of original organic media and metal nanoparticles. For example, dispersed nanoparticles of metal or semiconductor have been used in π-conjugated conducting polymers to produce electro conductive hybrid materials having the potential to be applied to organic thermoelectric materials. In recent years, titanium (TiO_2) NPs have been of considerable interest regarding their potential in materials and device applications. Chen and co-workers reported that insulating TiO_2 NPs as a dopant can reduce the impurity-ion concentration in LC cell, thereby lowering the threshold voltage as revealed by their transient-current data in conjunction with the transmittance–voltage measurements [5,9–12].

The properties, which can be varied by doping of nano-particles in the pure nematic LCs, are dielectric constant, dielectric loss, dielectric anisotropy, threshold voltage, and response time. Jeng et al. [13]. have studied the effect of adding Polyhedral Oligomeric Silsesquioxane (POSS) nano-particle on LCs. They have reported an enhancement in the switching properties of the POSS doped liquid crystals [13]. Martinez-Miranda et al. studied the properties of octylcyanobiphenyl (8CB) nematic LCs doped with ZnO nano-particle. They have reported the enhancement of electrical properties of the nematic LC sample [14]. Also, the nano-particles affect some parameters of the ferroelectric liquid crystal [15]. The anisotropic ordering of nematic LCs has been utilized in organizing copper doped ZnO nano-particle nematic LC system.

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http://dx.doi.org/10.1016/j.molliq.2015.05.020
0167-7322/

However, most of the studies based on nematic LCs and nano-particle nematic LC composites have been concentrated on their electro-optical properties [16]. In this work, we study the phase transition behavior of eutectic composition of pentylcyanobiphenyl (5CB) 55% and heptylcyanobipheny (7CB) 45% (E_{5CN7}) [17] LCs, which have crystal–nematic (C–N) and nematic–isotropic (N–I) phases doped (1%) with Fe_3O_4 ferroelectric and TiO_2 nonferroelectric nanoparticles as revealed by DSC technique. impedance spectroscopy was used to study the effects of Fe_3O_4 and TiO_2 NPs on semiconducting properties of nematic LCs at low-frequency range of 1 MHz-1 MHz. Finally, the effects of NPs texture and optic properties on nematic LC composites were studied using polarized light microscopy (POM).

2. Experimental details

2.1. Materials

All chemicals used are shown in Table 1. Eutectic composition of E_{5CN7} was formed of pure 5CB and 7CB purchased form Aldrich. TiO_2 NPs of 25 nm size particle purchased from Degussa AG. Fe_3O_4 NPs were synthesized using chemical co-precipitation in which Fe (II) and Fe (III) chloride salts were added to ammonium hydroxide [18,19].

Before the cell construction, the glass substrates covered with indium tin oxide (ITO) were spin coated with a polyamide layer about 180 nm thick then rubbed with a soft cloth in one direction to align the LC molecules. The ultimate form of the constructed cell was planar with a rubbing tilt of about 2^0. Each cell consisted of two glass slides separated by Mylar sheets, which is about 18 μm thick (Fig. 1). 0.02 g of TiO_2 (Fe_3O_4) was dissolved in 5 mL chloroform and then placed into ultrasonic bath for 2 h. Also, 1%(w/w) TiO_2 (Fe_3O_4) was added to E_{5CN7} eutectic system. Liquid crystal is completely soluble in chloroform solvent and is dispersed smoothly under the heat treatment [20]. The solvent was evaporated under a vacuum heat chamber at 90 °C. Finally, the nano doped liquid crystal samples were obtained through ITO cells.

2.2. Methods

(a) Differential scanning calorimetry (DSC): DSC measurements were made with NETZSCH DSC 200 F3 model in scan ramp rate of 5 $K \cdot min^{-1}$. 8 mg of each samples was placed into aluminum pans (dimensions: 8 mm diameter and 0.5 mm thick) and put into a differential scanning calorimeter along with an empty reference pans separately. The samples were first heated to 353 K for 7 min and immediately quenched to 173 K. The samples were also heated from 173 to 353 K and then cooled to 173 K at 5 $K \cdot min^{-1}$ ramp rate. The DSC thermograms showed endothermic and exothermic peaks in heating and cooling scan rates, respectively. In second measurement, heating and cooling of all samples gave identical results which show the reversibility of phase transition.

Table 1
Provenance and mass fraction purity of chemical samples studied.

Chemical name	Source	Molecular weight/($g \cdot mol^{-1}$)	Mass fraction purity
Heptylcyanobipheny (7CB)	Aldrich	249.35	0.98
Pentylcyanobiphenyl (5CB)	Aldrich	277.40	0.98
Titanium dioxide TiO_2	Degussa AG	79.86	0.99
Fe_3O_4 iron (III) oxide	Synthesis	231.53	0.95
Chloroform ($CHCl_3$)	Aldrich	119.37	0.99
Indium tin oxide (ITO)	Aldrich	–	–
Polyamide $C_{12}H_{22}O_2N_2$	Aldrich	226.32	0.99
Iron (II) chloride	Aldrich	198.8102	0.99
Iron (III) chloride	Aldrich	270.3	0.99
Ammonium hydroxide (NH_4OH)	Aldrich	34.05	0.99

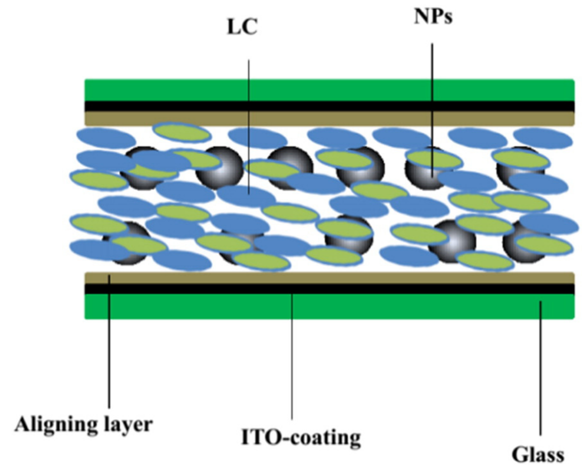

Fig. 1. Scheme of NP-doped LCs inside the ITO cell.

(b) Polarized light microscopy (POM): POM was used to monitor the thermal behavior and textures exhibited by the mesophases. POM measurements were made with LEICA DMRX LTS 350 and images were captured using a Nikon digital camera during heating or cooling at rates of 5 $°C \cdot min^{-1}$.

(c) Impedance spectroscopy: Impedance spectroscopy measurements were made at 1 MHz–1 MHz using EG & G model 273 connected with a personal computer.

(d) X-ray Diffraction: XRD measurements were carried out using Philips X'pert MPD model with Co tube, λ 4.7986 Å, step size 0.02°/s, V 40 kV and current 30 mA to obtain the phase and particle size of NPs.

(e) Scanning electron microscopy (SEM): scanning electron micrographs were recorded on a PHILIPS electron microscope CM120 model operated at 20 kV.

3. Results and discussion

3.1. Analysis of nanoparticles size and structure

Figs. 2 and 3 show the SEM and XRD pictures of two types of nanoparticles. SEM results show two types of spherical nanoparticles regarding the identical effect on phase transition of E_{5CN7}. The XRD results indicate that the TiO_2 phase is anatase phase having an average size of about 25 nm. The same particle size was obtained for Fe_3O_4 nanoparticle.

3.2. Phase transition study of E_{5CN7} composite using DSC

Phase transition of bulk E_{5CN7}, E_{5CN7}/1% TiO_2 and E_{5CN7}/1% Fe_3O_4 in cooling and heating ramp rate of 5 $k \cdot min^{-1}$ is shown in Fig. 4. The DSC thermograms showed endothermic and exothermic peaks in heating and cooling scan rates, respectively. In second measurement, heating and cooling of all samples gave identical results which show the reversibility of phase transition. C–N and N–I peaks were observed in heating process while I–N peaks were seen in cooling. The C–N phase transition was not observed in E_{5CN7}/1% TiO_2 and E_{5CN7}/1% Fe_3O_4 since the disordering is increased in colloidal system and the phase transition cannot be observed by DSC since an abrupt heating is needed to observe the phase transition phenomenon [17].

The N–I phase transition for all samples approximately occurs in the same temperatures since the nanoparticles shape is spherical and are not able to change the phase transition temperature noticeably. These results are in agreement with a similar research about doped spherical