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Magnetic-Field Induced Isotropic–Nematic Phase Transition in PDLC Doped with Magnetic Nanoparticles

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The paper presents a study of the polymer dispersed liquid crystals that consist of liquid crystal 4-trans-4'-n--hexyl-cyclohexyl-isothiocyanatobenzene (6CHBT) microdroplets dispersed in polyvinyl alcohol and doped with various kinds of magnetic particles. As magnetic nanoparticles there were used single walled carbon nanotubes and magnetite labeled single walled carbon nanotubes. The volume concentration of the particles was 2×10^{-3} . Magnetic properties were investigated by a SQUID magnetometer. The higher saturation magnetization has been achieved in sample polymer dispersed liquid crystal doped with magnetite labeled single walled carbon nanotubes. The phase transition temperature from isotropic to nematic phase at the external magnetic field 0 T and 12 T was monitored by precise capacitance measurements in the capacitance cell filled with prepared sample. The significant shift of the phase transition temperature $(0.2 \,^{\circ}C)$ at the external magnetic field 12 T has been observed in sample polymer dispersed liquid crystal doped with magnetite labeled single walled carbon nanotubes.

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1. Introduction

Polymer dispersed liquid crystals (PDLCs) are a novel class of optical composites [1-5], which consist of polymer and liquid crystal (LC) in an appropriate ratio. Micron sized nematic liquid crystal (NLC) droplets are uniformly dispersed in a transparent polymer matrix. The nematic texture of these droplets is randomly oriented with respect to the neighbouring droplets such that incoming light into the cell is scattered, and the PDLC appears opaque. When an electric field is applied across the cell, the liquid crystal droplets align and the PDLC is transparent if the ordinary index of refraction is matched to the index of the polymer. The voltage and speed at which the PDLC switches from opaque to transparency and the optical contrast between the opaque and transparent state is controlled by the size, shape, and anchoring energy of the liquid crystal droplets, as well as the dielectric anisotropy and viscosity of the liquid crystal.

In the past decade, PDLCs have found great interest because of their promising use in advanced optical device applications, such as large flexible displays, switchable windows or paper-like displays for electronic books. In our previous work [6] we studied dielectric properties of PDLCs doped with spherical and rod like nanoparticles. The goal of this work was to study the magnetic field induced isotropic- nematic phase transition in the PDLCs doped with single wall carbon nanotubes (SWCNT) and SWCNT functionalized with magnetite nanoparticles (so-called polymer dispersed ferronematics).

2. Experimental

The samples of PDLCs have been prepared by the following method. Liquid crystal (6CHBT) amount of 0.05 ml was added to 5 ml of 10% polyvinyl alcohol (PVA). This mixture was stirred at 10 000 rpm for 1 min. A creamy white emulsion was obtained. It was let to degas and a thin bead was placed on a slide. After the water evaporation we got a thin film.

This technique was used also for preparing the PDLC films doped with various kinds of magnetic particles. SWCNT and magnetite labeled SWCNT (SWCNT/ Fe_3O_4) have been used as magnetic nanoparticles. The prepared samples are illustrated in Fig. 1.

The samples thickness was 50 μ m. The structure of the films was investigated using the scanning electron microscope JSM-35 with an accelerating voltage of 35 keV.

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Fig. 1. The photo of the prepared samples.

To eliminate the effect of charging the surface, before the measurements a graphite film was deposited onto the surface of the PDLC film.

The magnetic properties of the samples were performed with a SQUID magnetometer (Quantum Design MPMS 5XL) up to 5 T at room temperature. The contribution of the 6CHBT in PVA was subtracted.

The phase diagram of the samples was obtained using the polarizing microscopy. Structural transitions in the samples were monitored by capacitance measurements. The capacitor was placed into a thermostated system. The distance between the electrodes (sample thickness) was $D = 50 \ \mu$ m. The capacitance was measured at the frequency of 1 kHz by the high precision capacitance bridge Andeen Hagerling.

3. Results and discussion

Polarizing microscopy analysis demonstrated that the size of 6CHBT microdroplets in the polymer matrix was from 5 to 8 μ m. The magnetization properties of PDLCs doped with different nanoparticles are illustrated in Fig. 2. The saturation magnetization, $M_{\rm s} = 3.9 \times 10^{-3}$ A m² kg⁻¹, has been achieved in PDLC doped with SWCNT/Fe₃O₄. The sample doped with SWCNT has lower value of saturation magnetization, $M_{\rm s} = 7.4 \times 10^{-5}$ A m² kg⁻¹.



Fig. 2. Magnetic properties of the samples with volume concentration of magnetic nanoparticles $\Phi = 2 \times 10^{-3}$ measured at room temperature.

During measurements of the temperature dependences of the capacitance, the magnetic field was applied parallel to the capacitor electrodes. The constant magnetic field was held, while the temperature was increased above the temperature of the transition from nematic to isotropic phase $T_{\rm N-I}$ and then slowly decreased. The dependence of the measured capacitance reflects the re-orientation of the molecules of the liquid crystal. Figure 3 shows the temperature dependence of the capacitance of PDLC doped with SWCNT/Fe₃O₄ measured without magnetic field and in magnetic field 12 T. There is a significant shift in the temperature of isotropic to nematic phase transition due to applying the external magnetic field. In the case of doping liquid crystals with SWNCTs no measurable shift of the transition from isotropic to nematic phase after application of the external magnetic field 12 T was observed.



Fig. 3. The temperature dependence of capacitance of the samples with volume concentration of magnetic nanoparticles $\Phi = 2 \times 10^{-3}$ measured without magnetic field and in magnetic field 12 T.

It has long been known the possibility to substantially alter the nematic-isotropic transition temperature in liquid crystals with the external fields. However, the effect could not been induced by magnetic field H until recently [7]. The principal reason is that the estimated critical fields are well over 100 T for traditional liquid crystal materials. The first experimental observation of the predicted magnetic-field dependence of the nematicisotropic phase transition temperature has been recently carried out [7] on a powerful electromagnet (H up to 30 T). To demonstrate the effect, besides the powerful electromagnet, the proper choice of a "non-traditional" (bent-core) nematic liquid crystal material was also necessary. The "non-traditional" nematic material chosen in Ref. [7], has considerably different physical properties from "traditional" calamitic nematics. These properties, combined with the high magnetic field, have contributed to the observation of the phase transition temperature shift that was ≈ 0.8 °C at the magnetic field of 30 T, but at the magnetic field of 12 T the shift was about 0.25 °C [7].

In our sample doped with SWCNT/Fe₃O₄, similar shift, about 0.2 °C, in the temperature of the phase transition from isotropic to nematic phase at the external magnetic field of 12 T was observed.

4. Conclusions

In this work we have studied PDLCs which have consisted of liquid crystal 6CHBT microdroplets dispersed in a PVA and doped with various kinds of magnetic nanoparticles. Magnetic measurements show ferromagnetic properties of the samples. The shift about $0.2 \,^{\circ}$ C in the temperature of the phase transition from isotropic to nematic phase at the external magnetic field of 12 T was observed in the PDLC doped with SWCNT/Fe₃O₄.

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