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The Influence of Magnetic Particles on the Nematic Droplets Formation in Liquid Crystal

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In this work the thermotropic nematic liquid crystal 4-*trans*-4′-*n*-hexyl-cyclohexyl-isothiocyanato-benzene (6CHBT) was dissolved in phenyl-isothiocyanate and doped with spherical magnetic particles with volume concentration $\phi_1 = 10^{-4}$ and $\phi_2 = 10^{-3}$. The influence of the volume concentration on the phase transitions from isotropic to nematic phase was studied by three experimental methods: optical microscopy, differential scanning calorimetry, and dielectric measurements. The obtained results confirmed the coexistence of isotropic and nematic phase, i.e. nematic or ferronematic droplets in isotropic phase in a wide temperature range between nematic and isotropic phase.

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1. Introduction

Liquid crystals (LCs), fascinating state of matter, represent materials in terms of their properties, importance for fundamental understanding of molecular self-assembly and their boom in commercial applications surrounding us everywhere [1]. The configuration of self-organized LC structures can be changed under the influence of different external stimuli, for example surfaces, electric, mechanical, and magnetic fields. Thus, LCs are able to assemble functional molecules into well-defined superstructures. A significant part of research is inspired by promising early results obtained by addition of nanomaterials into nematics, which indicated that nematic LC-nanoparticle composites could form basis for new electro-optical or composite materials and for molecular self-assembly in biosystems [2]. One of the most effective and versatile methods for the spontaneous self assembly of atoms, molecules, clusters and particles association is the application of magnetic field, which can induce alignment effect even for paramagnetic or diamagnetic materials with extremely small magnetic susceptibility [3]. To increase the magnetic susceptibility of LC, doping with magnetic nanoparticles (MNPs) is used. These suspensions of magnetic particles in nematic liquid crystals are called ferronematics. Brochard and de Gennes were the first, who suggested that doping liquid crystal by magnetic particles enhances their sensitivity to magnetic field [4]. Kedziora et al. [5] observed the coexistence of nematic and isotropic phases in 6CHBT LC dissolved in nonpolar medium benzene in the vicinity of the temperature of the isotropic–nematic transition. Due to the short-range orientational order of the mesogenic molecules, pseudonematic domains (droplets) were formed in the isotropic phase. Liquid crystal droplets have attracted strong interest due to the new applications. During the last few years the research focus has shifted from studying the director field and defect structure [6] to dynamic processes under the influence of external fields [7]. In our previous study it was shown that the embedding magnetic particles in a nematic LC causes orientational coupling between the magnetic moment of magnetic particle $\boldsymbol{m}$ and director of the nematic $\boldsymbol{n}$ [8]. We carried out investigation on the influence of volume concentration of MNPs on the shape of the droplets.

2. Experiment

Thermotropic nematic LC 6CHBT was dissolved in phenyl-isothiocyanate (PI). The temperature of the nematic–isotropic transition of 6CHBT is $T_{IN} = 42.8\,^{\circ}\mathrm{C}$. The spherical MNPs were prepared by co-precipitation method [9]. The MNPs with diameter $d \approx 10$ nm were coated with oleic acid. The doping was realized by adding MNPs to the LC in the isotropic phase under continuous stirring. The ferronematic samples were prepared with two different concentrations of spherical MNPs: $\phi_1 = 10^{-4}$ and $\phi_2 = 10^{-3}$. The structural transitions from the isotropic to the nematic phase were monitored by polarizing microscope, capacitance measurements, as well as differential scanning calorimetry (DSC) measurements.

For measurements with polarizing microscope the samples were put into a Linkam hot stage, heated to the isotropic state, then the samples were slowly cooled (at the rate of $1\,^{\circ}\mathrm{C}$/min) to the nematic state while monitoring their textures between crossed polarizers. The capacitance was measured at the frequency 1 kHz using a high precision capacitance bridge (Andeen Hagerling). The prepared samples were filled into a capacitor made of ITO-coated glass electrodes with the electrode area approximately 0.5 cm × 0.5 cm. The distance between the electrodes (sample thickness) was $D = 5$ μm. DSC measurements were carried out using a DSC8000 apparatus

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by Perkin Elmer. The samples were sealed in the volatile aluminium pans. They were heated to the temperature of 50 °C and after the stabilization of 2 min the samples were measured at cooling from the temperature of 50 °C to –40 °C with the rate of 10 °C/min in a flowing nitrogen as a protection atmosphere with the rate of 40 ml/min.

3. Results and discussion

The phase diagram of the transition from the isotropic to the nematic phase via the region of coexistence of the isotropic and nematic phases (droplet state) was found by observation under a polarizing microscope (Fig. 1). From this diagram it is clearly seen that the temperature of the nematic–isotropic transition in the mixture of the liquid crystal and phenyl isocyanate is shifted to lower values with increasing molar concentration of PI. For the next investigation the molar fraction of 6CHBT $x = 0.955$ was used for its wider coexistence of the isotropic and nematic phase.

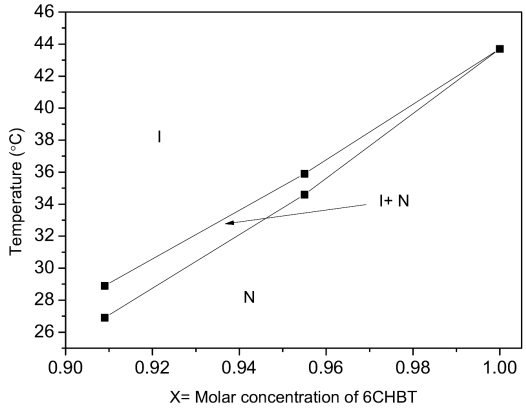

Fig. 1. The phase diagram of the transition from the isotropic (I) to nematic (N) phase obtained from observation under the polarizing microscope.

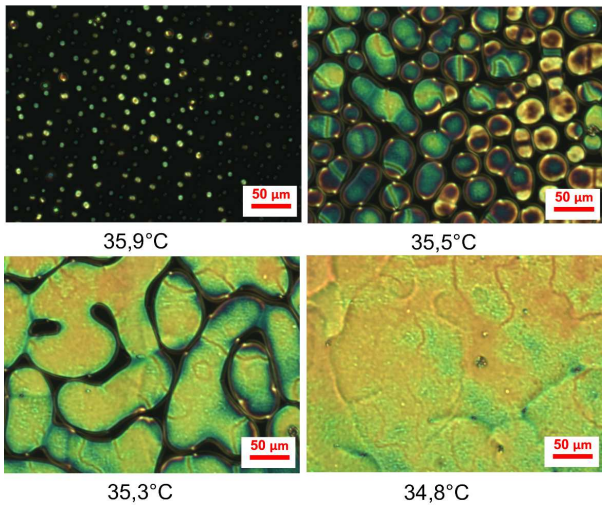

Fig. 2. Observation of the formation of the nematic droplets in 6CHBT mixed with PI by optical microscopy.

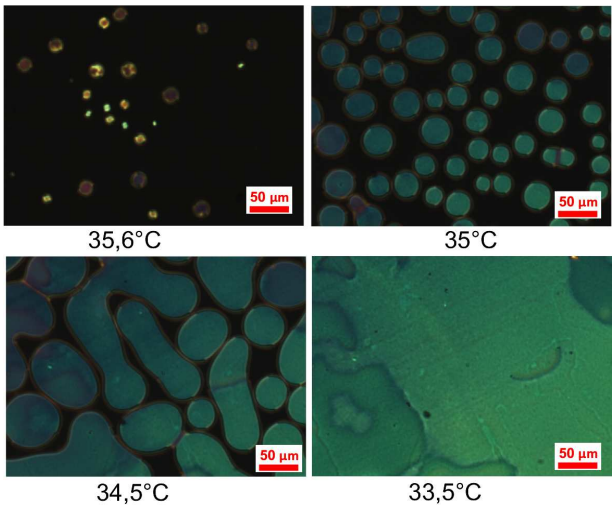

Fig. 3. Observation of the formation of the ferronematic droplets in 6CHBT mixed with PI doped with spherical MNPs for $\phi = 10^{-4}$ by optical microscopy.

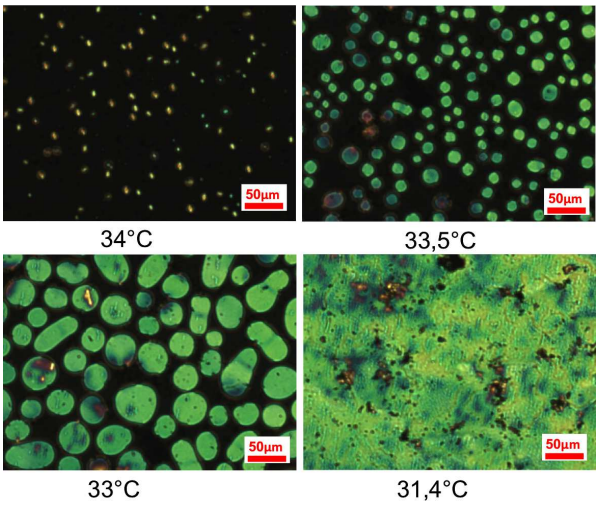

Fig. 4. Observation of the formation of the ferronematic droplets in 6CHBT mixed with PI doped with spherical MNPs for $\phi = 10^{-3}$ by optical microscopy.

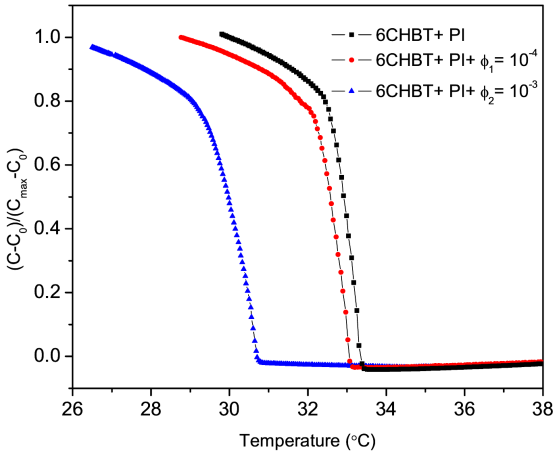

Fig. 5. Reduced capacitance vs. temperature for undoped 6CHBT in PI and for 6CHBT doped with spherical MNPs of different concentration ϕ in PI.

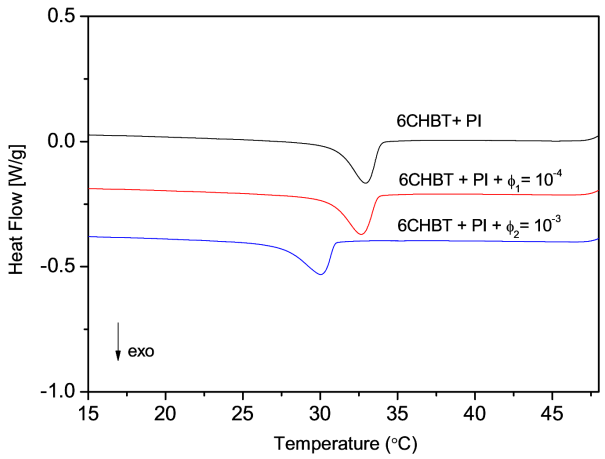

Fig. 6. DSC thermograms obtained for the 6CHBT and ferronematics with different volume concentration of spherical NPs during first cooling cycle.

The coexistence of droplet state was found by observation under a polarizing microscope. The samples were heated above the nematic–isotropic transition point and then slowly cooled. The transition temperature from isotropic to nematic phase (T_{IN}) was taken as the temperature, when nematic droplets occurred in isotropic phase during cooling process. By the temperature decrease the droplet size increases until the whole sample becomes nematic. Figures 2–4 show the observation of the formation of the droplets of the nematic phase in isotropic phase of the mixture 6CHBT and PI, the mixture doped with spherical magnetic particles with volume concentration $\phi = 10^{-4}$, and $\phi = 10^{-3}$, respectively. From the figures it can be seen that transition temperature is shifted to lower values depending on the volume concentration of MNPs and that number and shape of droplets was changed.

Figure 5 shows the temperature dependence of the reduced capacitance $(C - C_{\max})/(C_{\max} - C_0)$ for the undoped 6CHBT dissolved in PI and for the ferronematics containing spherical MNPs. Here C, $C_{\max}$ and C_0 correspond to the capacitances at the actual, at the highest and at the lowest temperatures, respectively. Obtained data clearly show that doping with spherical MNPs results in a shift of T_{IN} towards lower temperature. The shift becomes larger with increase of the volume concentration of MNPs.

TABLE I

The temperatures of isotropic–nematic phase transition obtained from polarizing optical microscopy (OM), DSC, and capacitance measurements.

Sample	OM	DSC	Cap.
6CHBT+PI	35.9	33.86	33.48
6CHBT+PI+$\phi_1 = 10^{-4}$	35.4	33.7	33.15
6CHBT+PI+$\phi_2 = 10^{-3}$	34	30.97	30.8

DSC thermograms of the structural transition from the isotropic to the nematic phase obtained for the pure 6CHBT as well as doped with magnetic particles can be seen in Fig. 6. The transition temperature from isotropic to nematic phase T_{IN} for the sample without the magnetic particles was found to be 33.86 °C. Doping with the magnetic particles caused the shift in the transition temperature towards the lower temperature. Whereas a small concentration of magnetic nanoparticles caused only a little change of the T_{IN}, higher concentration (10^{-3}) shifted the temperature by 2.89 °C (Table I).

4. Conclusion

In addition, quite interesting results have been obtained from our studies regarding the influence of magnetic particles on the quantity and shape of droplets of LC. Measurements using different experimental methods have shown that there is a shift in the isotropic–nematic transition via droplet phase. If the volume concentration of magnetic particles increases, the temperature of this transition decreases and temperature range of droplet phase is extended. We suppose that magnetic particles play the role of natural nucleation centres.

Acknowledgments

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