The structural transitions in 6CHBT-based ferronematic droplets

N Tomašovičová[1]**, P Kopčanský**[1]**, M Koneracká**[1]**, L Tomčo**[2]**,**
V Závišová[1]**, M Timko**[1]**, N Éber**[3]**, K Fodor-Csorba**[3]**,**
T Tóth-Katona[3]**, A Vajda**[3] **and J Jadzyn**[4]

[1] Institute of Experimental Physics, Slovak Academy of Sciences, Watsonova 47,
043 53 Košice, Slovakia

[2] Faculty of Aeronautics, Technical University, Rampová 7, 041 21 Košice, Slovakia

[3] Research Institute for Solid State Physics and Optics, Hungarian Academy of Sciences,
H-1525 Budapest, PO Box 49, Hungary

[4] Institute of Molecular Physics, Polish Academy of Sciences, Smoluchowskiego 17,
60179 Poznan, Poland

E-mail: nhudak@saske.sk (N Tomašovičová)

Abstract

In this work we describe the observations of structural transitions in ferronematics based on the thermotropic nematics 6CHBT (4-trans-4′-n-hexyl-cyclohexyl-isothiocyanato-benzene). The ferronematic droplets were observed in solutions of nematogenic 6CHBT dissolved in phenyl isocyanate and doped with fine magnetic particles. The phase diagram of the transitions from the isotropic phase to the nematic phase via a droplet state was found. Magneto-dielectric measurements of various structural transitions in this new system enabled us to estimate the type of anchoring of the nematic molecules on the magnetic particle surfaces in the droplets.

1. Introduction

Liquid crystals can be orientated under magnetic or electric fields due to their anisotropic properties. However, because of the small value of the anisotropy of the diamagnetic susceptibility ($\chi_a \sim 10^{-7}$), the magnetic fields necessary to align liquid crystals have to reach rather large values ($B \sim 1$ T). In an effort to enhance the magnetic susceptibility of liquid crystals, the idea of doping them with fine magnetic particles was introduced theoretically by Brochard and de Gennes [1]. The authors predicted that a rigid anchoring $m \parallel n$, where the unit vector n (director) denotes the preferential direction of the nematic molecules and the unit vector m denotes orientation of the magnetic moment of the magnetic particles, would result in ferromagnetic behaviour of the nematic matrix. Later, on the basis of the estimations given in [1], first lyotropic nematic and cholesteric [2, 3], then thermotropic nematic [4] and lyotropic smectic [5] systems were prepared and studied. These experiments confirmed the existence of considerable orientational and concentrational effects in liquid crystals doped with magnetic particles, but raised a lot of questions as well. The most essential feature

of these systems is a strong orientational coupling between the magnetic particles and the liquid crystal matrix. On the basis of the experiments, which excluded the presence of parallel orientation of m and n in thermotropic ferronematics, Burylov and Raikher's theory was constructed [6–8]. This theory considers the finite value of the surface density of anchoring energy W at the nematic–magnetic particle boundary. The finite value of W, like that of the parameter ω which is defined as the ratio of the anchoring energy to the elastic energy of the liquid crystal ($\omega = Wd/K$, where d is the size of the magnetic particles and K is the orientational–elastic Frank modulus), characterizes the type of anchoring of nematic molecules on magnetic particle surfaces. Parameter $\omega \gg 1$ characterizes rigid anchoring. Soft anchoring, characterized by parameter $\omega \leqslant 1$, unlike the rigid form, permits both types of boundary conditions ($m \parallel n$ and $m \perp n$); thus Burylov and Raikher's theory could be applied to thermotropic ferronematics. In its framework, the instabilities of the uniform texture in the ferronematics exposed to external magnetic or electric field (Freedericksz transitions) [6–8] were studied and the expressions for their critical fields in different geometries were found. Our previous experiments showed that the

critical magnetic field of magnetic Freedericksz transitions can either increase (8CB-based ferronematics) [9] or decrease (6CHBT-based and MBBA-based ferronematics) [10, 11] due to doping of nematic liquid crystals with fine magnetic particles, where the decrease or increase depends on the mutual initial orientation of the director n and the magnetic moment of the magnetic particles m. In the case of $m \parallel n$ a decrease was observed, while in the case of the perpendicular condition, the opposite behaviour was observed.

In the work of Kedziora *et al* [12] the coexistence of nematic and isotropic phases in 6CHBT liquid crystal dissolved in a nonpolar medium (benzene) was observed in the vicinity of the temperature of the isotropic–nematic transition. Due to the existence of a short-range orientational order of the mesogenic molecules (6CHBT), pseudonematic domains (droplets of 500–1000 nm in size depending on temperature) were formed in the isotropic phase. The size of these droplets increased as the temperature of the liquid decreased. The phase diagram of the mixture of 6CHBT and benzene was determined with a polarizing microscope. These results have inspired us to perform similar experiments with the nematogenic liquid crystal 6CHBT dissolved in phenyl isocyanate (which is more stable than benzene) doped with spherically shaped magnetic nanoparticles. The observations of the ferronematic droplets with a polarizing microscope revealed a behaviour similar to that in the case of pure droplets but with the occurrence of magnetically active droplets. The size of the droplets could be easily controlled by changing the temperature [14].

2. Experiment

The ferronematic samples studied were based on the thermotropic nematic 6CHBT 4-(trans-4′-*n*-hexyl-cyclohexyl)-isothiocyanato-benzene. 6CHBT is an enantiotropic liquid crystal with a low melting point and high chemical stability [13]. The temperature of the nematic–isotropic transition (clearing point) of the nematic studied is $T_{N-I} = 42.8\,°\mathrm{C}$. The nematic samples were doped with a magnetic suspension consisting of Fe_3O_4 particles (diameter $d \sim 10$ nm, standard deviation $\sigma = 0.28$) coated with oleic acid as a surfactant. The doping was simply done by adding this suspension, under continuous stirring, to the liquid crystal in the isotropic phase. Due to the small volume concentrations of the magnetic particles (10^{-5}–10^{-3}) and surfactant in the prepared ferronematic samples, interparticle dipole–dipole interactions are avoided. The homogeneity and stability of the samples were verified by optical microscopy and by dielectric measurements, indirectly [14]. The formation of the droplets and ferronematic droplets was achieved near the isotropic–nematic transition temperature, in the 6CHBT dissolved in phenyl isocyanate and in the mixture of 6CHBT dissolved in phenyl isocyanate with Fe_3O_4 particles coated with oleic acid. The structural transitions in ferronematic samples were indicated by capacitance measurements using a capacitor made of ITO-coated glass electrodes (LINCAM Co.). A capacitor with the electrode area of approximately 1 cm × 1 cm was connected to a regulated thermostat system; the temperature was stabilized
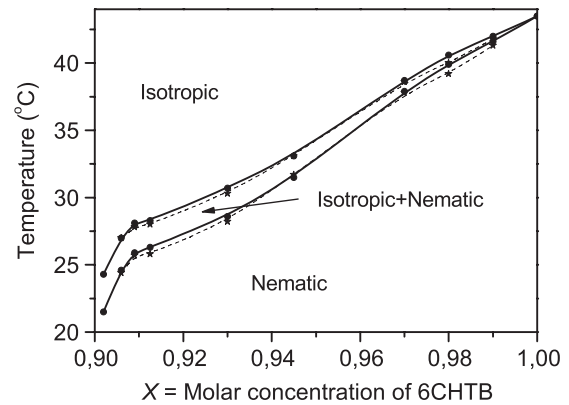
Figure 1. The phase diagram of the transition from the isotropic to the nematic phase obtained from observation under the polarizing microscope. The solid line represents the 6CHBT liquid crystal mixed with phenyl isocyanate, the dashed line represents the 6CHBT mixed with phenyl isocyanate and doped with magnetic particles ($\phi_2 = 10^{-3}$).

with the accuracy of 0.05 °C. The distance between the electrodes (sample thickness) was $D = 5\ \mu\mathrm{m}$. The capacitance was measured at the frequency 1 kHz using a high precision capacitance bridge (Andeen Hagerling). The stability of the samples in the strong magnetic fields was verified by repeating the capacitance measurements after five months on the same samples; the results were reproducible.

3. Results

Droplets were created in the 6CHBT liquid crystal dissolved in phenyl isocyanate and in the 6CHBT liquid crystal dissolved in phenyl isocyanate and mixed with a small volume concentration of fine magnetic particles, $\phi_1 = 5 \times 10^{-4}$ and $\phi_2 = 10^{-3}$, near the isotropic–nematic transition temperature. The phase diagram of the transition between the isotropic phase and the nematic phase via the region of coexistence of the isotropic and nematic phases ('droplet state') was found by observation under a polarizing microscope, JENAPOL U300 (figure 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 phenyl isocyanate.

Figure 2 shows the ferronematic sample observed under the polarizing microscope. The sample was deposited between two glass slides, heated above the nematic–isotropic transition point and then slowly cooled. When the temperature is decreased, microdroplets occur, and as the temperature decreases, the size of droplets increases until the whole sample becomes nematic. The droplets created were magnetically active and their size could be easily controlled by changing the temperature.

The magnetic Freedericksz transitions were studied in the experimental geometry shown in figure 3. The bias electric field was applied perpendicular to the capacitor electrodes and the external magnetic field was applied perpendicular to the bias electric field. The dependence of the measured
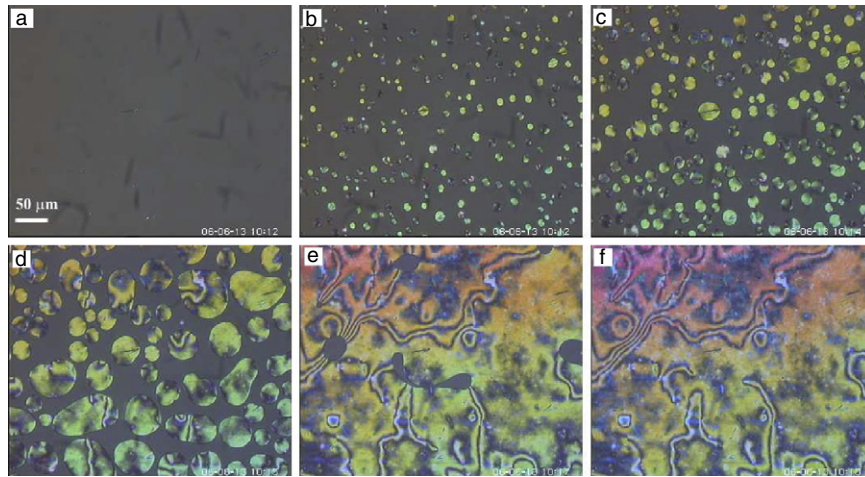
Figure 2. Observation of the formation of the ferronematic droplets in 6CHBT mixed with phenyl isocyanate (molar fraction $X = 0.906$) and doped with magnetic particles ($\phi_1 = 5 \times 10^{-4}$), by optical microscopy. (a) Isotropic phase at temperature 30 °C. (b) Sudden appearance of the ferronematic droplets at temperature 27.1 °C. (c) 26.5 °C. (d) 25.5 °C. The size of the ferronematic droplets is increasing as the temperature is decreasing. (e) 24.8 °C. The ferronematic droplets are expanding. (f) Homogeneous nematic state almost everywhere at temperature 24.5 °C. (This figure is in colour only in the electronic version)
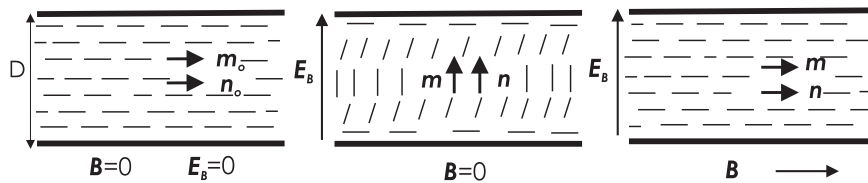
Figure 3. Cross section of the cell in the initial state, after application of the electric field $E_B > E_c$ and after application of the external magnetic field $B > B_c$.
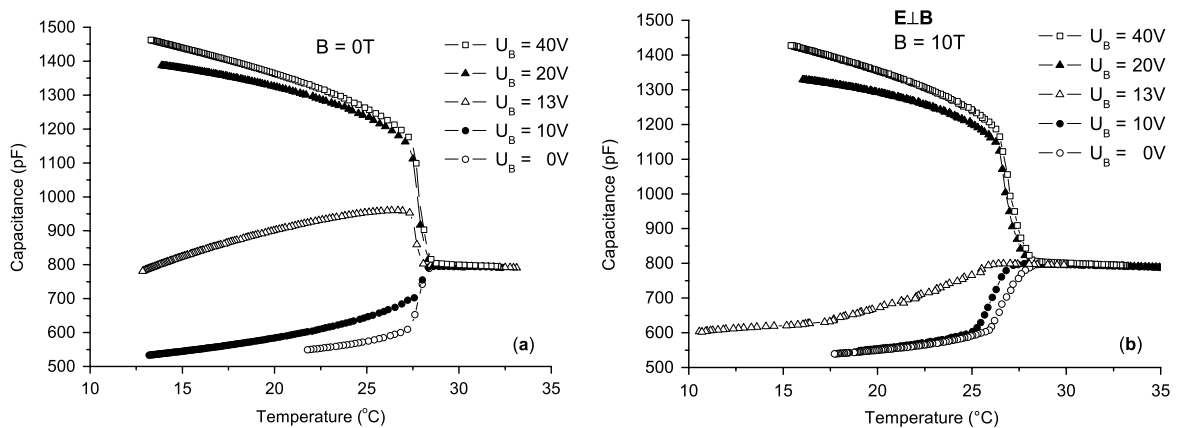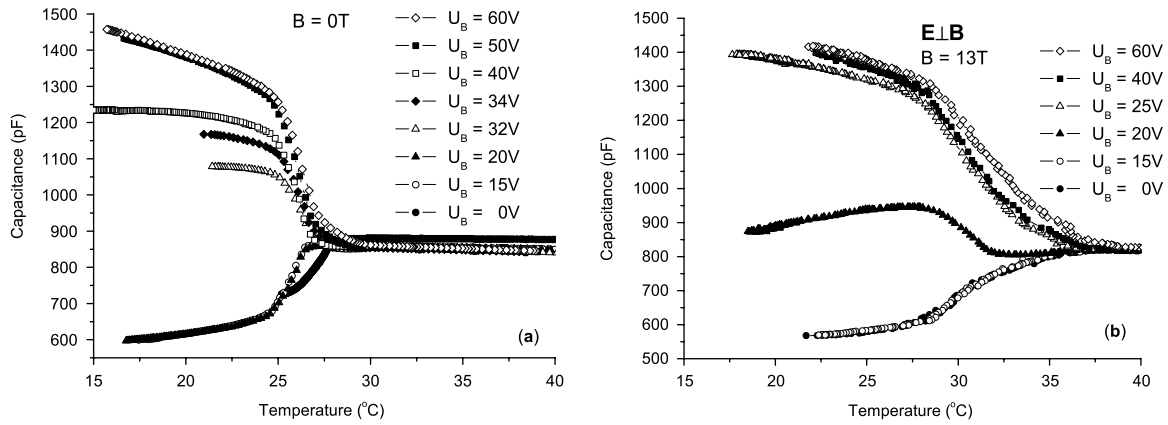

Figure 4. Temperature dependence of the capacitance for 6CHBT dissolved in phenyl isocyanate (molar fraction 0.906) (a) without the external magnetic field and (b) in the external magnetic field $B = 10$ T.

capacitance on the external magnetic field reflects the reorientation of the nematic molecules in the strong magnetic field.

Performing the above mentioned measurements for the sample without magnetic particles and for the samples containing magnetic nanoparticles, the type of anchoring can be evaluated. There are two theoretical assumptions on the initial orientation of the director and the magnetic moment of the magnetic particles: that they are perpendicular or that they are parallel.

From our previous measurements on 6CHBT-based ferronematics we have obtained parameter $\omega = 10^{-2}$, which characterizes soft anchoring, and the boundary condition between m and n was found to be that they are parallel [14]. However, our experiments on droplets indicate that the orientation of the nematic molecules in the droplets could be more complicated.
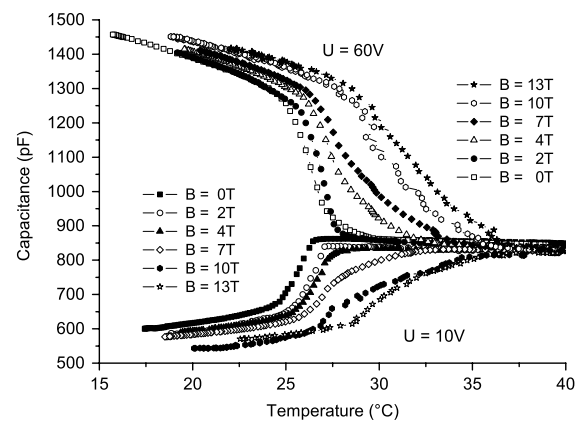
Figure 4 shows the temperature dependence of the capacitance for the sample without the magnetic particles (molar fraction of liquid crystal $X = 0.906$) for different

Figure 5. Temperature dependence of the capacitance of the sample (molar fraction 0.906) with the volume concentration of magnetic particles $\phi_1 = 5 \times 10^{-4}$ (a) without the external magnetic field and (b) in the external magnetic field $B = 13$ T.

applied voltages in the absence of an external magnetic field ($B = 0$) and for an external magnetic field ($B = 10$ T). As is seen from this figure, for $U < U_c$ (U_c is the critical electric field of the electric Freedericksz transition; for 6CHBT liquid crystal $U_c = 13.6$ V) and for $T < T_{N-I}$ the molecules of the liquid crystal are oriented parallel to the surface of the electrodes (the capacitance decreases with decreasing temperature) since the electric field is not strong enough to turn the molecules away. For $U \gg U_c$ the electric field rotates the director to its direction, i.e. the liquid crystal molecules are oriented perpendicular to the electrodes (the capacitance increases with decreasing T). The competition between the influences of the electrode surfaces and the external electric field results in another interesting phenomenon near T_{N-I} as depicted in figure 4. In the nematic phase the director is preferentially oriented parallel to the surface of the electrodes due to the surface treatment. However, close to T_{N-I} in the two-phase region the nematic droplets are surrounded by the isotropic phase, so the influences of surfaces are negligible. As a consequence even a weaker electric field can turn the director inside the nematic droplets created to its direction. As the temperature decreases and the droplets grow and come into contact with the electrodes, the interaction with the aligning surfaces becomes more effective and finally the director turns back towards the direction parallel to the electrodes (see the change in the slope in figure 4(a) for $U_B = 13$ V). From figure 4(b) it is seen that this effect is absent for the same voltage if a strong external magnetic field ($B = 10$ T) is applied, as it keeps the molecules of the liquid crystal parallel to B (and thus to the electrodes) also for $U_B = 13$ V.

The situation is changed if the sample is doped with magnetic nanoparticles. Figure 5 shows the temperature dependence of the capacitance for the sample with a volume concentration of the magnetic particles $\phi_1 = 5 \times 10^{-4}$ at different applied voltages without an external magnetic field and for $B = 13$ T oriented perpendicular to the electric field. For $B = 0$ the behaviour is similar to that for the droplets without the magnetic particles. The situation seems to be the same also for $B = 13$ T but the temperature where the capacitance becomes voltage dependent indicating a Freedericksz transition is shifted to higher values. The amount

Figure 6. Temperature dependence of the capacitance of the sample (molar fraction 0.906) with the volume concentration of magnetic particles $\phi_1 = 5 \times 10^{-4}$ for $U = 10$ V $< U_c$ (lower part of the figure) and for $U = 60$ V $> U_c$ (upper part of the figure) for the external magnetic fields $B = 0, 2, 4, 7, 10$ and 13 T. (The magnetic field is applied perpendicular to the electric field.)

of this shift depends on the value of the external magnetic field. With increasing external magnetic field the temperature of the phase transition increases as is seen from figure 6, which shows the temperature dependence of the capacitance of the sample with the volume concentration of the magnetic particles $\phi_1 = 5 \times 10^{-4}$ for $U = 10$ V $< U_c$ (lower part of figure) and for $U = 60$ V $> U_c$ (upper part of figure) for various external magnetic fields ($B = 0, 2, 4, 7, 10$ and 13 T).

We propose the following explanation for this behaviour. We assume that there is an interaction between the magnetic particles and the liquid crystal molecules which favours a parallel initial orientation of the magnetic moments of the magnetic particles and the director around them (see figure 7(a)). If the temperature of the sample is higher than T_{N-I}, the sample is in the isotropic phase, and in the absence of external fields ($B = 0$, $U = 0$) the molecules as well as the magnetic moments are disordered. Switching on a strong external magnetic field, the energy of the thermal excitation may be overcome and the magnetic moments of the nanoparticles will tend to align parallel to B, themselves

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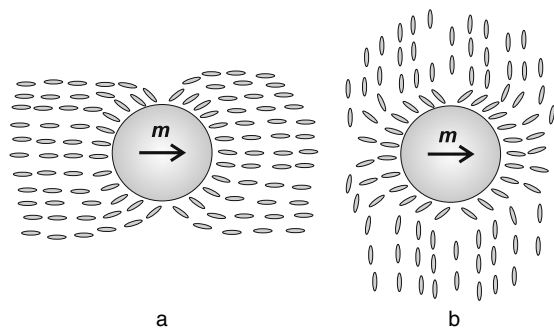
Figure 7. The orientation of director and magnetic moment of magnetic particles indicated by the experiments.

turning the molecules of the liquid crystal too. Thus a nematic order is induced by the magnetic field around the nanoparticles already above T_{N-I}, i.e. the isotropic–nematic phase transition is apparently shifted to higher temperatures. At low applied voltages ($U < U_c$) this induced order is seen in figure 6 as a capacitance decreasing with decreasing temperature. The higher the magnetic field, the higher the temperature where the induced order appears. Once the induced order is established at a given temperature, at high enough applied voltages ($U > U_c$) the electric field can reorient the director (a Freedericksz transition can occur) just as in the regular nematic phase below T_{N-I}. That is seen in figure 6 as an increasing capacitance as the temperature decreases. As the electric field does not exert a direct torque on the magnetic moment of the nanoparticles, for $B > 0$ one expects m to be held firmly by the strong external magnetic field. Therefore at high voltages the mutual orientation of the magnetic moment of the magnetic particles and director of the bulk director of the liquid crystal changes. For $B > 0$ and $U \gg U_c$ the liquid crystal molecules are still oriented along the external magnetic field near the surface of the magnetic particle for the nematic droplets, but the rest of the molecules change their orientation to parallel to E as depicted in figure 7(b). Moreover, it is seen from figure 6 that the temperature dependence of the capacitance becomes weaker (the slope of the curves in figure 6 decreases) for higher magnetic fields. This suggests that the temperature interval in which the isotropic–nematic phase transition occurs via a droplet state (i.e. the width of the two-phase region) increases as the external magnetic field increases. Microscopic observation under a magnetic field would be required to justify this assumption.

4. Conclusion

Embedding magnetic particles in a nematic liquid crystal causes an effective orientational coupling between the magnetic moment of the magnetic particle and the director of the nematic. This coupling may come from the anisotropy of the anchoring of the nematic molecules on the particle surface. The results obtained show, for the case of the ferronematics based on the 6CHBT liquid crystal, that though the anchoring of the liquid crystal molecules on the surface of magnetic particles is soft, their orientation is parallel to the magnetic moment. However, the director of the liquid crystal at some distance from the surface of the magnetic particles in the droplets already depends on the strength of the applied external electric and magnetic fields, and m may be either parallel or perpendicular to n. Moreover, the temperature of the phase transition increases with increasing value of the external magnetic field due to a field induced nematic order.

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