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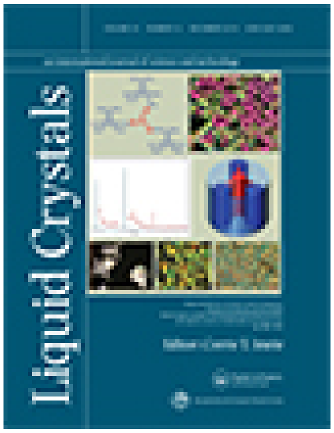

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Influence of the anisometry of magnetic particles on the isotropic–nematic phase transition

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The influence of the shape anisotropy of magnetic particles on the isotropic–nematic phase transition was studied in ferronematics based on the nematic liquid crystal (LC) 4-(trans-4-*n*-hexylcyclohexyl)-isothiocyanato-benzene (6CHBT). The LC was doped with spherical or rod-like magnetic particles of different size and volume concentrations. The phase transition from isotropic to nematic phase was observed by polarising microscope as well as by capacitance measurements. The influence of the concentration and the shape anisotropy of the magnetic particles on the isotropic–nematic phase transition in LC are demonstrated here. The results are in a good agreement with recent theoretical predictions.

Keywords: liquid crystal; magnetic nanoparticles; ferronematics; anisotropy

1. Introduction

Doping liquid crystals (LCs) with nanoparticles (NPs) in low volume concentrations has been shown as a promising method to modify the properties of LCs. The presence of NPs in LC changes the properties of the mesophase and/or introduces some new features of the composite mixtures. After introducing the idea theoretically by Brochard and de Gennes [1] several reports have shown that the doping of LCs with magnetic NPs can either increase or decrease the critical field of the magnetic Fréedericksz transition, [2–5] depending on the host–guest combination. It has also been proven [6,7] that ferronematics respond to low magnetic fields (below 0.1 T) due to doping with magnetic particles. Furthermore, the theoretically predicted magnetic field-induced isotropic–nematic phase transition [8] was observed in calamitic LCs at relatively low magnetic fields (below 12 T) when they are doped with magnetic NPs.[9]

Properties of magnetic NPs significantly depend on their size, shape and structure. Therefore, the properties of ferronematics composed of them are also expected to be sensitive to the same factors. As an example, in our previous work [2] it was shown that doping the LC 4-(trans-4-*n*-hexylcyclohexyl)-isothiocyanato-benzene (6CHBT) with spherical magnetic particles results in soft anchoring ($\omega \sim 1$), while in the case of doping with rod-like magnetic particles rigid anchoring ($\omega \sim 10^4$) was obtained at the LC–NP interface, even though both kinds of magnetic particles were coated with the same surfactant (oleic acid). Here, the parameter $\omega = WR/K$ is the ratio of the interfacial (anchoring) to the bulk (elastic) energies; W is the anchoring energy density, R is the reference size of the NPs [10] which in case of cylindrical particles coincides with their mean radius $D/2$,[10,11] and K is the corresponding elastic modulus of the host LC.

Recently, a mean-field theory has been developed by Gorkunov and Osipov [12] to describe the influence of embedded NPs on the orientational order and on the isotropic–nematic phase transition of the host LC. They considered relatively large, uniaxial NPs of oblate or prolate shape, where the interaction between the LC molecules and the NPs may be described by an anisotropic surface potential depending on the coupling between the surface normal of the particle and the long molecular axis of the host. It has been shown that spherically isotropic NPs effectively dilute the LC medium and decrease the isotropic–nematic transition temperature. On the contrary, anisotropic NPs become aligned by the nematic host and, reciprocally, improve the LC alignment, thus extending the nematic order to higher temperatures.

This theory has inspired us to perform measurements with the nematic LC 6CHBT doped with spherical or rod-shaped magnetic NPs. The present work is devoted to an experimental study of how the shape as well as the volume concentration of magnetic NPs affect the temperature of the isotropic–nematic phase transition. The obtained results indicate a significant effect in accordance with the theoretical expectations described in [12].

2. Experiment

The spherical magnetic NPs were prepared by the co-precipitation method described in [2]. The rod-

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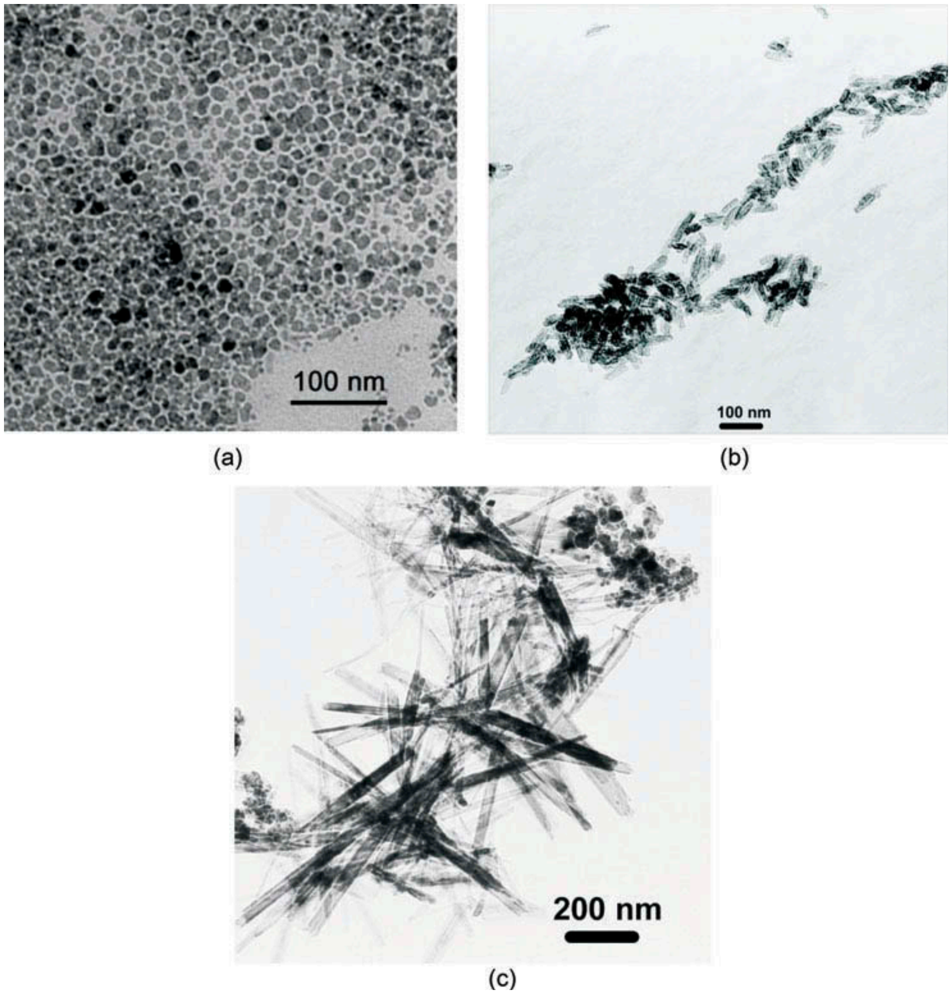

Figure 1. (colour online) TEM images of (a) spherical, (b) short and (c) long rod-like magnetic nanoparticles.

like iron oxide NPs were synthesised through smooth decomposition of urea.[5] The smaller particles were synthesised by co-precipitation of Fe^{3}+ and Fe^{2}+ in oleic acid micelles. The synthesis of the longer iron oxide particles utilised precipitation of Fe^{2}+ in the presence of oleic acid as stabiliser. The morphology and size distribution of the prepared NPs were determined by transmission electron microscopy (TEM). Figure 1 shows the TEM images of the prepared spherical and rod-like NPs. The mean diameter of the spherical magnetic NPs was D = 10 nm. The average diameter of the shorter rod-like NPs was D = 8 nm and the mean length was L = 40 nm. The longer rod-like NPs had the average diameter of D = 11 nm and their mean length was L = 240 nm.

The ferronematic samples were based on the thermotropic nematic 6CHBT which is a low-temperature-melting enantiotropic LC with high chemical stability.[13] The phase transition temperature from the isotropic liquid to the nematic phase (the clearing point) of the studied nematic was found by polarising optical microscopy at T_{IN} = 43.3°C. The doping was done by adding NPs (spherical or rod-like) to the LC in the isotropic phase under continuous stirring. The NPs were coated with oleic acid as a surfactant to suppress their aggregation. The ferronematic samples were prepared with three different volume concentrations of the spherical as well as of the rod-like magnetic particles: $\phi_1 = 1 \times 10^{-5}$, $\phi_2 = 5 \times 10^{-5}$ and $\phi_3 = 1 \times 10^{-4}$.

The structural transition from the isotropic to the nematic phase was monitored by polarising microscope as well as by capacitance measurements. The prepared samples were filled into a capacitor made of indium-tin-oxide-coated glass electrodes with the electrode area approximately 1 cm × 1 cm. The distance between the electrodes (the sample thickness) was d = 5 μm. The samples (the undoped 6CHBT, or 6CHBT doped with various NPs) were filled into the cells in the isotropic phase due to capillary forces. A rubbed polyimide coating on the electrodes ensured planar orientation.

For all samples the measurements started with polarising microscopic observations. 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°C/min) to the nematic state while monitoring their textures between crossed polarisers. The transition temperature T_{IN} was taken as the temperature, where nematic droplets appeared in the isotropic melt in the cooling process. Next, the temperature dependence of the capacitance of the same samples was measured in the same cells at the frequency of 1 kHz by a high precision capacitance bridge Andeen Hagerling (the accuracy at 1 kHz is 0.8 aF). The samples were first heated to the isotropic phase and then they were again slowly cooled to the nematic phase (at the rate of 1°C/min).

3. Results and discussion

Figure 2 shows the temperature dependence of the reduced capacitance $(C-C_{\max})/(C_{\max}-C_{\min})$ for the undoped 6CHBT and for the ferronematics containing spherical magnetic NPs in different volume concentrations. Here C, $C_{\max}$ and $C_{\min}$ correspond to the capacitances at the actual, at the highest and at the lowest temperatures, respectively. Each curve exhibits a monotonic decrease of the capacitance with diminishing temperature. In the isotropic phase the capacitance is nearly constant. The sudden drop of the capacitance indicates the appearance of the orientational order (and hence the increase of the anisotropy), i.e. the phase transition to the nematic phase.

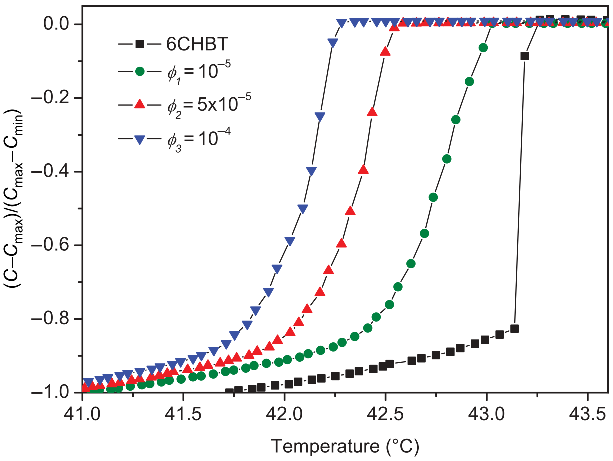

Figure 2. (colour online) Reduced capacitance vs. temperature for undoped 6CHBT and for 6CHBT doped with spherical magnetic nanoparticles of different concentrations ϕ.

The decrease of C occurs due to the planar alignment and the positive dielectric anisotropy of 6CHBT and the 6CHBT-based ferronematics. Figure 2 clearly shows that doping with spherical NPs results in a shift of T_{IN} towards lower temperatures; the shift becomes larger with increasing the volume concentration of magnetic NPs. This is in accordance with the expectations, as NPs behave as impurities introducing disorder and thus reducing T_{IN}. Figures 3 and 4 also show the temperature dependence of the reduced capacitance, however, for ferronematics doped with short and long rod-like magnetic NPs, respectively. The monotonicity of the temperature dependence and the easy detectability of the isotropic–nematic phase

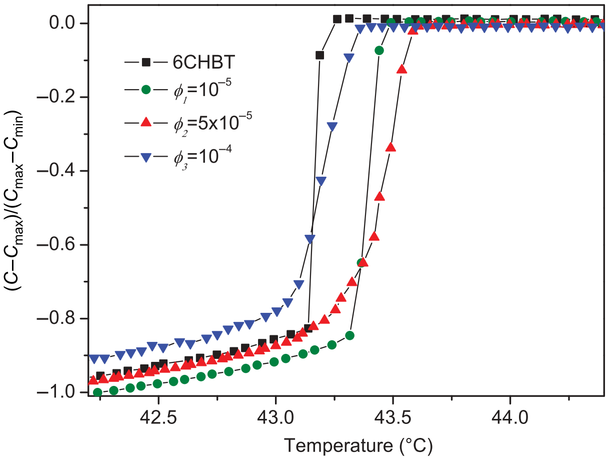

Figure 3. (colour online) Reduced capacitance vs. temperature for undoped 6CHBT and for 6CHBT doped with short rod-like magnetic nanoparticles of different concentrations ϕ.

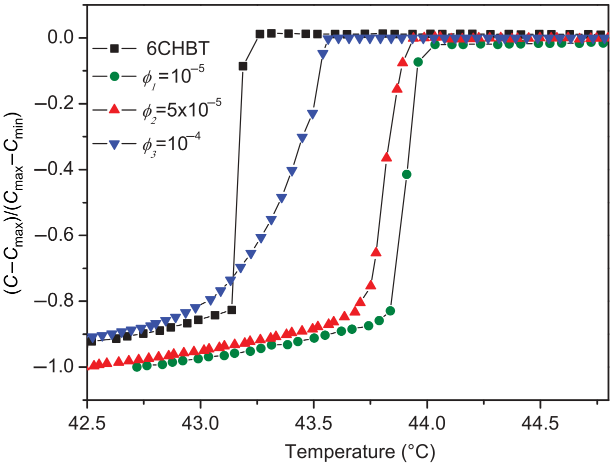

Figure 4. (colour online) Reduced capacitance vs. temperature for undoped 6CHBT and for 6CHBT doped with long rod-like magnetic nanoparticles of different concentrations ϕ.

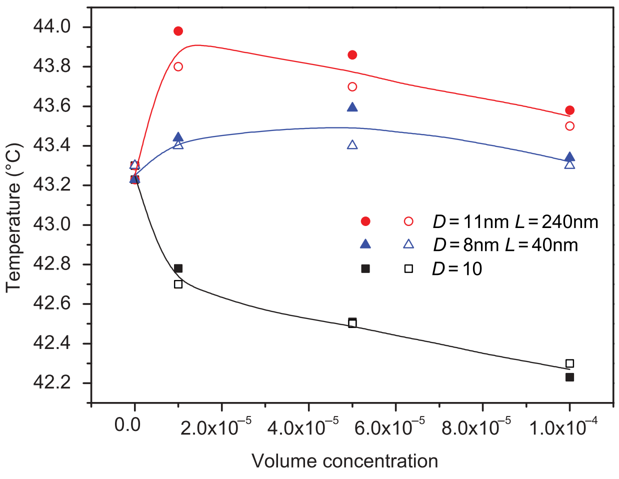

Figure 5. (colour online) Dependence of the isotropic to nematic phase transition temperature on the volume concentration for spherical and rod-like magnetic nanoparticles (as indicated in the legend), obtained by capacitance measurements (full symbols) and determined by polarising microscopy (open symbols). The solid lines are guides to the eye.

transition temperature hold here too. However, in the case of doping 6CHBT with rod-like magnetic NPs, T_{IN} shifts towards higher temperatures. Moreover, though the increasing volume concentration of NPs initially enhances the shift, this tendency turns over for higher concentration. Nevertheless, T_{IN} still remains higher for the samples doped with rod-like NPs than that for the undoped LC.

The differences between the behaviour of ferronematics containing NPs of different shape is even more perceptible in Figure 5 which shows the dependence of the T_{IN} on the volume concentration of NPs, obtained by capacitance measurements and by polarising microscopy. As one can see, the results provided by the two independent techniques are in good agreement. Figure 5 clearly shows that the increase of the phase transition temperature is more pronounced when long rod-like NPs are used for the doping instead of the short ones. In order to understand these features one has to recall the recent theory of Gorkunov and Osipov.[12] They have developed a mean-field molecular description of the thermodynamics of nematic LCs mixed with NPs, which may be anisotropic due to their shape, their surface treatment and/or their spontaneous polarisation. As it has been shown, the large shape anisotropy of NPs (namely the rod-likeness) enhances the nematic order and, as a consequence, increases the phase transition temperature. In contrast to that, spherical NPs reduce the orientational order and thus lower T_{IN}. These conclusions are in agreement with our experimental findings presented in Figures 2–5 and explain the different signs of the shift of T_{IN} for spherical and rod-like NPs. Moreover, it is evident from our TEM measurements that longer rod-like NPs have a larger length/diameter ratio (≈22) than the shorter NPs (≈5); i.e. longer NPs have higher anisotropy and thus larger shift in T_{IN}.

In order to prevent aggregation of NPs, they are usually coated with surfactants during the preparation. In a recent work, various ligands were used for this purpose for two different NPs of spherical shape dispersed in a polymorphic LC.[14] A slight, though measurable change in the phase transition temperatures has been reported in these dispersions. However, the influence of the type and concentration of the NPs as well as the type of the surfactant on the phase transition temperature shift could not be distinguished clearly from these measurements. Therefore, we have coated all magnetic NPs (spherical and rod-like) with the same surfactant (oleic acid). The theoretical description in [12] remains valid if the surface of the NPs is coated by organic molecules. However, one has to take into account that, in general, the surfactant dilutes the LC, reduces its order and thus lowers the isotropic–nematic phase transition temperature in itself. In the case of doping with coated magnetic NPs, the increasing volume concentration of NPs increases the concentration of the surfactant as well. When spherical NPs are used as dopants, the surfactant and the NPs have a similar effect on T_{IN} resulting in its decrease, as shown in Figure 2. In contrast to that, using rod-like dopants the NPs and the surfactant counteract; the effect of the surfactant (which decreases T_{IN}) seems to prevail at higher concentrations. This may explain the nonmonotonic concentration dependence of T_{IN} as seen in Figure 5, and is also in good qualitative agreement with the Gorkunov–Osipov theory.

Finally, we note that in ferronematics based on 6CHBT, the magnetic moment (which is in case of rod-like NPs parallel with their long axis) coincides with the nematic director as it has been shown in our previous work.[2] However, because of the low volume concentration (order of 10^{-5}–10^{-4}) and small value of the magnetic moment (order of 10^{-24} Tm^3) of NPs their magnetic interaction can be considered negligible, and therefore, does not influence the LC order significantly.

4. Conclusion

We have found that the shape as well as the volume concentration of magnetic NPs have a significant influence on the temperature of the isotropic to nematic phase transition of ferronematics. We have justified that ferronematics doped with rod-like magnetic NPs have higher T_{IN} than the host nematic or ferronematics containing spherical NPs. We have found that doping with rod-like NPs yields a nonmonotonic concentration dependence of T_{IN}, which could be attributed to the competing influence of the NPs and of the organic surfactants they are coated with. Our results provide a firm experimental proof for the main conclusion of the recent mean-field theory of Gorkunov and Osipov.[12]

Funding

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