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Structural changes in the 6CHBT liquid crystal doped with spherical, rodlike, and chainlike magnetic particles

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In this work the 4-(trans-4′-*n*-hexylcyclohexyl)-isothiocyanatobenzene (6CHBT) liquid crystal was doped with differently shaped magnetite nanoparticles. The structural changes were observed by capacitance measurements and showed significant influence of the shape and size of the magnetic particles on the magnetic Fréedericksz transition. For the volume concentration $\phi=2\times10^{-4}$ of the magnetic particles, the critical magnetic field was established for the pure liquid crystal, and for liquid crystals doped with spherical, chainlike, and rodlike magnetic particles. The influence of the magnetic field depends on the type of anchoring, which is characterized by the density of anchoring energy and by the initial orientation between the liquid crystal molecules and the magnetic moment of the magnetic particles. The experimental results indicated soft anchoring in the case of spherical magnetic particles and rigid anchoring in the case of rodlike and chainlike magnetic particles, with parallel initial orientation between the magnetic moments of the magnetic particles and director.

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I. INTRODUCTION

Liquid crystals can be oriented under magnetic or electric fields due to their anisotropic properties. However, because of the small value of the anisotropy of 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 theoretically introduced by Brochard and de Gennes [1]. They predicted that a rigid anchoring with $\boldsymbol{m}\parallel\boldsymbol{n}$, where the unit vector $\boldsymbol{n}$ (director) denotes the preferential direction of the nematic molecules and the unit vector $\boldsymbol{m}$ denotes the orientation of the magnetic moment of the magnetic particles, would result in ferromagnetic behavior of the mixture. In the first experimental paper by Rault *et al.* [2], the basic magnetic properties of a suspension of rodlike γ-Fe_2O_3 particles in 4′-methoxybenzylidene-4-*n*-butylaniline (MBBA) liquid crystal were reported. Later, based on the estimations given in [1], first lyotropic [3,4] and then thermotropic [5] ferronematics were prepared and studied. These experiments confirmed the existence of considerable orientational and concentration effects in liquid crystals doped by magnetic particles, but raised a lot of questions as well.

Ferronematics are stable colloidal suspensions of fine magnetic particles in nematic liquid crystals. They attract considerable interest of investigators because their response to an external magnetic field considerably exceeds that of pure nematics. The most essential feature of these systems is a strong orientational coupling between the magnetic particles and the liquid crystal matrix. Based on the experiments, which excluded the presence of parallel orientation of $\boldsymbol{m}$ and $\boldsymbol{n}$ in thermotropic ferronematics, Burylov and Raikher's theory was constructed [6–8]. This theory considers the finite value of the surface density of the anchoring energy W at the nematic–magnetic particle boundary. The finite value of W and the parameter ω, which is defined as the ratio of anchoring energy to 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), characterize the type of anchoring of nematic molecules on magnetic particle surfaces. A parameter $\omega\gg 1$ characterizes rigid anchoring. Soft anchoring is characterized by a parameter $\omega\leq 1$ and, unlike rigid anchoring, permits both types of boundary conditions ($\boldsymbol{m}\parallel\boldsymbol{n}$ and $\boldsymbol{m}\perp\boldsymbol{n}$). Thus Burylov and Raikher's theory could be applied for thermotropic ferronematics. In its framework, the instabilities of the uniform texture in ferronematics exposed to external magnetic or electric fields (Fréedericksz transitions) [6–8] can be studied, and the expressions for their critical fields in different geometries have been derived.

II. EXPERIMENT

The synthesis of the spherical magnetic nanoparticles was based on coprecipitation of Fe^{2+} and Fe^{3+} salts by NH_4OH at 60 °C. To obtain a Fe_3O_4 precipitate, $FeCl_2\cdot4H_2O$ and $FeCl_3\cdot6H_2O$ were dissolved in deionized water by vigorous stirring (the ratio $[Fe^{3+}]:[Fe^{2+}]$ was 2:1). The solution was heated to 80 °C and 25% NH_4OH was added. The precipitate was isolated from solution by magnetic decantation by wash-

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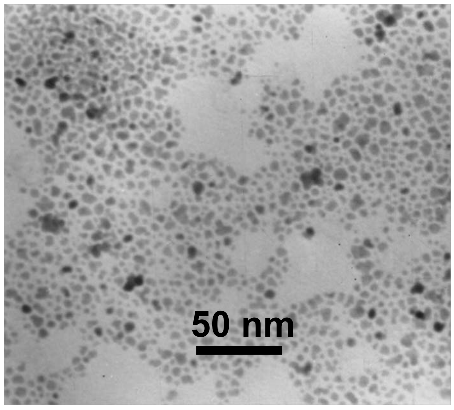

FIG. 1. TEM image of spherical magnetic particles.

ing with water. The magnetic properties were estimated by magnetization measurements using a vibrating sample magnetometer and the size and morphology of the particles were determined by transmission electron microscopy (TEM) (Fig. 1) and atomic force microscopy working in tapping mode. A histogram of the size distribution of the spherical magnetic particles obtained is shown in Fig. 2. The mean diameter of the magnetic nanoparticles obtained was 11.6 nm.

Magnetite nanorods were synthesized through hydrolysis of $FeCl_3$ and $FeSO_4$ solutions (the Fe^{3+} to Fe^{2+} molar ratio was 2:1) containing urea. In a typical experiment $FeCl_3 \cdot 6H_2O$, $FeSO_4 \cdot 7H_2O$, and $(NH_2)_2CO$ were all dissolved in purified deoxygenated water. This mixture was added to a flask with reflux condenser and heated in a water bath for 12 h at 90–95 °C. A dark precipitate was formed. The sample was cleaned several times with purified and deoxygenated water, and then it was dried at a lower pressure at 50 °C for 3 h. The morphology and size distribution of the prepared nanorods were measured by transmission electron microscopy (Tesla BS 500) (Fig. 3). The sample dispersed in diluted ethanol was dropped on a copper grid and dried in air. The average diameter of rodlike particles was 80 nm and the mean length determined from the histogram of the size distribution was 1200 nm (Fig. 4). Their magnetic properties were investigated by using a vibrating sample magnetometer at room temperature.

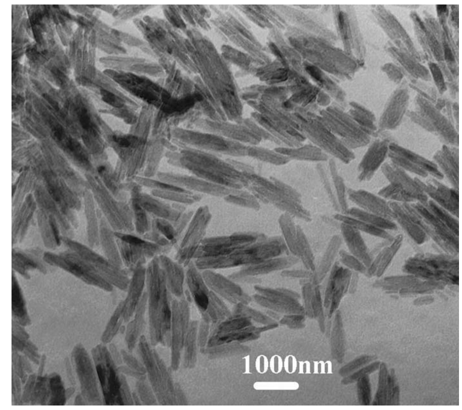

FIG. 3. TEM image of rodlike magnetic particles.

The chainlike particles were obtained from the magnetotactic bacterium *Magnetotacticum magnetospirillum* (AMB-1). For the cultivation of AMB-1, a medium consisting of Wolfe's vitamin solution, Wolfe's mineral solution, KH_2PO_4, sodium succinate hexahydrate, sodium tartrate dihydrate, sodium acetate trihydrate, 0.2% (w/v) resazurin (aqueous), $NaNO_3$, ascorbic acid, and 0.01*M* ferric quinate was used. Resazurin was added to the medium as a colorimetric indicator of the redox potential. The *p*H was adjusted to 6.75 with NaOH. This medium was prereduced under nitrogen for a period of 1 h, using copper as reducing agent, and was subsequently dispensed into culture tubes in an anaerobic hood. Inoculated tubes were incubated at 25 °C for a period of 4 days. For isolation of magnetosomes, *M. magnetospirillum* cells suspended in 20 m*M* 4-(2-hydroxyethyl)piperazine-1-etha (HEPES)–4 m*M* chelaton 2 (EDTA), *p*H 7.4, were disrupted by sonification. The unbroken cells and the cell debris were removed from the sample by centrifugation (10 min, 3036 rpm). The cell extract was placed on NdFeB magnets for 1 h. The black magnetosomes sedimented at the bottom of the tube and the residual con-

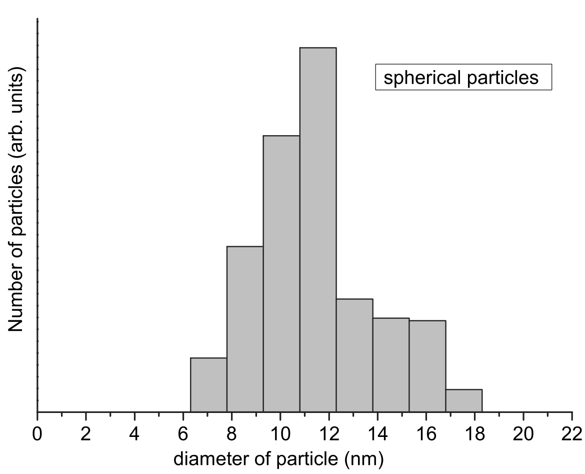

FIG. 2. Histogram of size distribution of spherical magnetic particles.

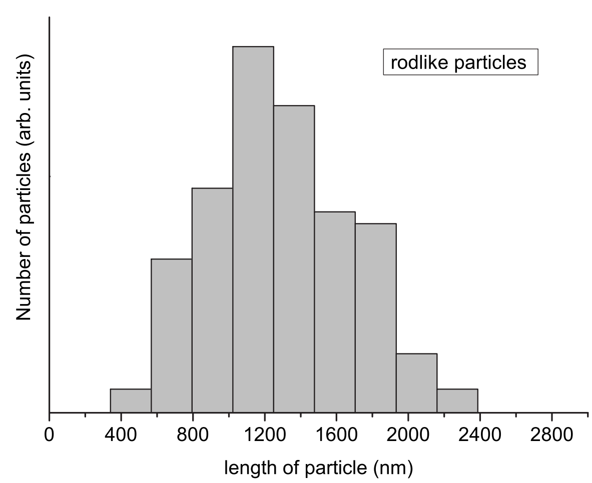

FIG. 4. Histogram of length distribution of rodlike magnetic particles.

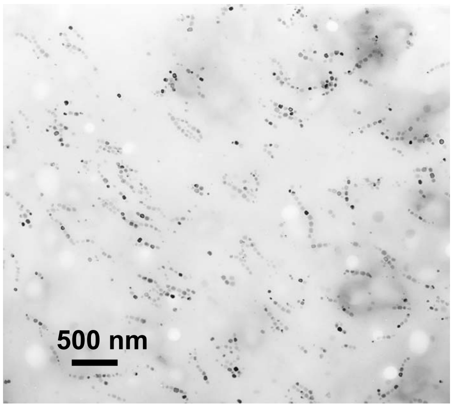

FIG. 5. TEM image of chainlike magnetic particles.

taminating cellular material was retained in the upper part of the tube and decanted. To eliminate electrostatically bound contamination, magnetic particles attached to the column were rinsed first with 50 ml of 10 m*M* HEPES–200 m*M* NaCl, *p*H 7.4, and subsequently with 100 ml of 10 m*M* HEPES, *p*H 7.4. After removal of the column from the magnets, magnetic particles were eluted from the column by flushing with 10 m*M* HEPES buffer. The magnetosome suspension (the black sediment) was centrifuged (18 000 rpm, 30 min, 4 °C). After centrifugation the cell extract was placed on the magnet for 30 min. The magnetic particles were sedimented at the bottom of the tube, whereas residual contaminating cellular material was retained in the upper part of the tube. The last procedure was repeated ten times to obtain well-purified magnetosomes. The TEM image of the chainlike magnetic particles is shown in Fig. 5. The mean size of a single magnetic particle coated with surfactant, i.e., of the magnetosome, was 34 nm (Fig. 6), so the mean length of the chainlike particles as a whole was 446 nm.

The studied ferronematic samples were based on the thermotropic nematic 4-(trans-4′-*n*-hexylcyclohexyl)-isothiocyanatobenzene (6CHBT). 6CHBT is a low-melting enantiotropic liquid crystal with high chemical stability [9]. The temperature of the nematic-to-isotropic transition (clearing point) of the studied nematic is T_{NI}=42.8 °C. The nem-

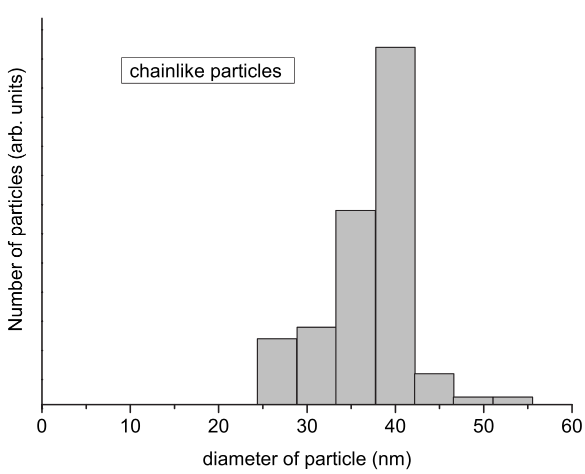

FIG. 6. Histogram of diameter distribution of the magnetosome.

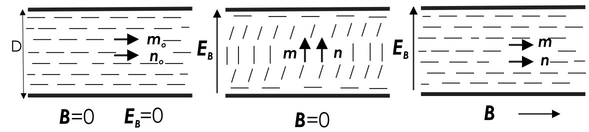

FIG. 7. Cross section of the cell in the initial state, after application of the electric field $E_B > E_C$ and after application of the external magnetic field $B > B_C$.

atic samples were doped with a magnetic suspension consisting of Fe_3O_4 particles 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 (2×10^{-4}) and surfactant in the prepared ferronematic samples, the interparticle dipole-dipole interactions are avoided. The calorimetric scans were performed by using a differential scanning calorimeter (DSC) (Mettler FP80HT) at a scan rate 4 °C min^{-1} in the temperature range from 20 up to 90 °C. No influence of the admixture of magnetic particles on the temperature of the nematic-to-isotropic transition has been observed. The structural transitions in the ferronematic samples were indicated by capacitance measurements in a capacitor made of indium tin oxide–coated glass electrodes (LINCAM Co.). A capacitor with an electrode area approximately 1×1 cm^2 was connected to a regulated thermostat system; the temperature was stabilized with an accuracy of 0.05 °C. The distance between the electrodes (sample thickness) was D=5 μm. The capacitance was measured at the frequency of 1 kHz by a high-precision capacitance bridge (Andeen Hagerling). The stability of the samples in strong magnetic fields was verified by repeating the capacitance measurements after 5 months on the same samples, with reproducible results.

The Fréedericksz transition in combined electric and magnetic fields was studied in the assumed experimental geometry shown in Fig. 7 at temperature 35 °C. In the experiments an initial alignment of the magnetic moments was achieved by applying a strong magnetic field temporarily before starting the measurement. Then the external magnetic field was switched off and the initially planar nematic layer was realigned by a strong electric field applying a bias voltage $U_B > U_F$ at B=0, where U_F is the critical voltage of the electric Fréedericksz transition,

$$U_F = \pi\sqrt{\frac{K_1}{\epsilon_0\epsilon_a}}. \tag{1}$$

Then the magnetic field was applied perpendicular to $\boldsymbol{E}$, along the initial surface alignment. The magnetic field increased the electric Fréedericksz threshold $U_c(B)$, where

$$U_c(B) = U_F\sqrt{1+\frac{B^2}{B_F^2}}, \tag{2}$$

with

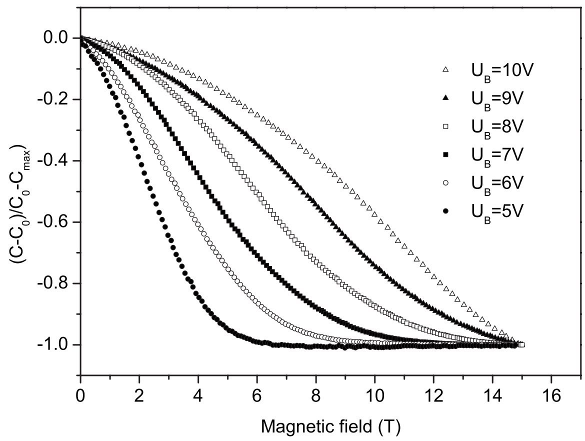

FIG. 8. Reduced capacitance dependence of 6CHBT doped with rodlike particles on external magnetic field measured at different bias voltages.

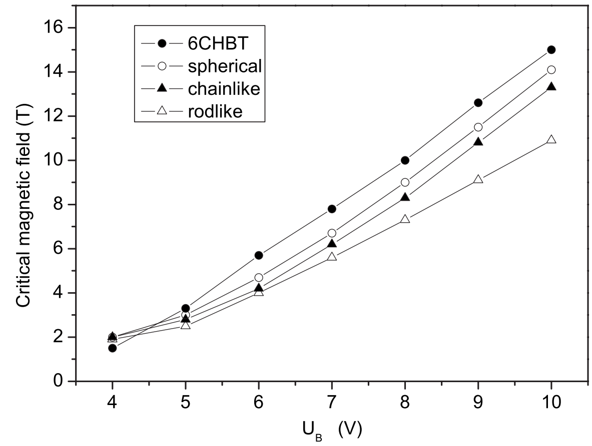

FIG. 9. Dependence of critical magnetic field on the bias voltage for pure 6CHBT and 6CHBT doped with spherical, chainlike, and rodlike particles.

$$B_F = \frac{\pi}{D}\sqrt{\frac{\mu_0 K_1}{\chi_a}}, \tag{3}$$

reducing therefore the distortion angle in the cell. At a critical magnetic field B_c, where $U_c(B_c)=U_B$, the distortion of the director disappeared and the initial planar texture was restored.

III. RESULTS AND DISCUSSION

The influence of the shape of magnetic particles on the structural transition in the 6CHBT liquid crystal was studied. The magnetic particles used were spherical, rodlike, and chainlike. In all cases the size of the magnetic particles was much greater than the dimensions of the liquid crystal molecules, i.e., the magnetic particles can be regarded as macroscopic objects floating in the liquid crystal. The surface of the magnetic particles is able to orient the adjacent liquid crystal molecules. The degree of that anchoring is characterized by the surface density of the anchoring energy W.

Observations of the structural transitions in ferronematics in an external field can be used for determination of the type of anchoring of nematic molecules on magnetic particle surfaces as well as of the surface density of the anchoring energy W at the nematic–magnetic particle boundary. During measurements 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 capacitance on the external magnetic field reflects the reorientation of the nematic molecules in a strong magnetic field. Figure 8 shows the dependence of the reduced capacitance of 6CHBT liquid crystals doped with rodlike magnetic particles on the external magnetic field at different bias voltages. From this figure it is seen that the critical magnetic field, i.e., the magnetic field that turns the molecules of liquid crystal in its direction, is shifted to higher values with increasing bias voltage. Similar dependences were observed for all samples. The values of the critical magnetic field for all samples were determined from the dependences $(C-C_0)/(C_0-C_{\max})$ versus B, where C, C_0, and $C_{\max}$ are the capacitance at the given magnetic field, the capacitance at $B=0$, and the capacitance at B when the initial planar texture is completely restored, respectively. B_c was determined as the value when the distortion of the director disappeared and the initial planar texture was restored. The values of the critical magnetic fields obtained for different values of bias voltage are summarized in Fig. 9, which shows the dependence of the critical magnetic field on the applied bias voltage for pure 6CHBT and 6CHBT doped with spherical, chainlike, and rodlike magnetic particles.

By means of Burylov and Raikher's expression for the free energy of ferronematics [8], the formula for the critical magnetic field was estimated as follows:

$$B_{CFN}^2 - B_C^2 = \frac{\epsilon_0 \epsilon_a \mu_0 U_B^2}{D^2} - \frac{2\mu_0 W \phi}{\chi_a d}, \tag{4}$$

where B_C and B_{CFN} are the critical fields of the magnetic Fréedericksz transition of the pure liquid crystal and ferronematic, respectively, U_B is the applied electric field, ϵ_0 is the permittivity of vacuum, ϵ_a is the anisotropy of the dielectric permittivity (for 6CHBT $\epsilon_a=7$), D is the thickness of the sample, d is the mean diameter in the case of spherical particles or length of magnetic particles in the case of rodlike and chainlike particles, ϕ is the volume concentration of magnetic particles in the liquid crystal (in these experiments the volume concentration of magnetic nanoparticles was $\phi=2\times10^{-4}$), μ_0 is the permeability of vacuum, and χ_a is the anisotropy of diamagnetic susceptibility of the liquid crystal (for 6CHBT $\chi_a=4.805\times10^{-7}$ at the temperature 35 °C). The surface density of the anchoring energy W at the nematic–magnetic particle boundary for different magnetic particles was determined from measurements of the critical magnetic fields for pure 6CHBT and for different magnetic particles and for different U_B at the temperature $T=35$ °C. The calculated values of surface density of the anchoring energy for spherical particles is $W_s \sim 10^{-5}$ N m^{-1}, for chainlike particles is $W_c \sim 10^{-3}$ N m^{-1}, and for rodlike particles is $W_r \sim 10^{-2}$ N m^{-1}.

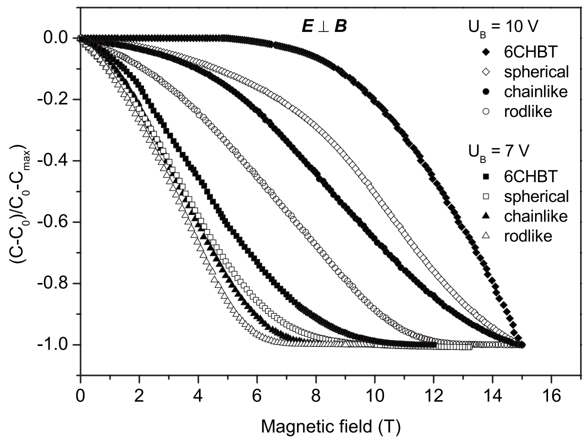

FIG. 10. Reduced capacitance dependence of pure 6CHBT and 6CHBT doped with spherical, chainlike, and rodlike particles on external magnetic field measured at $U_B=7$ V and $U_B=10$ V.

The values of W obtained were used for calculating the parameter ω (for pure 6CHBT $K_1=6.71$ pN). For spherical particles the obtained value is $\omega \sim 10^{-1}$, i.e., $\omega < 1$, which characterizes the soft anchoring of nematic molecules on magnetic particle surfaces. For chainlike particles we have obtained $\omega \sim 10^2$ and for rodlike particles $\omega \sim 10^4$, i.e., $\omega \gg 1$, which characterizes rigid anchoring.

Figure 10 shows the reduced capacitance dependence of pure 6CHBT and 6CHBT doped with spherical, chainlike, and rodlike particles on external magnetic fields measured at $U_B=7$ and 10 V. These results show that the shape and size of the magnetic particle play an important role in ferronematics and significantly influence the structural transitions in these materials. We suppose two effects that influence the behavior of ferronematics in the external magnetic field. The first one is the shape of the magnetic particles. Because the initial boundary condition for 6CHBT ferronematics was found to be parallel, magnetic particles shaped similarly to the liquid crystal molecules can better influence the orientation of adjacent molecules of the liquid crystal. The other effect could be connected to the size of the magnetic particles. The highest value of the parameter ω was found for rodlike magnetic particles that are shaped similarly to the molecules of the liquid crystal, but on the other hand their size is the largest. In order to separate the two contributing effects it will be interesting in future work to prepare and study ferronematic samples doped with magnetic particles of the same shape but of different size.

IV. CONCLUSION

The influence of the shape of magnetic particles on the critical magnetic field in 6CHBT-based ferronematics was studied. Doping with magnetic particles reduced the critical magnetic field. When the shape of the particles was changed from spherical to chainlike, the reduction increased. The largest decrease of B_C was obtained for rodlike particles. From these results it can be seen that the shape and the size of the magnetic particles significantly influence the degree of anchoring of the nematic molecules on the surface of magnetic particles and the behavior of ferronematics in the external magnetic field. The experimental results indicated soft anchoring in the case of spherical magnetic particles and rigid anchoring in the case of rodlike and chainlike magnetic particles, with parallel initial orientation between the magnetic moment of the magnetic particles and the director. It can be concluded that doping with magnetic particles shaped similarly to the liquid crystal molecules is advantageous for ferronematics in applications where the magnetic field is necessary to control the orientation of the liquid crystal molecules.

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