SANS Study of Liquid Crystal Doped with CoFe$_2$O$_4$ Nanoparticles

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In the present paper, small-angle neutron scattering results from measurements performed on 4-n-pentyl-4'-cyanobiphenyl liquid crystal and magnetic spherical cobalt ferrite CoFe$_2$O$_4$ nanoparticles suspension are presented. To prevent aggregation, the nanoparticles were coated with mesogenic ligands. Samples with two nanoparticle concentrations of 0.0854 wt% and 0.0623 wt% as well as pure liquid crystal were investigated. Measurements in zero magnetic field and in magnetic field up to 2.2 T were carried out. The samples were oriented in the cells in zero magnetic field and aligned when large enough magnetic field was applied. Moreover, the results showed a presence of elongated objects in the samples.

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1. Introduction

Liquid crystals (LC) are materials that in mesophase combine both solid crystal and liquid properties. In nematic LC molecules are oriented in a certain direction, which relates to boundary conditions. While the anisotropy of dielectric permittivity ($\varepsilon_a$) is high and therefore small electric field is needed to reorient LC molecules, high magnetic fields (≈ 1 T) [1] are necessary for reorientation due to small anisotropy of magnetic permeability ($\chi_a$). In 1970 Brochard and de Gennes proposed addition of small magnetic particles into LC [2] that led to enhanced sensitivity of LC to magnetic field due to strong coupling between LC molecules and nanoparticles. Stable suspensions of LC and magnetic nanoparticles (MNPs) are called ferronematics. Interaction of nanoparticles in ferronematics has been studied [3–6], but it is still not fully understood and the preparation of a stable suspension is still a challenge. Understanding of interaction among nanoparticles is necessary for preparing stable ferronematics with a high sensitivity to magnetic field. The present paper is focused on studying interaction of spherical CoFe$_2$O$_4$ MNPs with 4-n-pentyl-4'-cyanobiphenyl (5CB) LC by small-angle neutron scattering (SANS).

2. Materials and methods

CoFe$_2$O$_4$@mesogenic ligand(ML)-MNPs were synthesized and mixed in 5CB liquid crystal via method described in Ref. [7]. In brief, rapid injection of FeCl$_3$ solution and CoCl$_2$ solution into NaOH solution was applied to produce CoFe$_2$O$_4$-MNPs with size < 5 nm and narrow size distribution. Hydrodynamic diameter of CoFe$_2$O$_4$-MNPs, according to dynamic light scattering measurements, was 5.6 nm, that is the diameter of a particle with a shell. CoFe$_2$O$_4$-MNPs were then purified, peptized in perchloric acid and subsequently functionalized with a solution of the promesogenic ligand 16-((4'-cyano-[1,1'-biphenyl]-4-yloxy)hexadecanoic acid in dimethylformamide. After functionalization CoFe$_2$O$_4$@ML-MNPs with particle core size 3.0 (± 0.5) nm (according to transmission electron microscopy) were dispersed in ethanol. The CoFe$_2$O$_4$@ML-MNPs in ethanol were mixed in 5CB. Subsequently, ethanol was evaporated but simultaneously agglomerates arose. After evaporation the agglomerates were eliminated with a Nd$_2$Fe$_{14}$B laboratory magnet that leaves stable solution with concentration of 0.0854 wt% (sample OA). By adding 5CB to the solution the sample OB was prepared with concentration of 0.0623 wt%. The concentrations were determined by inductively coupled plasma optical emission spectroscopy.

The SANS experiments were carried out at KWS-1 instrument [8, 9] operated by Jülich Centre for Neutron Science (JCNS) at Heinz Maier–Leibnitz Zentrum (MLZ).
in Garching near Munich, Germany. The neutron wavelength of $\lambda = 5 \text{ Å}$ with wavelength spread of $\Delta \lambda / \lambda = 10\%$ was chosen. The samples in 1 mm quartz cells were placed in an automatic sample changer of the electromagnet and measured at three sample-to-detector distances, 1.5, 8, and 20 m, at room temperature. Magnetic field up to 2.2 T was applied to the samples.

3. Results and discussion

The initial 5CB LC sample and its mixture with MNPs with concentration of 0.0854 wt% (OA) and 0.0623 wt% (OB) have been measured as reference samples in zero magnetic field. The corresponding 2D images are presented in Fig. 1. Two peaks of shape like an arc appear at $q = 0.25 \text{ Å}^{-1}$, for all three samples which correspond to the distance, $d = 25 \text{ Å}$ between the liquid crystal molecules along the long axis. This can be explained by an initial orientation of the samples in the cells.

Figure 2 shows the data in the middle $q$-range for zero magnetic field. The additional scattering contribution is present only in the case of OA and OB samples, i.e., after the addition of the MNPs, and it has anisotropic shape with the maximum scattering along the direction of the LC director.

Upon the application of an external vertical magnetic field of 0.5 T the two peaks shift and align along the direction of the applied field (see Fig. 3). The measurements were repeated for the fresh OB sample with smaller magnetic field steps and we observed orientation of the LC already at 0.01 T.

We would like to point out the additional scattering contribution, upon the application of the magnetic field, orients along the field direction and becomes stronger (see Fig. 4). Further increase in the magnetic field does not lead to any qualitative changes in the scattering in the whole $q$-range.

The initial slope of the SANS curve averaged in the sector parallel to the magnetic field (see Fig. 6) is close to the power-law type with an exponent of $-1$ pointing out
to the existence of elongated objects formed by MNPs. The length of such object can be estimated only from the minimum available $q$ and is at least 130 nm. The corresponding fit with a model of cylinder gives a radius of the cross-section, which is 6.3 nm. The estimated length of the elongated object corresponds to the one obtained from SAXS (small-angle X-ray scattering) [10]. However, the obtained cross-section size is significantly smaller. The discrepancy in the diameter of aggregates acquired from SANS and SAXS may be caused due to different conditions used for fitting the SANS and SAXS curves. The samples in the isotropic phase without alignment were used for size estimation from SAXS measurements. Under these conditions the $p(r)$ function and ab initio model approach can be used. For the estimation from SANS the oriented particles were used. The SANS data were fitted by an averaged cylindrical model, i.e., non-oriented cylinder, which is a rough approximation.

4. Conclusions

The reference SANS measurements in zero magnetic field showed that 5CB LC sample and its mixture with spherical CoFe$_2$O$_4$ MNPs with two concentrations of 0.0854 wt% and 0.0623 wt% were initially oriented in the cell. When magnetic field of 0.5 T was applied both samples were aligned by field due to anchoring of LC molecules on nanoparticle surface. Moreover, further measurements with smaller magnetic field steps performed on diluted sample showed that the sample was already aligned at 0.01 T. In addition, corresponding averaged intensities in directions parallel and perpendicular to magnetic field showed a presence of elongated objects in the samples in the case of both mixtures with the length at least of 130 nm. This corresponds to SAXS measurements [10], and radius of the cross-section is $\approx 6.3$ nm.

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