SANS Study of Liquid Crystal Doped with CoFe₂O₄ 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 CoFe₂O₄ 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.

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 (ε_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 (χ_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 CoFe₂O₄ MNPs with 4-n-pentyl-4'-cyanobiphenyl (5CB) LC by small-angle neutron scattering (SANS).

2. Materials and methods

CoFe₂O₄@mesogenic ligand(ML)-MNPs were synthesized and mixed in 5CB liquid crystal via method described in Ref. [7]. In brief, rapid injection of FeCl₃ solution and CoCl₂ solution into NaOH solution was applied to produce CoFe₂O₄-MNPs with size < 5 nm and narrow size distribution. Hydrodynamic diameter of CoFe₂O₄-MNPs, according to dynamic light scattering measurements, was 5.6 nm, that is the diameter of a particle with a shell. CoFe₂O₄-MNPs were than purified, peptized in perchloric acid and subsequently functionalized with a solution of the promesogenic ligand 16-((4'-cyano-[1,1'-biphenyl]-4-yl)oxy)hexadecanoic acid in dimethylformamide. After functionalization CoFe₂O₄@ML-MNPs with particle core size 3.0 ($\pm$ 0.5) nm (according to transmission electron microscopy) were dispersed in ethanol. The CoFe₂O₄@ML-MNPs in ethanol were mixed in 5CB. Subsequently, ethanol was evaporated but simultaneously agglomerates arose. After evaporation the agglomerates were eliminated with a Nd₂Fe₁₄B 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)

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in Garching near Munich, Germany. The neutron wavelength of $\lambda = 5$ Åwith 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 $q = 0.25$ Å^{-1}, for all three samples which correspond to the distance, $d = 25$ Åbetween 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.
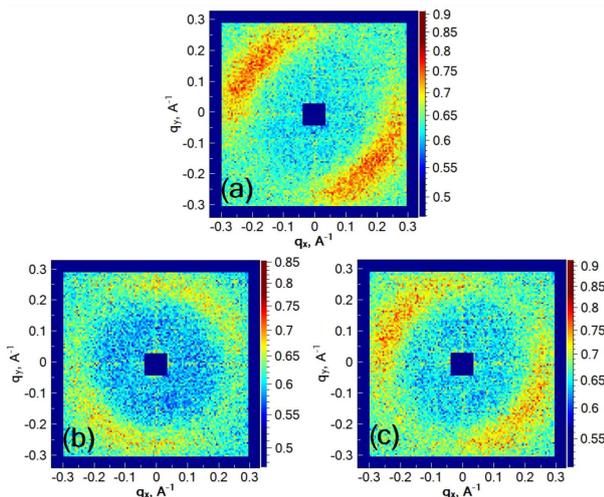
Fig. 1. 2D SANS images of (a) the 5CB LC sample and its mixture with MNPs of (b) 0.0854 wt% and (c) 0.0623 wt% in zero magnetic field.
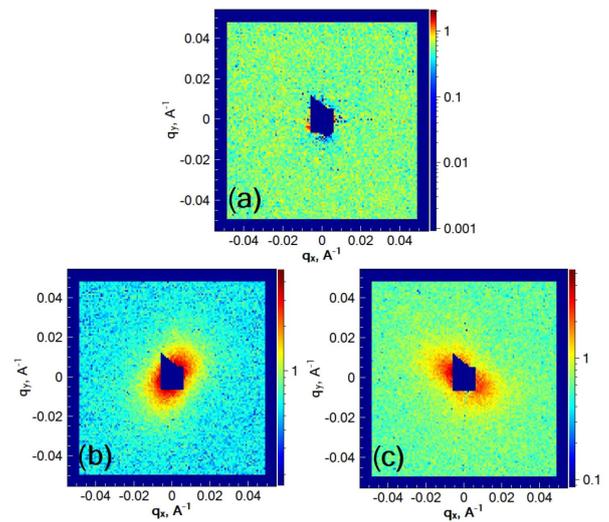
Fig. 2. 2D SANS images of the (a) 5CB, (b) OA and (c) OB sample in zero magnetic field for the middle q-range. A part of a reflex occurring in the empty cell measurement, which influenced the subtracted data, is masked.
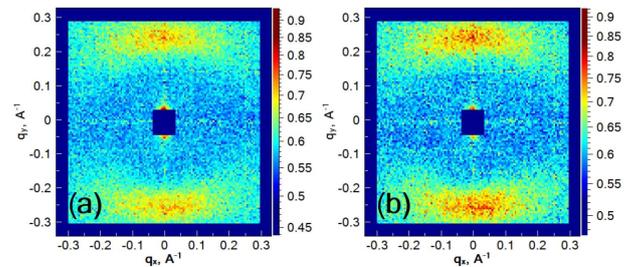
Fig. 3. 2D SANS images of (a) OA and (b) OB samples under an applied magnetic field of 0.5 T.
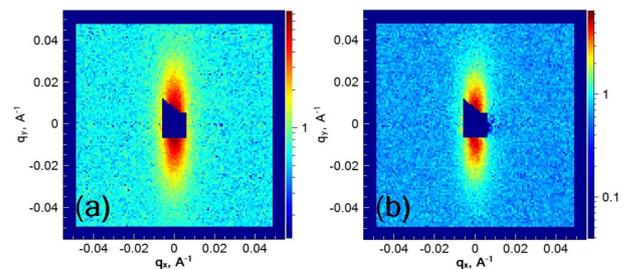
Fig. 4. 2D SANS images of (a) OA and (b) OB samples under an applied magnetic field of 0.5 T for the middle q-range. A part of a reflex occurring in the empty cell measurement, which influenced the subtracted data, is masked.

The corresponding averaged intensities in the direction perpendicular and parallel to the applied magnetic field are presented in Fig. 5.

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
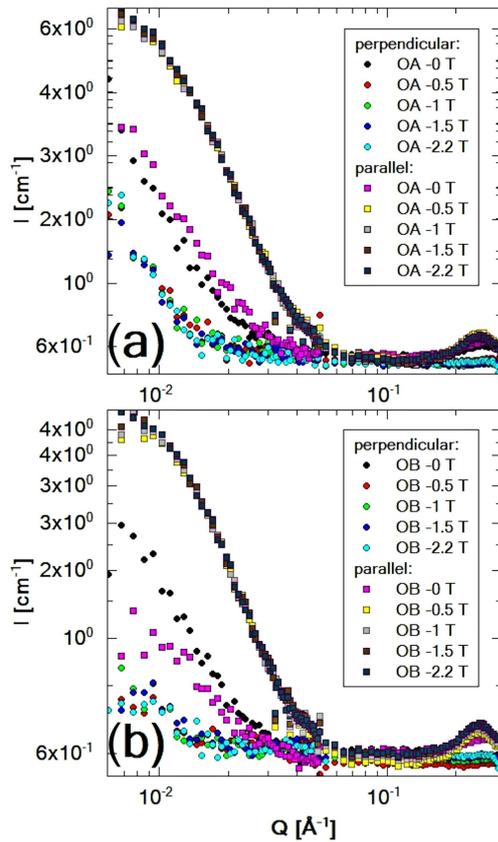
Fig. 5. Averaged scattering intensities along the directions perpendicular and parallel to the applied magnetic field for the sample (a) OA and (b) OB.

Fig. 6. Full q-range radially averaged SANS data in in sectors parallel and perpendicular to magnetic field direction for the case of (a) OA sample and (b) OB sample in 0 T and 0.5 T. Solid blue line represents a corresponding fit and solid red line represents a q^{-1} dependence of scattering intensity.

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 CoFe₂O₄ 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 ≈ 6.3 nm.

References

[1] P.G. de Gennes, *Mol. Cryst.* **7**, 325 (1969).

[2] F. Brochard, P.G. de Gennes, *J. Phys. (France)* **31**, 691 (1970).

[3] M. Skarabot, M. Ravnik, S. Zumer, U. Tkalec, I. Poberaj, D. Babic, N. Osterman, I. Musevic, *Soft Matter Phys.* **77**, 031705 (2008).

[4] J.-I. Fukuda, H. Stark, M. Yoneya, H. Yokoyama, *Phys. Rev. E* **69**, 041706 (2004).

[5] I. Musevic, M. Skarabot, U. Tkalec, M. Ravnik, S. Zumer, *Science* **313**, 954 (2006).

[6] A.T. Juhl, D.K. Yang, V.P. Tondiglia, L.V. Natarajan, T.J. White, T.J. Bunning, *Opt. Mater. Expr.* **1**, 1536 (2011).

[7] I. Appel, H. Nadasi, Ch. Reitz, N. Sebastian, H. Hahn, A. Eremin, R. Stannarius, S. Behrens, *Phys. Chem. Chem. Phys.* **19**, 12127 (2017).

[8] A.V. Feoktystov, H. Frielinghaus, Z. Di, S. Jaksch, V. Pipich, M.-S. Appavou, E. Babcock, R. Hanslik, R. Engels, G. Kemmerling, H. Kleines, A. Ioffe, D. Richter, T. Brückel, *J. Appl. Crystallogr.* **48**, 61 (2015).

[9] Heinz Maier-Leibnitz Zentrum, H. Frielinghaus, A. Feoktystov, I. Berts, G. Mangiapia, *J. Large-Scale Research Facilities (JLSRF)* **1**, A28 (2015).

[10] V. Gdovinová, M.A. Schroer, N. Tomašovičová, I. Appel, S. Behrens, J. Majorošová, J. Kováč, D.I. Svergun, P. Kopčanský, *Soft Matter* **13**, 7890 (2017).