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Effect of Magnetic Nanoparticles and Their Functionalization on Liquid Crystal Order

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We have added magnetic nanoparticles with a different surface termination (functionalization) to smectic A 8CB liquid crystals and studied their effects on the order of the liquid crystal. This is done by looking at the liquid crystals both with polarized optical microscopy and by X-ray scattering. Adding the magnetic nanoparticles improves the liquid crystal's response to a magnetic field by at least one to two orders of magnitude. We have performed the experiments with four types of organic compounds covering the nanoparticles and have found that with 11 nm particles covered with polyethelene glycol (PEG) 3000 the liquid crystal exhibits the largest effect as a function of the applied magnetic field.

Keywords: liquid crystal reorientation; magnetic field; magnetic nanoparticles; surface termination

INTRODUCTION

Liquid crystals are known to be diamagnetic molecules. When a magnetic field in the order of 3–4 T is applied to them, the liquid crystals

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align with the magnetic field [1]. In 1970, Brochard and de Gennes proposed a theory in which liquid crystals were doped with small magnetic particles [2]. These had the effect of reducing the magnetic field at which the liquid crystal oriented with the magnetic field [2–6]. Fabre *et al*. [6] worked with a hybrid lytropic system that consisted of γ-Fe_2O_3 particles, sodium dodecyl sulfate and 1-pentanol, and observed an anisotropic response to magnetic fields, suggesting an anisotropic alignment of the magnetic moments within the lamellae. The mixture of liquid crystals and magnetic nanoparticles is known as a ferrosmectic or a ferronematic, depending on which is the phase of the liquid crystal.

The inorganic magnetic nanoparticles need to be surface treated in order to mix them with the organic liquid crystal, otherwise they phase separate [7]. Surface-treated iron oxide particles intercalate in the oily (hydrophobic) region between the organic molecules double layer [6]. Intercalation of iron oxide particles results in an increased anisotropic response to magnetic fields. This interaction can induce a reorientation of the organic lamellae, depending on the applied magnetic field direction. This involves a rupture of the lamellae sheets and a reorganization of the molecules within these. The reorientation can be observed under the polarizing optical microscope by looking at the birefringence change as a function of the magnetic field [4,6]. Once the magnetic field is removed the original orientation is recovered [6].

The surface treatment can also determine with which molecules the magnetic nanoparticle will interact more strongly. In this way, the surface treatment can be used as an identifier of either the liquid crystal or a material it supports, such as the proteins in the cell walls. In this study, we have observed the response the liquid crystal exhibits to an 11 nm particle of $Fe_{48}Co_{52}$ (FeCo) covered with four different surface treatments, as a function of the strength of the magnetic field. Recently, we have observed the response of the liquid crystal in the magnetic field when particles of a different size (2 nm) are mixed with the liquid crystal.

EXPERIMENTAL

The magnetic nanoparticles were synthesized using the polyol process. Iron (II) chloride, cobalt acetate and sodium hydroxide were refluxed for 1 hour in 1,2 propanediol and then allowed to cool to room temperature. The mixture was then centrifuged, the supernatant discarded and the precipitate redispersed in ethanol. The resulting powder was washed three times with ethanol and then magnetically separated out. The particle size was determined by differential light scattering

(DLS), transmission electron microscopy (TEM) and X-ray diffraction. The particles of FeCo, 11 nm in size, were then surface functionalized with, 1. mPEG-SPA, (MW 3400, Shearwater), or n-hydroxy succinimide/polyetheleneglycol (NHS/PEG); 2. Polyetheleneglycol molecular weight 3000(Fluka), or PEG(3000); 3. 3-Aminopropyltriethoxysilane (APTS) (Gelest), and NHS/PEG, or APTS/NHS/PEG; and 4. Mercaptohexadecanoic acid (MHDA) (Aldrich), and NHS/PEG, or MHDA/NHS/PEG. These were chosen to be able to identify either different liquid crystals or different materials in the liquid crystals.

The liquid crystal octylcyanobiphenyl (8CB) was then mixed with the nanoparticles. 8CB was obtained from British Drug House and used as received. This liquid crystal has a double layer spacing of 3.15 nm. The magnetic nanoparticles are added until they are approximately 30% weight of the mixture with 8CB. We have found that less than 30% weight does not give us significant results when we observe the liquid crystal-particle system with the microscope. The mixture is placed in an ultrasound and is sonicated at the smA – Nematic transition temperature for 8CB, which is 35°C, for eight hours [6]. The temperature is raised and the mixture is sonicated at 40°C, the nematic-isotropic transition temperature, for five hours.

Once mixed, a drop is placed in a microscope slide to observe the mixture in the microscope. The microscope is in polarizing mode and observations are made with a 200x magnification. To make observations in the presence of the magnetic field, two neodynium magnets placed in an aluminum holder in the microscope are used. The magnetic field strength is determined by how close the magnets are placed with respect to each other. The microscope lenses limit how close we can place the magnets. The magnetic field strength obtained with the magnets with the lens limitation is 127 mT.

The same microscope slide is placed in another aluminum holder to observe the changes that occur with the X-rays. In this holder the magnetic field can be varied up to 423 mT and above depending on the size of the microscope slide. The holder is placed in the X-rays, and the orientation of the liquid crystal is monitored in the direction parallel to the field H, as illustrated in Figure 1. The X-ray experiments were performed using a Rigaku rotating anode with a Cu (1.54 Å) source, and a bent graphite monochromator with a resolution of $\Delta q = 0.012 q_o(\text{Å}^{-1})$, operating at 50 kV and 100 mA. In the magnetic field, we scan five times to observe if there are any changes that occur as a function of time. All measurements were taken at room temperature, where the 8CB is in the Sm-A phase. We heat the sample that has been in the magnetic field to the isotropic and let it cool before we repeat the measurements to repeat the experiment.

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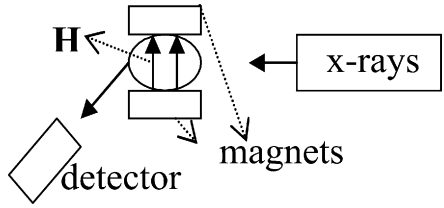

FIGURE 1 Top view of the experiment, showing the position of the magnets, the direction of the magnetic field, and the X-rays. The liquid crystal reorients according to this direction.

RESULTS AND DISCUSSION

The microscope experiment served to confirm that there was a rearrangement before putting the samples in the X-rays. Under cross polarizers we see that the sample darkens when we apply the magnetic field. We then heat the sample into the isotropic, and place the same microscope slide in the X-rays to do the detailed structural

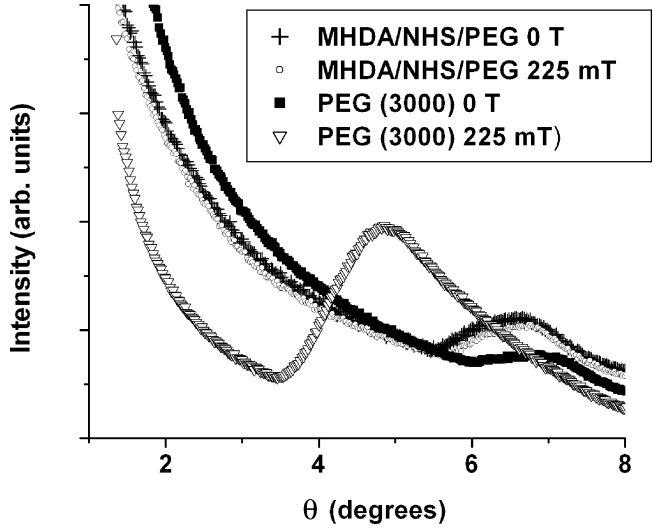

FIGURE 2 comparison of the 8CB and the PEG (3000) covered 11 nm FeCo nanoparticles with 8CB and the MHDA/NHS/PEG covered nanoparticles. The graphin an X-ray scan of the intensity versus the angle 2θ. Note that the nanoparticles covered with PEG (3000) have the largest effect on the 8CB whereas the MHDA/NHS/PEG covered particles have no effect in a 225 mT magnetic field.

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measurement. Figure 2 presents the results for two samples, the one where the 11 nm particle is covered with PEG (3000) and the one where it is covered with MHDA/NHS/PEG with and without a field of 225 mT. Note that 225 mT is about one order of magnitude smaller than the magnetic field needed to realign the liquid crystal alone. We observe that in the absence of a magnetic field the liquid crystal does not lie in the plane. The length or layer spacing observed is 1.298 nm as opposed to 3.15 nm. This corresponds to a tilt of 65.7° with respect to the direction of the magnetic field, which corresponds to the plane of the microscope slide. When a field of 225 mT is applied the sample with PEG (3000) aligns along the plane of the microscope slide. The length observed is 1.839 nm as shown in Table I, which corresponds to a tilt of 54.3°. The field of 225 mT does not have an effect with the sample covered with MHDA/NHS/PEG. The other two surface functionalization covers lie intermediate between these two extremes, as can be seen in Table 1.

The sample covered with PEG (3000) has the highest molecular weight and longest molecular length covering the particle. However, it only has one compound surrounding the nanoparticle, as opposed to the other surface coverages, which may mean that the liquid crystal interacts with a "smooth" surface particle that can drag it and realign it more easily. The other surface coverages consist of smaller molecules of different lengths that can effectively make the nanoparticle uneven and almost invisible to the liquid crystal such that at low magnetic fields it does not react to the magnetic field, as in the MHDA/NHS/PEG or barely does, as in the case of the other two surface coverages.

If we take the PEG (3000) and increase the magnetic field to 362 mT we observe two peaks, one at 4.412 nm and the other at 1.512 nm, as can be seen in Figure 3. The first peak corresponds to two molecules of 8CB, which have a layer spacing of 2.2 nm and the second corresponds to the higher of the two peaks which make up the peak at

TABLE 1 Effect of the Functionalization Compound on the Rotation of the Liquid Crystal Under a Magnetic Field of 225 mT. The Angle 2θ is Read Directly from the X-rays Scans, such as Figure 2 and 3

Functionalization	2θ(°)	Layer separation (nm)
NHS/PEG	5.75	1.535
PEG (3000)	4.80	1.839
APTS/NHS/PEG	5.80	1.522
MHDA/NHS PEG	6.80	1.298

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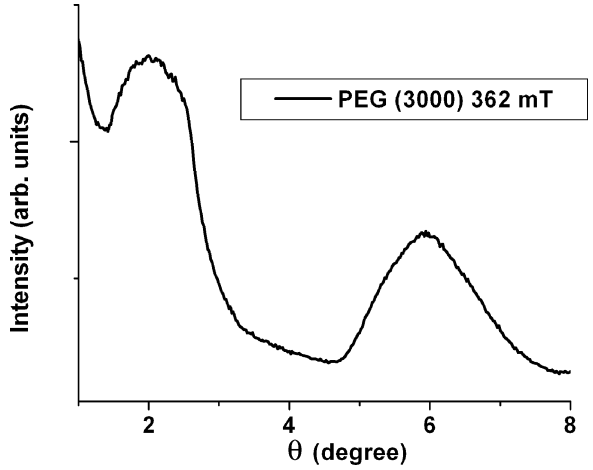

FIGURE 3 The PEG (3000) covered nanoparticles and 8CB under a field of 362 mT. The figure is an X-ray scan of the intensity versus the anlge 2θ. Note that part of the sample has rotated such that the liquid crystal is parallel to the field and shows a length of 4.412 nm.

225 mT for the PEG (3000) sample (see Fig. 2). The fact that the first peak is at 4.412 nm and not the 3.15 nm length of the double layer of the liquid crystal probably means that the nanoparticles go in between the −CN group of the liquid crystal, disrupting the double layer. This has to be further studied as well as the fact that we still have a peak at 1.512 nm. We are still in the process of looking at the other surface terminations in the 362 mT field.

Recently, we have begun to investigate the effect of the particle size in the reorientation of the liquid crystal. The preliminary study shows that for 2 nm particles covered in PEG (3000) the effect of the magnetic field is not as large as with the 11 nm particles we have presented here in Figures 2 and 3 and that part of the liquid crystal rotates to a larger angle. In other words the liquid crystal tends to reorient with its long axis perpendicular to the direction of the magnetic field. This needs to be looked at in more detail.

CONCLUSIONS

In this study we have found that the surface cover (functionalizing compound) influences how a nanoparticle of a certain size realigns the sm-A liquid crystal. This effect depends on the particular functionalizing compound, and how many functionalizing compounds

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surround the nanoparticle. We have preliminary evidence that the functionalizing compound combined with the size of the nanoparticle influences and changes how the liquid crystal behaves. We have found that the magnetic field at which the liquid crystal realigns with the magnetic nanoparticles is about one order of magnitude smaller than the one needed to realign it with the liquid crystal alone.

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