ESRF	**Experiment title:** **Nano-structured and oriented hybrid materials from magnetic nanorods**	**Experiment number**: 02-01-799
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Report:

The purpose of this experiment was to study hybrid systems consisting of rodlike magnetic particles suspended in a polymer matrix, aiming to obtain **homogeneous** and **stable** materials with a **controlled anisotropy** given by the variable degree of alignment of the inserted particles.

Experimental

Goethite is an iron hydroxide with the general formula FeOOH. Following a well-established synthesis, it can form rodlike, polydisperse nanoparticles[1]. At low volume fractions, aqueous suspensions of goethite nanoparticles are isotropic. At concentrations above 6.7 vol%, the suspensions become nematic. Moreover, the suspensions have interesting magnetic properties. The nanoparticles align with their long axes parallel to a low-strength magnetic field (B<250 mT), and perpendicular to a high-strength magnetic field (B>250 mT).

For this experiment, the goethite nanoparticles were dispersed in a mixture of water and 2-hydroxyethyl methacrylate (HEMA) and a few weight percent of an initiator. The orientation of the particles was controlled by the application of an external magnetic field during sample preparation.

The experiment was performed in the standard SAXS configuration of D2AM, at an energy of 10.7 keV and a sample-detector distance of 1.62 m. In these conditions, the accessible wave vector range was about $0.007-0.16$ Å^{-1}, very well adapted to the relevant length scales in the sample. We used the motorized sample changer available at the beamline.

Results

We were able to prepare hybrid materials for concentrations $\phi \leq 5.56$ %, at which the goethite dispersions are isotropic; above this threshold (in the nematic phase) the samples demix upon polymerization. For each concentration, we prepared samples in flat glass capillaries (50 µm thick and 1 mm wide) and polymerized them under UV light while applying a constant magnetic field *B* along the width of the capillary. As expected, the particles align along the field at low *B* values and perpendicular to it at high field (see Fig. 1.) We emphasize that all measurements were performed after polymerization, in the absence of the field, showing that the final materials preserve the particle orientation imparted upon preparation.

[1] B. J. Lemaire et al., *Eur. Phys. J. E* **13**, 291-308 (2004)

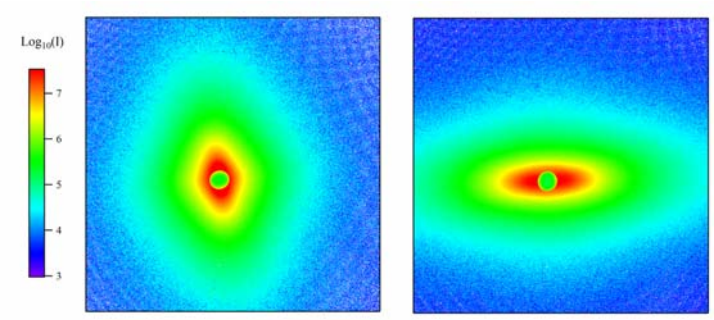

Figure 1: SAXS patterns for two samples polymerized under magnetic field. Left: ϕ=5.58 % and B=0.2 T (alignment along the field, S>0). Right: ϕ=4.31 % and B=1.5 T (alignment perpendicular to the field, S<0). No magnetic field was applied at the time of the measurement.

In Figure 2 we show the order parameter S induced by the presence of the field, determined by analysis of the SAXS patterns (left) and by measuring the optical birefringence of the samples.

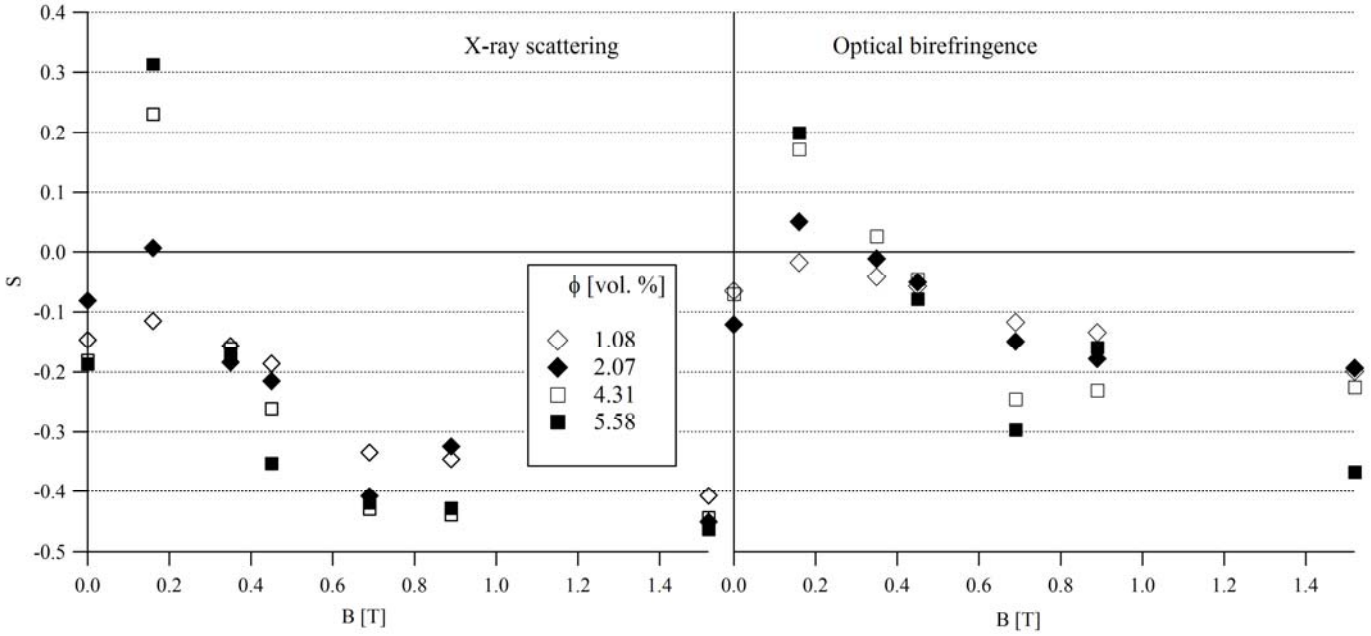

Figure 2: Order parameter S as a function of the magnetic field B applied during polymerization. (Left) Determined from the SAXS patterns. (Right) Determined from the optical birefringence of the samples, Δn. Different symbols correspond to different volume fractions ϕ of goethite, indicated in the legend.

The two methods yield reasonably close values. It should however be emphasized that the SAXS patterns yield additional (more microscopic) information, which is completely lost at optical length scales: on the one hand, we are thus able to confirm that the particle distribution is indeed homogeneous; a more detailed analysis of the structure factor for the system of rods is under way. On the other hand, we can discriminate between unimodal orientational distributions (such as those shown in Fig. 1) and defective samples where a bimodal distribution is encountered, due to preparation problems.

In summary, we were able to complete the experimental program detailed in the proposal, obtaining hybrid materials with up to 5 vol.% magnetic nanorods. The results presented above are being prepared for publication[2]; they also open the perspective of more complex formulations, based for instance on doped lamellar phases[3], where the orientational order of the rods is combined with the positional (layered) order imposed by the surfactant membranes.

[2] F. Périneau et al., in preparation.
[3] D. Constantin, P. Davidson, and C. Chanéac, *Langmuir* **26**, 4586-4589 (2010).