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Orientational behavior of an assembly of superparmagnetic rods

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Abstract

In a previous article, we described the synthesis and magnetic characterization of superparamagnetic elongated assembly of iron oxide nanoparticles and block copolymers by electrostatic interactions. We demonstrated that those rod-like aggregates preserved the superparmagnetic behavior of the magnetic nanoparticles that are included in it. Here we investigate the dynamic behavior of those rods using optical dynamic birefringence measurements on rods samples made from different lengths. Herein we confirme the superparamagnetic behavior of the magnetic rods and emphasize a new method for the determination the ensemble averaged length of the rods by a macroscopic optical method.

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Keyword: Superparmagnetic; nanorods; nanoparticle; optical birefringence; controlled aggregation

1. Introduction

Magnetic nanoparticles (MNPs) inspired a lot of research in order to use there intrinsic properties to build supported drug delivering cargos, local probes or MRI contrast agents by combining organic molecular activities and magnetic driving forces[2]. Magnetic properties of magnetic architectures can also been enhanced by a local increase of the nanoparticle concentration, such as preparing nanoparticles aggregates with well controlled sizes and shapes.

In a previous article, we described the synthesis of rod-like aggregates made by attractive electrostatic interactions between a neutral / positively charged block copolymer and maghemite nanoparticles to prepare dense aggregates from 1 µm to 100 µm long with a diameter of 100 to 300 nm. By measuring the rotational dynamics of the reorientation of magnetic rods initially perpendicular to the applied magnetic field by optical microscopy, we demonstrated that the rods preserved the superparamagnetic behavior of the nanoparticles. Here we compared those reorientation measurements to macroscopic experiments consisting in detecting the optical birefringence originating from the uniaxial symmetry induced by the application of a magnetic field. We measured the characteristic time to

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orientate all rods and reach a maximum birefringence intensity on several samples of rods differing by their magnetic field value during preparation and hence by their distribution of long axis values.

2. Measurement details

2.1. rods preparation

The protocol for the elaboration of nanostructured rods has been reported recently. Solutions of a double hydrophilic block copolymer $PTEA_{11k}$–*b*-PAM_{30k} (Rhodia Inc. France) and of PAA_{2k}-coated iron oxide nanoparticles[3] were first prepared in 1 M ammonium chloride (NH_4Cl) at weight concentration c = 0.2 wt%. The two solutions were then mixed at a ratio X of iron oxide compared to copolymer, yielding a disperse solution where polymers and particles were not yet associated (figure 1). The absence of interactions between particles and polymers at high salt content was carefully checked by dynamic light scattering. The screening of the electrostatic interactions was then suppressed by a slow removal of the salt by dialysis under controlled magnetic field.

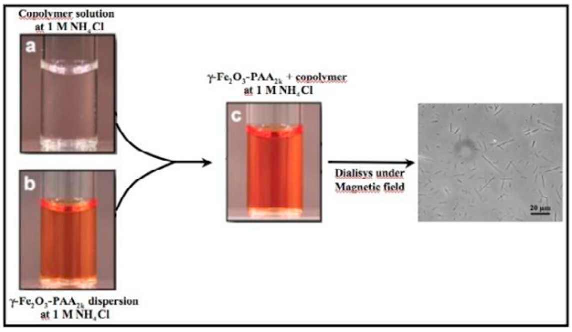

Figure 1: Synthesis pathway of superparamagnetic nanostructured rods

Once the ionic strength of the dialysis bath reached its stationary value (typically 10^{-2} M), the magnetic field was removed and the rods solutions are stored as prepared. Electronic scanning images of the rods are shown in figure 2.

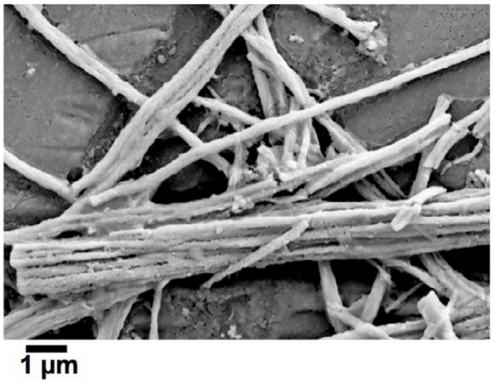

Figure 2: SEM images of superparamagnetic rods

2.2. orientation measurements

In a previous article[1], we studied the rotation of superparamagnetic rods in water due to a π/2-flip of the magnetic field. We determined a scaling law between the characteristic time of the rotation and the ratio H/L (where H is the magnetic field amplitude and L is the length of one rod). Those experiments were achieved using an optical microscope to observe each rods rotating in the π/2-flip magnetic field. The rotational angle was compiled versus time. Experiments were carried out for rod lengths 5–50 µm and magnetic fields 10^3 –10^4 A m^{-1}. The decrease of the reorientation was found to depend mainly on two parameters: on the one hand the strength of the magnetic field H and on the other hand the length L of the rod. More precisely, the decay time τ of the tangent of the orientation angle scales with the ratio $(H/L)^2$ (figure 4 : open symbols).

When inertial terms are neglected, the rod relaxation results from the balance between the magnetic and the hydrodynamic torques, yielding a differential equation for the time evolution that are given elsewhere[1,4]. The scaling law can be understood "with the hands" by the fact that the magnetic torque is proportional to $\Delta\chi H^2 D^2 L\sin(2\theta)$ (where $\Delta\chi$ is the susceptibility and D the rod diameter) while the viscous torque varies like $\eta L^3 d\theta/dt$ (according to J. Perrin's law).

As all these results were obtained looking at rods one by one, a statistical study is really time consuming to characterize a whole sample of polydisperse rod lengths. We emphases to measure this rotation decay time for a larger population of rods. Because the alignment of a huge number of micrometric rods induces optical anisotropy, we used optical birefringence to analyze the orientation of rod samples due to the application of an external magnetic field.

2.3. Dynamical birefringence measurements

Birefringence measurements were achieved using a home made system made with a 632.8 nm laser, a polarizer, the sample cell in a solenoid, an analyzer and the photodiode. Different current amplitudes in the coil are applied to vary the magnetic field amplitude. The magnetic field is maintained until the optical signal reaches a plateau (figure 3). The plateau level is directly proportional to the magnetic field amplitude.

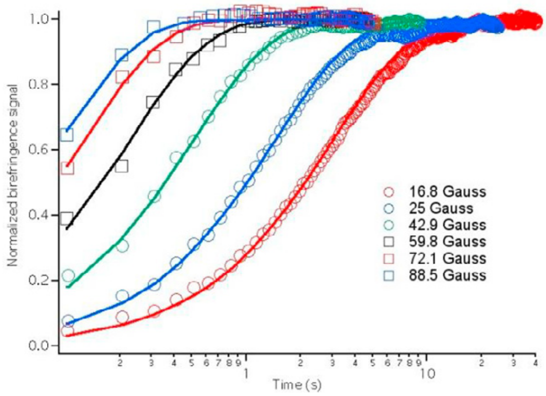

Figure 3 : Normalized birefringence signal for 8,45 µm length rods versus time for different magnetic field amplitudes (solid lines : exponential fits)

The birefringence signal is analyzed in terms of alignment of the rods when the magnetic field is switched on (*field raise-up*) and their orientation randomization when the magnetic field is switched off (*field relaxation*). Here we only focused on the field raise-up experiments. Figure 3 showed the typical signal obtained for the increase of signal due to the magnetic field. All signals are normalized to unity in order to compare the relaxation process for different magnetic field amplitudes. For each sample, up to 8 magnetic amplitudes are used in order to obtain different values of the H/L ratio defined previously.

3. Discussion

The birefringence characteristic time is measured for different samples that have increasing mean lengths from 5.84 µm to 11.86 µm. Those means lengths are obtained by analyzing the lengths of rods in a sample and by fitting the length distribution by a lognormal law. Results of optical microscope analysis are shown in table 1.

Table 1: Synthesis magnetic field amplitude, length and dispersity of a lognormal law for 5 rod samples

Sample	Synthesis B (Gauss)	L (µm)	Sigma
1	280	5,84	0,26
2	370	7,1	0,39
3	580	8,91	0,45
4	1780	11,86	0,49
5	4880	9,71	0,45

For each orientation signal, the decay time τ is determined by a mono-exponential fit. The inverse of those characteristic times are plotted *versus* H/L, where H is the magnetic field amplitude and L the mean length of the rods in the sample. Results for 5 samples are plotted on figure 4. The diameter D of the rods are assumed to be all in the same range, so that the scaling law take the following expression:

$$\frac{1}{\tau} = \frac{\chi^2}{2+\chi} \frac{\mu_0 g(L/D)}{2\eta} D^2 (\frac{H}{L})^2 \qquad (1)$$

A model is developed to explain the birefringence results. The birefringence experiments fit well with the optical measurement data, due to a common orientational process. Those experiments give us the opportunity to have several ways to determine both the magnetic susceptibility and mean size of an unknown sample, so that the characterization of magnetic rods can be achieved easily.

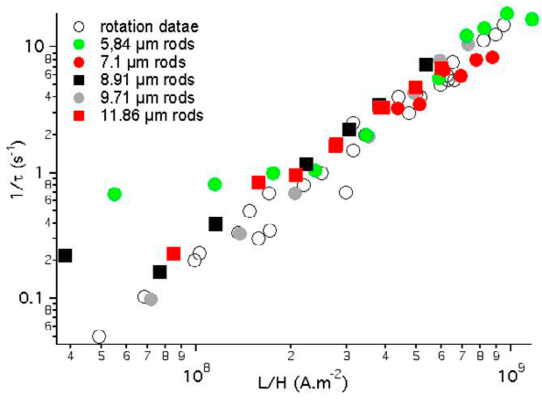

Figure 4: Master curve of the relaxation rates (inverse of relaxation times) versus *H/L* determined either from π/2 flips of rods studied individually by optical microscopy or from ensemble averages given by dynamic birefringence experiments

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