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SELF-ALIGNMENT OF INORGANIC BIOMIMETIC LIQUID CRYSTALS: MAGNETIC FIELD EFFECTS

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The Al-Fe hydroxide system is one of a limited number of inorganic liquid crystals systems. It is a biomimetic analoque to collagen, and has the advantage that it can be prepared with a specific size, so its self-alignment can be studied as a function of size. It responds to surface forces as well as magnetic fields. For a grated surface, we find that the smaller (<300 nm) and intermediate (2-3 μm ellipsoidal plates) particles align following the contour of the surface, whereas the large particles (>2 μm equiaxed plates) tend to agglomerate and sit on the surface with no order at all. When we apply a magnetic field to the particles on the surface, we find that, for the smaller particles, there is a competition between the magnetic field and the surface. The top particles will align with the magnetic field. The intermediate particles act as though they are large particles, and tend to agglometrate in the magnetic field, even in the presence of a grated surface. The large particles behave the same as in contact with the surface. The smaller particles behave like an organic liquid crystal.

Keywords: biomimetic particle; interface structure; inorganic liquid crystal; magnetic field behavior; size dependence

INTRODUCTION

Smectic ordering has been observed in colloidal systems, such as dried $\beta - FeOOH$ colloidal crystals, [1,2] and solutions of materials consisting of hard-rod-like particles, such as the tobacco mosaic virus (TMV) [3].

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Elongated, spherocylindrical particles undergo liquid crystal transitions as the density of particles in solution increases [4,5]. This behavior has also been observed in a novel Al-Fe mixed oxide system (AlFe) [6], which exhibits the following transitions as a function of decreasing water concentration in a grated surface: isotropic–self alignment–hometropic (smectic)–and striped domain (smectic) liquid crystal transitions. A similar transition was observed in nematic liquid crystals on rubbed surfaces [7]. This is true of the $15\times150\,\mathrm{nm}^2$ sample (short) [6] and the $150\,\mathrm{nm}\times2\,\mu\mathrm{m}$ ellipsoidal plate sample (intermediate). The large ($>2\,\mu\mathrm{m}$) sample does not exhibit this transition, in part because the particles are more rounded (circular) than spherocylindrical. Because the particles contain Fe^{3+} atoms, they also respond to a magnetic field and go into competition with the surface forces when the magnetic field is applied.

The AlFe inorganic polymer was modeled after the collagen macromolecule and exhibits self assembly behavior similar to that of collagen. Depending on the type of self-alignment, collagen can form bone or skin. Like collagen, its ability to self align depends on its size and surface interactions. Unlike collagen, the self assembly behavior of AlFe is easier to classify according to its self-alignment, since it can be synthesized in specific sizes, with a narrow size variation [8]. This feature of AlFe particles along with the unique magnetically induced liquid crystal behavior, makes this system suitable for studying aspects of biological self assembly such as hierarchical structure development in collagen and bone reconstruction.

EXPERIMENTAL

Solutions of AlFe hydroxy macromolecule particles have been prepared in by a chemical synthesis procedure [8]. These samples are diamagnetic through the Fe^{3+} atom. The particles are ellipsoidal in shape, except the larger ones. This implies that the presence of an anisotropic substrate as well as the application of a magnetic field will reorient the particles. It also means that we can study this reorientation by observing their birefringence under a polarizing microscope. Three characteristic samples have been observed: $15\,\mathrm{nm}\times150\,\mathrm{nm}$ cigar-shaped rods (short); $500\,\mathrm{nm}\times2\,\mu\mathrm{m}$ ellipsoidal plates (intermediate); and $>2\,\mu\mathrm{m}$ in diameter equiaxed plates (large). The observed transformations are lyotropic in nature. The controlling parameter for the observed phase transformations in the AlFe particles is the change of density of the particles as a function of time [4,6]. In order to monitor the particle alignment induced phase transformations of the AlFe particle suspensions, an Olympus BLX polarizing microscope, with a 200X, 500X and 2500X magnification, connected to a CCD camera and video system was used. AlFe particle suspensions were placed

between the crossed polarizers of the microscope, and its transformation was recorded as a function of time. During the time we recorded the transformation, the AlFe suspension was allowed to dry so the particles could settle in the grating.

The AlFe suspensions are of interest in the field of bone reconstruction, which makes it interesting to see how they align with different substrates and whether they can be handled with external fields. In the initial study of surface interactions of the AlFe suspensions, photolithographed gratings were used similar to those used in our studies of liquid crystal alignment, because of the morphological similarity between the AlFe system and nematic [7] and smectic [9] liquid crystals. The gratings have proved effective in aligning smectic liquid crystals [9]. The grating walls aligned the long axis of the liquid crystals with the long axis of the grating's grooves. The gratings were prepared following a modified etching procedure [10]. The grating period used was 9 μm, with an average channel size of 5–6 μm and a depth of 1.5 μm.

The samples were observed with and without adding a small amount of a 0.005 M HNO_3 solution. The acid enhanced the colloidal stability of the AlFe particle suspensions and prevented the particles from clumping together. The samples were exposed to a 2mT magnet from the beginning of the experiment. The magnet was oriented perpendicular to the gratings and in the plane of the sample. The magnet covered an area that was larger than the grating's, which guaranteed its homogeneity over the sample. The order imposed by the magnet was retained by the sample after the transformation occurred.

RESULTS AND DISCUSSION

We have shown previously [6,9,10] that the surface force arising from the grating reorders the sample such that it aligns with its long axis along the edge of the grating. The external forces sometimes result in a striped domain phase, where the orientation of the liquid crystal alternates between being perpendicular or homeotropic and being parallel or homogenous [7].

The short sample exhibited a competition between the grated surface and the magnetic field, as shown in Figure 1. The time to finish the alignment was twenty-five minutes. We show in Figure 1a the final structure after the transition of the suspension without the magnetic field. The picture was taken under crossed polarizers. The striped domain phase is the result of the particles aligning with the walls of the gratings. In Figure 1b, the suspension has been exposed to the 2mT magnetic field perpendicular to the gratings. The experiment was repeated several times,

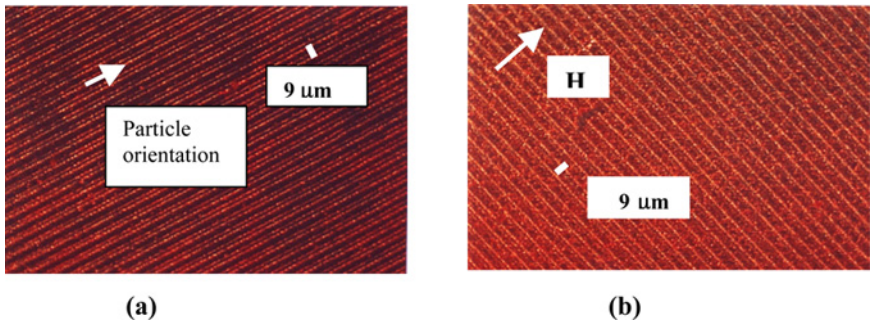

FIGURE 1 (a) The short sample without a magnetic field after the transition. The striped domain is due to the particles aligning with the corners of the grating. The white arrow shows the orientation of the long axis of the molecule. (b) The short sample under a 2 mT magnetic field. The orientation of the magnetic field is shown in the white arrow. The top particles align (see the top of the picture) with the magnetic field while there is still a weak striped domain at the bottom of the film. (See COLOR PLATE V)

and all times the result was the same. Compared to Figure 1a, the structure shows birefringence in the direction of the magnetic field (see arrow) as well as along the gratings. The particles at the top of the film align with the magnetic field whereas the particles at the bottom of the figure align with the grating, forming a striped domain surface (see the top of Fig. 1b). When the magnetic field is oriented parallel to the grooves of the grating, the order along the grooves is further enhanced and the sample does not exhibit a twist. The depth at which the sample twists has not been determined yet. We will try different magnetic field strengths to see if there is a point where the striped domain phase is broken.

The intermediate sample with acid completed its transformation in twenty-five minutes. Without the magnetic field, one can observe a weak striped domain, as shown in Figure 2a. However, with the magnetic field the particles do not align with the grating. Thus Figure 2b is all dark under cross polarizers. This implies it has transformed into a homoetropic phase or it has disordered. We tried to clarify this by using a $\lambda/4$ wavelength filter. This revealed that the particles tended to clump together and move towards the magnet when the magnetic field was applied. The clumps did not follow the grating, even though the individual particles were elongated. These clumps underwent a transition whereas they turned darker (more homeotropic) within ten to fifteen minutes, and afterwards continued to grow in size until twenty minutes passed. After twenty-five minutes, the sample was completely dry.

The large sample tended to clump together, with or without the magnetic field similar to the intermediate sample under the magnetic field.

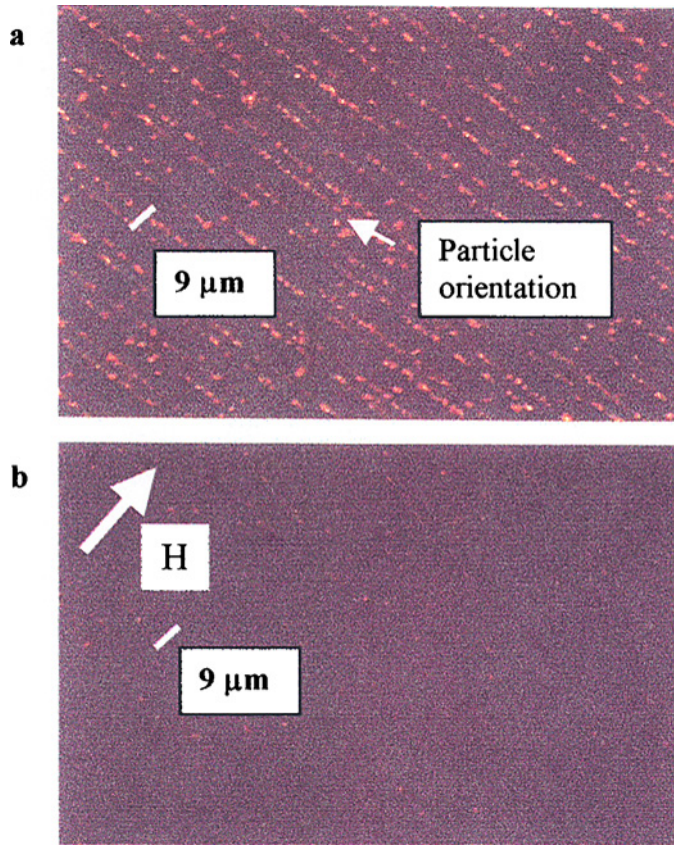

FIGURE 2 The intermediate particle without a magnetic field (a) and with a magnetic field (b). The striped domain phase in (a) is weaker than for the shorter particle. Note the absence of the striped domain phase in the sample with the magnetic field (b) pointed perpendicular to the gratings, except for a few spots. (See COLOR PLATE VI)

These clumps tended to get darker in forty minutes and followed the magnetic field lines. However, a striped domain phase was not formed. A more careful study at higher magnification (with the 2500x objective lens) shows that these particular particles are quasi circular, instead of being ellipsoidal. This can be seen in Figure 3.

The intermediate particle exhibited behavior in between the short and the large particle. It behaved like the short particle in the absence of a magnetic field, forming the striped domain phase, but it tended to clump like the large particle in the presence of a weak magnetic field. The striped domain phase observed was weaker than in the short sample, so the surface

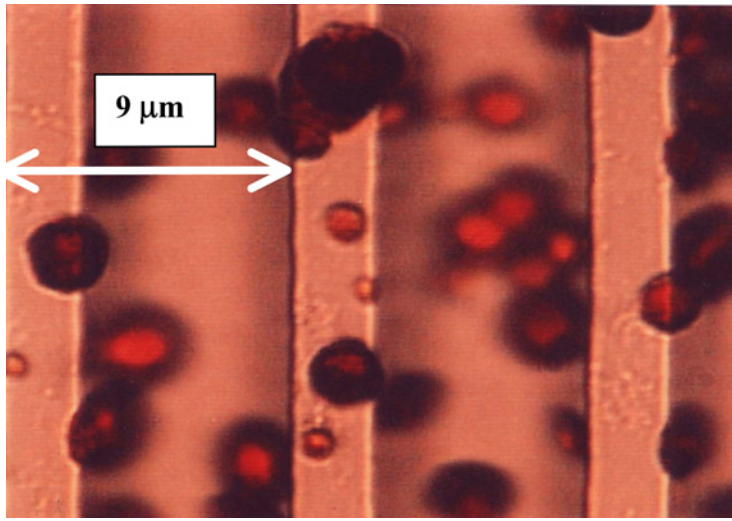

FIGURE 3 A 2500x image taken of the large sample, just as it dries (t = 1 hr). Note the circular nature of the particles. The photograph was taken with the polarizers off. (See COLOR PLATE VII)

forces were not strong enough to hold it in place and a very weak magnetic field was sufficient to overcome them. The particles that were aligned in the striped domain seemed to be the particles immediately close to the walls of the gratings. The alignment did not propagate much farther. Several attempts at trying to quantify this and to compare it to the short particles were made, but they yielded inconclusive results. The intermediate particles consisted of elongated, ellipsoidal particles, but they tended to clump like the more circular particles that characterized the large particle sample. We have not tried to re-hydrate the particles in either case once they dry out to see if the transformation is reversible.

CONCLUSION

We have looked at AlFe oxide particles of different sizes under a magnetic field to see the effect that particle size, substrate, and magnetic field have on the way they respond to the field. The short particles reoriented with the magnetic field and went into competition with the aligning forces of the grating. The short sample exhibited a twisted arrangement of the molecules in the field. The intermediate particles exhibited a behavior that fell between the short particles and the large particles. They aligned with the substrate in the absence of a magnetic field, but tended to cluster together in the presence of a magnetic field. The resulting striped domain

phase in the absence of a magnetic field was weaker than for the short particles. The large particles tended to cluster together in the homeotropic-like phase both with and without a magnetic field. These particles are inorganic analogues of collagen. Thus the AlFe particles can serve as a model system to help one understand and model the self assembly behavior of collagen. The smaller particles and intermediate particles behave like organic liquid crystals.

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