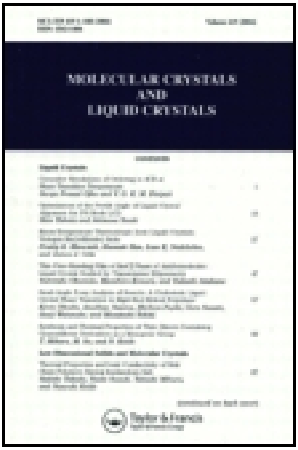

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Evidence of Surface Segregation in the Organization of Metallic Nanoparticles Dispersed in a Cholesteric Liquid Crystal

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Platinum nanoparticles dispersed in a cholesteric liquid crystal can form periodic ribbons which mimic the well-known fingerprint texture. The distance between ribbons is directly correlated to the helical pitch and therefore to the molecular chirality. Here we show how the particles are organized in volume by transmission electron microscopy investigations of cross-sections. A selective segregation takes place at the periphery of the anisotropic film and the particle ordering is localized close to the film-air interface. Potential applications of these results to build periodic ribbon-like patterns of nanoparticles on various substrates are emphasized.

Keywords: cholesteric liquid crystals; fingerprint texture; nanoparticles; nanostructured materials; pattern formation; self-assembly

1. INTRODUCTION

Studies of matter at a nanometer scale are increasing due to the development of technologies leading to significant reduction in the size of electronic and optical devices. Of particular importance is the ability to assemble nanoparticles (np) into well-defined spatial arrangements to build complex structures. The unusual optical, electronic or magnetic properties of np-based composite materials can then be used in

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a large range of applications including high-density information storage media, sensors, magnetic fluids, membranes and catalysts, etc... [1]. Different approaches towards the fabrication of ultrasmall structures are investigated which rely on soft materials and self-assembly rather than traditional optical lithographic techniques [2]; the aim is to explore a variety of these methods in order to produce simple structures (lines, arrays or grids) from soft material with a resolution on the order of 10–100 nm. Among these methods, mixing particles and a liquid crystal (LC) is a wide field of investigations with several practical and fundamental problems; new colloidal assemblies have been observed in liquid crystalline solvents which allow a controlled organization of the particles [3]. Recently, we have provided evidence of a long-range ordering of assemblies of platinum np in a cholesteric LC, which patterns present strong analogies with the well-known fingerprint texture [4]. Due to glass-forming materials, the investigation of nanostructures was made possible by transmission electron microscopy (TEM). The np do not decorate the cholesteric texture but create a novel structure with a larger periodicity. By varying the molar fraction of cholesterol-containing mesogen in the LC host, we have shown that the distance between ribbons is correlated to the pitch which thus becomes a simple control parameter to tune the np structuring. Here we report how the particles are organized in volume by TEM investigations of cross-sections. A peculiar segregation takes place at the boundaries of the anisotropic film and the particle ordering is localized close to the film-air interface. Potential applications of these results to build periodic ribbon-like patterns of np on various substrates are emphasized.

2. EXPERIMENTAL

Cholesteric LCs we used are oligomers with two types of side-chains attached to a siloxane cyclic chain via spacers: a non-chiral mesogen and a chiral one [5]. The pitch of the helical structure, and the related Bragg reflection wavelength, depends on the molar ratio in chiral mesogens. Here we used as-called silicon-red (SR) compound with a molar fraction in chiral mesogens equal to 31%. As an advantage for our purpose, the materials can be quenched at room temperature and the mesomorphic order permanently stored within a solid film at room temperature. Np are platinum nanocrystals which were synthesised via an electrochemical reaction using the zwitterionic surfactant sulfobetain [6]; the use of this surfactant leads to the np being soluble in polar solvents. The blend was sonicated during 3 hours to favorize the dispersion of particules. A drop was deposited on a TEM carbon-coated grid and the chloroform was evaporated at room temperature. The grid was annealed in an oven at 130°C during 16 hours. The purpose of the annealing step is double: the np have to diffuse inside the thin film and the cholesteric organization has to be achieved. Due to the low glassy transition temperature (50°C), a quenching was realized at 25°C by putting the grid on a metallic plate. At the end, the np are embedded in a solid film in which the cholesteric order is stored. For investigations of cross-sections, the specimen was embedded in epoxy resin cured at 40°C and cut at room temperature with an ultramicrotome (Reichert Ultracut) in a direction perpendicular to the surface and then retrieved on a TEM grid. The microstructure, size distribution and periodicity of the ribbons were studied by TEM on a CM30 Philips microscope.

3. RESULTS

SR was dissolved in chloroform with a concentration of 10 wt.% and the platinum particles were mixed with a concentration of 1.5 wt.% compared to the SR content. A drop of this solution was deposited on a TEM grid which was annealed and then quenched. TEM images showed periodic np ribbons which mimic the fingerprint texture

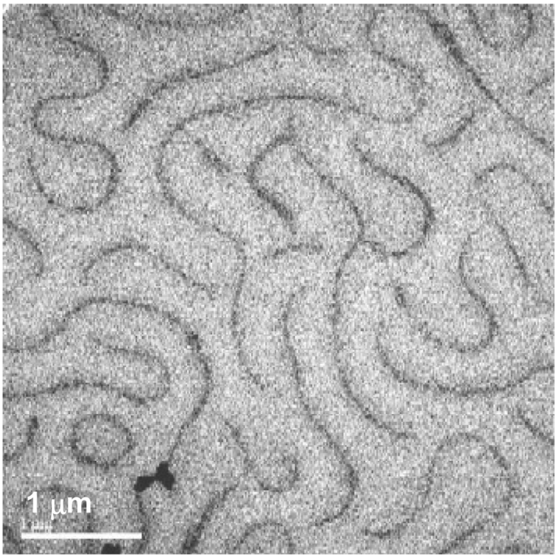

FIGURE 1 TEM micrograph of cholesteric LC SR doped with np. Particle assemblies are structured into ribbons which mimic the fingerprint texture.

(Fig. 1). To localize the np assemblies in volume we observed a cross-section of the doped SR film by TEM. Figure 2 shows the embedding resin and the transversal cut of the film with the two interfaces: the air-material and the substrate-material interfaces; close to the grid, the film was in contact with a thin polymer film (substrate-material interface). Band-like patterns perpendicular to the interfaces are due to the vibrations of the knife which was displaced in a direction parallel to the interface lines. From Figure 2, we can notice that: (i) most of np are rejected close to the interfaces; (ii) spaced sets of np (dash-like patterns) are present at the air-material interface; and (iii) np are dispersed without visible patterns at the substrate-material interface. Therefore, it appears that the fingerprint patterning is a surface phenomenon occuring at the free surface of the film.

To understand the origin of spaced sets of np at the air-material interface, we suggest a three-dimensional scheme of the sample depicting the fingerprint patterning of np in the film plane and the dash-like patterns as observed in the cross-section (Fig. 3). When the knife intercepts the film in a perpendicular direction, it cuts the ribbons perpendicularly to their length but also in many other

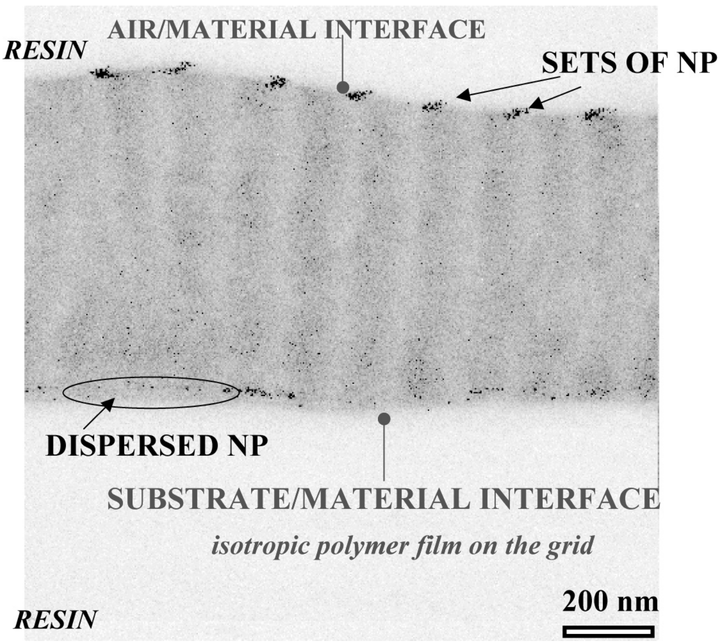

FIGURE 2 TEM micrograph of a cross-section of cholesteric LC SR doped with np.

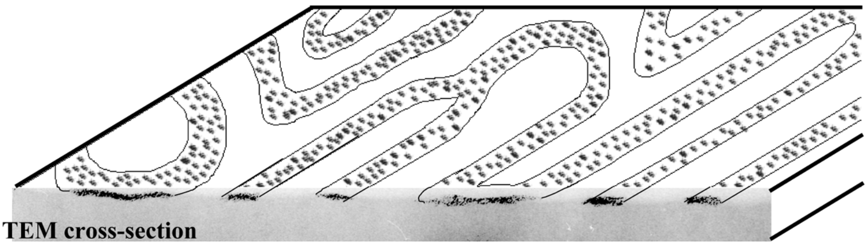

FIGURE 3 A possible sketch of np ribbons from the film plane to the cross-section.

directions. This would explain why the sets of np shown in Figure 2, while being separated, have differents widthes. To continue the correspondence between the array of np ribbons as seen in Figure 1 and the dash-like patterns observed in Figure 2, we measured the ribbon and dash widthes for some patterns (120 ribbons and 120 dashes). The results are reported in Figure 4. In one hand, most of ribbon widthes are between 50 and 250 nm with a main peak in the 150–200 nm

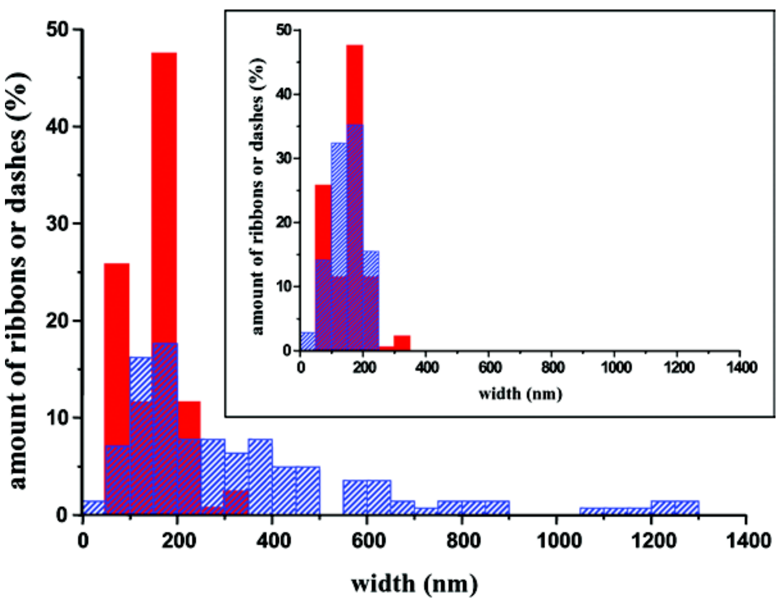

FIGURE 4 Amount of np ribbons or dashes (▨) of given specific width. Inserted graph: data by rejecting dash widthes greater than 250 nm.

range. In an other hand, the dispersion of measurements is much larger in the case of the dash width; this dispersion is not surprizing by working on the hypothesis that a cut intercepts ribbons perpendicularly to the length as well as in various directions (oblique cuts). In the case of the analysis of micrographs of film plane, we know that we effectively measure ribbon widthes; however, the measurement of dash widthes only partially addresses this case. To supplement this analysis, it was decided to reconsider the measurements of dash widthes by using the following selection criterion: if the dash width is larger than 250 nm (this value was chosen by refering to the measurements in the plan views), then it is rejected as a ribbon width. Corresponding results are displayed in the inserted graph in Figure 4: the cover between the curves is good. This analysis strengthens the hypothesis on the origin of dash-like patterns as illustrated in Figure 3.

4. DISCUSSION

On the phase separation of np, their fingerprint patterning and affinity with regions in which the LC molecules are parallel to the film plane at the air-material interface, we can expect that several mechanisms are at work. Among several parameters, the phase separation of np from the bulk LC depends on concentration, solubility, diffusivity and, as of paramount importance, the orientational order of the LC solvent. Firstly, we would like to do an analogy with the physical principle of positive staining of polymers for electron microscopy investigation purposes [7]; the polymer sample is treated with heavy-metal-containing compounds such as osmium tetroxide OsO_4 or ruthenium tetroxide RuO_4 and peculiar regions can be stained dark by a selective physical absorption of the staining agent inside the polymer film; here, the platinum np can have preferably migrated in parts of the structured film containing the more free volume, hence a higher diffusion rate of particles in these regions corresponding to liquid crystalline elongated molecules which are lain down in the film plane and not perpendicular to it. In an other hand, because the LC is an elastic medium, the phase separating material might accumulate in the sites with the highest energy of director distortions. The director field can influence the phase-separated patterns in an anisotropic solvent: the regions with the strongest distorsions attract the phase-separating component. Such effects were previously described from confocal microscopy observations in the case of a cholesteric mixture with a large pitch (10 μm) [8]. Because the mixture contains a few percent of a UV-curable prepolymer, a phase separation morphology is induced by nonpolarized UV-light and modulated in accordance with the fingerprint texture. The stained polymer particles tends to accumulate in the polymer content rather than in the LC and by being located near the bounding plates in the places with the maximum distortion energy. In our system, – which is a rather different one (as regards as the nature of constituents as well as the scale of structures) – many particles could migrate toward the domain boundaries with strong distortions of the director, which explains the accumulation of particles at the interfaces. In the bulk, the director has a favourable helical structure whereas near the boundaries, perpendicular boundary conditions require energetically costly bend and splay.

5. CONCLUSION

We have reported the fingerprint patterning of np dispersed in a cholesteric LC as a surface phenomenon close to the air-material interface. With the aim to form periodic lines of nano-objects, such a self-assembly process could be an interesting alternative to the use of ridge-and-valley structured surfaces which require the existence of a periodic relief of pre-chosen substrates [9]; by the very principle of our approach, the hybrid fluid could be deposited on various surfaces provided that the film presents a cholesteric organization. The result that extended parallel ribbons of np assemblies are formed with an interdistance correlated to the cholesteric pitch illustrates the potential of our approach for the formation of diverse periodic structures. With suitable materials having various pitches, it could then be possible to extend it for the production of np architectures with controlled periodicity.

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