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Fingerprint patterning of solid nanoparticles embedded in a cholesteric liquid crystal

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Abstract

Metallic nanoparticles dispersed in a cholesteric liquid crystal can order in accordance with the helical structure of the chiral phase. Since the liquid crystals we used have a glassy state, the nanostructures may be examined by transmission electron microscopy. The platinum nanoparticles form periodic ribbons which mimic the well-known fingerprint cholesteric texture. The particles do not decorate the pristine texture but create a novel structure with a larger periodicity. The distance between the ribbons is directly correlated to the helical pitch which therefore becomes a simple control parameter to tune the structuring of nanoparticles. Investigations of cross-sections show how the particles are arranged in the volume; a selective segregation proceeds at the periphery of the film and the particle ordering is localized close to the film–air interface. On the fingerprint patterning of nanoparticles, we do an analogy with the positive staining of polymer films with heavy-metal-containing compounds for transmission electron microscopy investigations and we discuss the accumulation of particles in the sites with the highest energy of director distortions.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

New phases and colloidal assemblies have been observed in liquid crystalline solvents which allow a controlled organization of the particles [1]. Liquid crystals (LCs) have been doped with the aim of achieving new physical properties in potentially useful composite materials. Mixing particles and an LC is a wide field of investigations related to several practical and fundamental

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problems; it is especially interesting to know how the interaction between foreign particles is influenced by the presence of an intrinsic structure of LC. A huge effort has been concerned with micron-sized objects (solid particles or liquid droplets) embedded in lyotropic lamellar smectic-like LCs and nematic LCs (with a uniaxial orientational order). Few investigations on solid particles in chiral LC media exhibiting a long-range helical structure have been carried out. In previous studies, cholesteric LCs (CLCs) with pitches in the micrometre range have been doped with colloidal particles and the corresponding textures investigated by optical microscopy [2]. As an interesting result, a stabilized network of oily streak defects was obtained for inclusions of size exceeding the pitch and this gave rise to gel-like rheological behaviour of materials; however no long-range ordering related to the helical structure has been reported. Atomic force microscopy has been used to investigate the patterning of hydrophobic aerosil particles with a mean diameter of about 7 nm when dispersed in a cholesteric LC [3]; at all concentrations the aerosil aggregates are inhomogeneously distributed and no particle structuring was detected. Our goal was to investigate the experimental conditions which lead to the long-range structuring of nanoparticles (np) in accordance with the helical organization of the cholesteric phase. For this purpose, we chose particles with a diameter in the same range as the mesogen length and CLC oligomers which have the property to become solid films due to a simple quenching at room temperature. Therefore, transmission electron microscopy (TEM) investigations of structures at the nanometre scale were made possible. We tried to investigate the correlation between the organization of the CLC carrier and the patterns formed by the particle assemblies.

2. Experimental conditions

2.1. Materials

Cholesteric liquid crystals. The molecule is an oligomer with two types of side-chains attached to a siloxane cyclic chain via spacers: a non-chiral mesogen and a chiral one [4]. On a glass or plastic plate, the material shows typical iridescent colours (Bragg reflections) ranging from blue to red simply by tuning the molar percentage of chiral mesogens from 50% to 31%. The cholesteric phase appears between 180/210 °C (isotropic transition) and 40/50 °C (glassy transition). The pitch of the helical structure, and therefore the reflection wavelength, depends on the molar ratio in chiral mesogens. Here we used so-called silicon-blue (SB) and silicon-red (SR) compounds with reflection wavelengths respectively equal to 450 and 675 nm. As an advantage for our purpose, the materials can be very easily quenched at room temperature and, as a consequence, the mesomorphic order is permanently stored within a solid film.

Nanoparticles. The nanoparticles (np) are platinum nanocrystals which were synthesized via an electrochemical reaction using the sulfobetain ($C_{19}H_{41}NSO_3$) which is a zwitterionic surfactant (a zwitterionic molecule is globally non-ionic but presents a positively charged head N^+R_4 and a negative one S^-O_3); the use of a zwitterionic surfactant leads to np soluble in polar solvents. The synthesis has been published elsewhere [5, 6].

2.2. Transmission electron microscopy

The microstructure, size distribution and periodicity of the ribbons were studied by TEM on a CM30 Philips microscope fitted with a 1024 × 1024 Gatan CCD camera at a magnification of about 1500, giving a resolution of 114 587 pixels μm^{-1}. For investigations of cross-sections (see section 3.3), the specimen was embedded in epoxy resin cured at 40 °C and cut at room

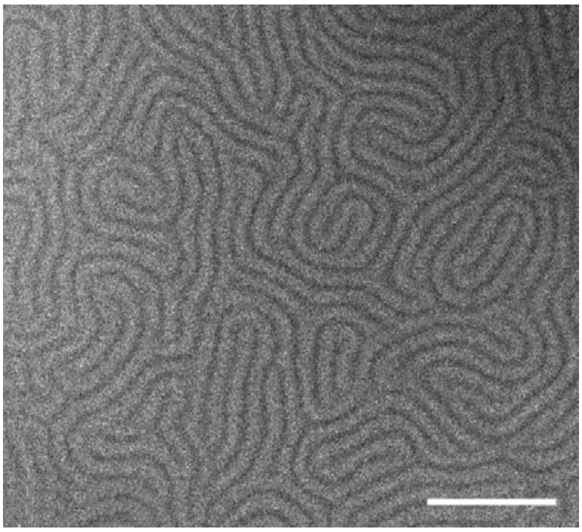

Figure 1. TEM micrograph showing the fingerprint cholesteric texture for the pure SB cholesteric material; scale bar: 1 μm.

temperature with an ultramicrotome (Reichert Ultracut) in a direction perpendicular to the surface and then retrieved on a TEM grid.

3. Results

3.1. Cholesteric film

SB was dissolved in chloroform with a concentration of 10 wt%. 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 for 16 h. Due to the low glassy transition temperature, a quenching was realized at 25 °C by putting the grid on a metallic plate. The viscous film became a glassy solid one. TEM images showed an array of periodic bright and dark lines which is called the fingerprint texture (figure 1).

This texture is mainly the result of mass loss during irradiation by the electron beam which acts as a selective etch depending on the initial molecular orientation [7, 8]. The distance between two dark or bright lines is of the order of the half-pitch. The mean value is equal to about 148 nm. The molecular orientation in dark (bright) lines is parallel (perpendicular) to the picture plane. The helical axis is everywhere perpendicular to the lines.

3.2. Cholesteric film doped with nanoparticles

SR was dissolved in chloroform with a concentration of 10 wt%. The particles were then mixed with a concentration of 1.5 wt% compared to the SR content. The blend was sonicated for 3 h to promote the dispersion of particles. The grid was annealed in an oven at 130 °C for 16 h. The purpose of this annealing step is here double: the np have to diffuse inside the thin film and concomitantly the cholesteric organization has to be achieved. A quenching was then realized at 25 °C by putting the grid on a metallic plate. Finally, the particles are embedded in a solid film in which the cholesteric order is stored. TEM images showed periodic ribbons of np assemblies which mimic the cholesteric fingerprint texture (figure 2).

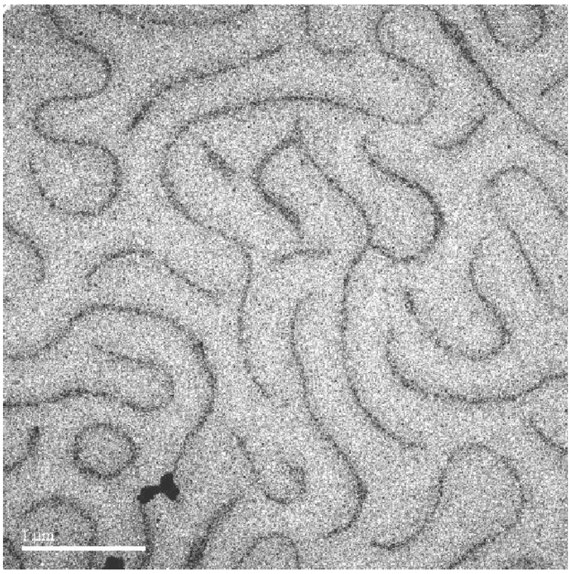

Figure 2. TEM micrograph of cholesteric liquid crystal material SR doped with nanoparticles (1.5 wt%); scale bar: 1 μm. Particle assemblies are structured into ribbons which mimic the fingerprint texture.

The particle structuring does not only reflect the long-range ordering but also the topological constraints of the organized fluid: the assembling follows the well-known defects of the cholesteric phase called disclinations [9]. The kind of organization and patterns (parallel ribbons, worm-like ribbons, number of defects, etc) can be controlled by the film thickness and the LC anchoring on the substrate. If the time for the sonication is insufficiently long, the np could stay as aggregates or the association of particles to the cholesteric order could only be partial; when a particle ribbon is intermittent, a dark line intrinsic to the pure LC film continues [10].

The particles are significantly localized in the darker areas; like an equilibrium configuration, the particles seem preferentially to fit into these parts, in which the orientation of LC molecules is parallel to the film plane. The distance between ribbons is equal to about 410 nm whereas the periodicity exhibited by the pure SR film was equal to about 200 nm. It is thus larger than the periodicity exhibited by the undoped cholesteric film (more than twice the value here). We reached the same conclusion when we mixed SB and SR compounds at different concentrations to obtain cholesteric films with different pitches and doped them with np. We showed that the periodic distance between ribbons decreases when the molar fraction in chiral mesogens present in the cholesteric host increases [9].

We chose different cases of cholesteric hosts: SB, SR and three intermediate blends (in wt%: 75 of SB + 25 of SR, 50 of SB + 50 of SR, and 25 of SB + 75 of SR). The variation of the periodic distance between lines and ribbons compared to the molar fraction in chiral mesogen is reported in figure 3. The distance between two identical lines decreases from about 200 to 150 nm when the molar fraction in cholesterol-containing mesogen in the cholesteric host increases from 31% to 50%. In parallel, for doped liquid crystalline materials with a constant concentration of np of 1.5 wt%, the distance between ribbons decreases from 410 to 225 nm. It is thus important to point out that the np do not simply decorate the cholesteric texture but are intimately combined with the liquid crystal carrier; they experience specific interactions and create a novel helical structure with a larger pitch.

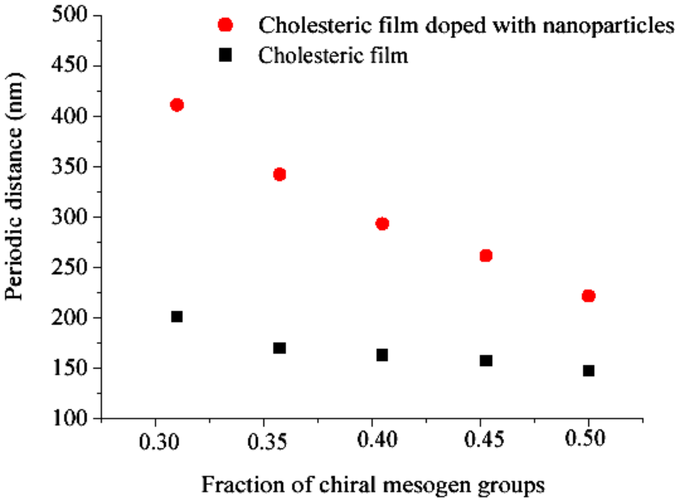

Figure 3. The periodic distance between lines (np ribbons) versus the molar fraction in chiral mesogens present in the pure (doped) cholesteric host.

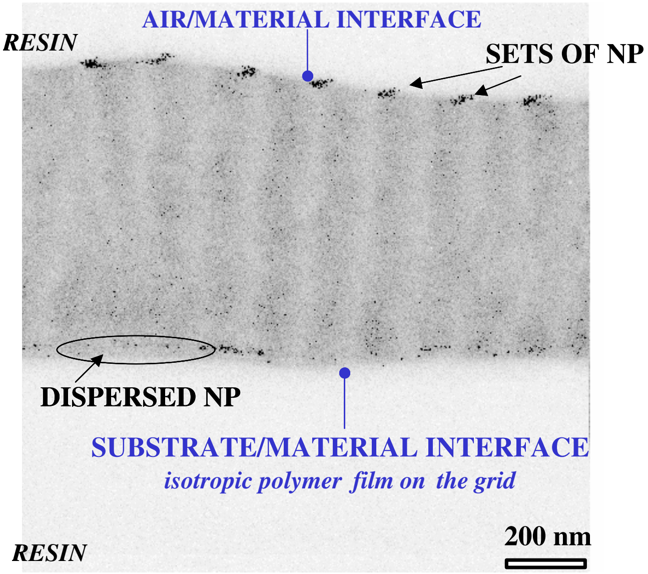

Figure 4. A TEM micrograph of a cross-section of cholesteric liquid crystal material SR doped with nanoparticles (1.5 wt%).

3.3. Study of a cross-section

In order to localize the np assemblies in the volume we investigated a cross-section of the doped SR film by TEM. Figure 4 shows the embedding resin and the transversal cut of the thin film with the air–material and substrate–material interfaces; close to the grid, the film was in contact with a thin polymer film (substrate–material interface).

The band-like patterns perpendicular to the interfaces are simply due to the vibrations of the knife which displaced in a direction parallel to the interface lines. From figure 4, we notice:

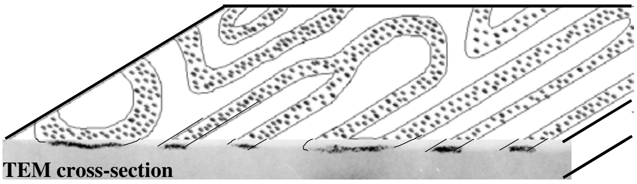

Figure 5. A possible sketch of np ribbons from the film plane to the transversal section.

(i) most of the np are rejected close to the interfaces;
(ii) spaced sets of np are present at the air–material interface;
(iii) np are dispersed without visible patterns at the substrate–material interface.

Thus, it appears that the fingerprint patterning is a surface phenomenon occurring at the free surface of the film.

In order to understand the patterns existing at the air–material interface, we suggest in figure 5 a three-dimensional scheme of the sample showing the fingerprint patterns of np in the film plane and dash-like patterns of np in the section. When the knife intercepts the film in a perpendicular direction, it cuts the ribbons perpendicularly to their length but also in many various directions. This would explain why the sets of np seen in figures 4 and 5, while being spaced, have different widths.

4. Discussion

(i) On the phase separation of np, their fingerprint patterning and affinity with regions in which the LC molecules are parallel to the film plane, 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, of paramount importance, the orientational order of the LC solvent.

First, and as a general behaviour, we would like to make an analogy with the physical principle of positive staining of polymers for electron microscopy investigation purposes [11]; the polymer sample is treated with heavy-metal-containing compounds such as osmium tetroxide OsO_4 or ruthenium tetroxide RuO_4 and peculiar regions are stained dark by either a chemical interaction or a selective physical absorption of the staining agent inside the polymer film. In the latter case, and as an example, the longitudinal periodicity of nylon was revealed by the differential absorption of the staining agent (iodine) in the crystalline and noncrystalline regions [12]. In our case, and during the annealing process, the platinum np can have preferentially migrated in parts of the structured film containing the more free volume, hence giving 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.

Secondly, 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 distortions 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) [13]. Because the mixture contains a few per cent 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. To progress the understanding of the np fingerprint patterning at the air–material interface rather than at the substrate–material one, it is necessary to progress in the study of the director distribution at the two distinct interfaces. From figure 4, we notice the absence of fingerprint patterns in the cross-section view of the cholesteric matrix. This is due to the fact that the helical structure in the direction perpendicular to the film plane is frustrated. Indeed, let us consider the confinement ratio $C = d/p$ where d is the film thickness and p is the pitch. From figure 4, we measure d as varying from the left to the right of the picture between roughly 710 and 640 nm. By taking p for SR equal to about 400 nm, C is around $1.6/1.8$, which means that the periodic structure cannot even develop on a length equal to twice the pitch. We emphasize this fact because the expelling of a helicoidal structure in a direction perpendicular to the film plane for reasons of geometrical frustration could also contribute to the expelling of particles close to the bounding surfaces; forthcoming investigations will have to consider the effect of the film thickness (and consequently the volume helicity) on the np distribution and patterning.

(ii) Let us now discuss the present modus operandi as a technique for organizing np in ordered arrays. Different approaches towards the fabrication of ultrasmall structures are investigated which rely on soft materials and self-assembly rather than traditional optical lithographic techniques [14]. 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 of the order of 10–100 nm. The arrangement of np ribbons in our study is tuned by the choice of the helical pitch of the sustaining cholesteric matrix and the achievement of a well-organized texture. By the very principle of our approach, the hybrid fluid could be deposited on various surfaces provided that the film presents a cholesteric organization. A route to complex nanostructures is the use of templates onto which the particles can assemble in a predetermined fashion. An example of this approach is the formation of periodic lines of np by using ridge-and-valley structured surfaces [15]; the structures are thus likely to reflect the direction of valleys. By contrast with these methods, using the periodic relief of pre-chosen substrates, our self-assembly mechanism is the result of a cooperative process during the annealing step as a compromise between the organization of the anisotropic fluid and the presence of solid foreign particles. 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. If suitable cholesteric materials with various pitches are available, it could be possible to extend it to the facile production of np architectures made of ribbons of controlled periodicity.

5. Conclusion

Periodic ribbon-like assemblies of np can be fabricated by dispersing the particles in a cholesteric LC which presents a long-range helical structure. The particle assemblies mimic the fingerprint texture and lead to the formation of a novel structure with a larger periodicity. The tuning of the distance between np ribbons is correlated to the molecular chirality and hence to the helical pitch of the cholesteric carrier. Therefore the pitch becomes a simple parameter for controlling the distance between particle ribbons. The fingerprint patterning of np appears to be a surface phenomenon at the air–material interface. We intend to progress in the understanding of pitch changes when the CLC host is doped with particles, in the study of the distribution of the LC molecules director at the interfaces in relationship with the local patterning, and to deposit the hybrid film on various substrates to investigate physical properties.

Acknowledgments

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