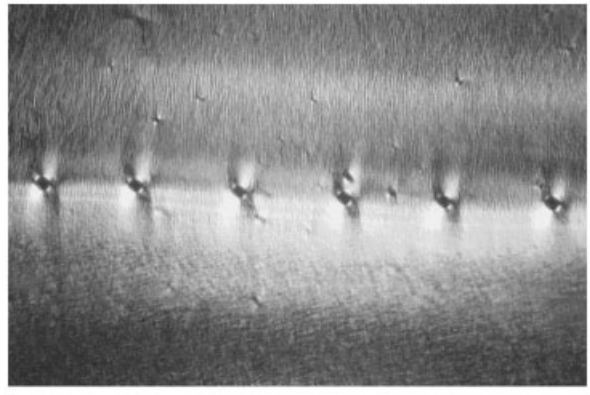
Summary: Organisation behaviours of spherical particles suspended in sheared, lyotropic, liquid-crystalline polymer solutions have been investigated using polarizing optical microscopy. We find that in a nematic phase the particles phase separate and adopt anisotropic chain-like structures along the director. An earring defect is observed around a single particle whereas a cross or strings defect between neighbouring particles is found to serve as a repulsive barrier to prevent the particles from contacting each other. A theoretical analysis is presented to explain this new phenomenon.



An optical micrograph of 0.01 wt.-% glass spheres suspended in a nematic solution of 40 wt.-% ethyl cellulose in chloroform under an external shear force.

Phase Separation and Organisation of Colloidal Spheres Suspended in Sheared Lyotropic Liquid-Crystalline Polymers

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Introduction

In recent years, studies of dispersions of colloidal spherical particles in anisotropic host fluids, such as liquid crystals (LCs), have received great interest because of a wealth of phase behaviour and spatial organisation.[1–5] Instead of being randomly dispersed, as they are in isotropic fluids, the particles adopt a specific anisotropic arrangement in the LC matrix. This behaviour reflects the long-range ordering of the LCs and the topological constraints of the particles. As a result, exotic physical phenomena and properties have been observed.[6–8] One of the most important applications for such a system is the moulding of filled liquid-crystalline polymers. However, the organisational behaviour of spherical particles in liquid-crystalline polymers is still far away from being understood.

In commercial mouldings and fibres of liquid-crystalline polymers, whether lyotropic or thermotropic, one microstructure most commonly observed is the so-called banded texture.[9–11] The banded texture perpendicular to the external force direction shows alternate bright and dark stripes under polarizing optical microscopy. It has been suggested that the orientation of the molecules in this texture is uniform along the force direction with misorientation within the sample plane.[11–13] In this work, we report organisation behaviours of colloidal spheres dispersed in sheared lyotropic polymer solutions.

Experimental Part

The system studied here is a mixture of glass spheres (''Spheriglass 3000'', Potters Europe) and ethyl cellulose

(''EC7'', Aldrich) in chloroform. The particles have a hydrophobic surface and vary in size from 5 to 0.5 μ in radius. The hydrophobic surface provides a normal (homeotropic) director to anchor boundary conditions. We added the glass spheres into the chloroform solution of the ethyl cellulose in isotropic and nematic phases under ultrasonication. Drops of the mixture were put between two glass slides and then mechanically sheared at room temperature. After removing the shear, the specimen was used for direct observation by polarizing optical microscopy (Zeiss Axioplan).

Results and Discussion

Figure 1 shows typical optical micrographs of the system in isotropic and nematic phases. As in classical isotropic fluids, the glass spheres were randomly dispersed in the isotropic polymer solution even though the sample was sheared (Figure 1a). This phase behavior indicates that the mixing entropy dominates the system and the solution is miscible.[2] In contrast, we observed anisotropic organisation of the glass spheres in the sheared nematic polymer solution (Figure 1b and 1c). The sheared nematic polymer solution exhibited a banded texture, which is a unique characteristic for nematic polymers. Within the bands, the polymer chains adopt a uniform orientation along the shear direction.[12] The banded textures in Figure 1b and 1c indicate that director fields in sheared nematic polymer solutions are uniformly aligned. Under such uniform director fields, the glass spheres attract each other over a long range, resulting in long, linear, chain-like structures along the director. Because of the high viscosity of the polymer system, the distance between two particles may be distant from that at equilibrium as observed for a low concentration of glass particles (Figure 1b). When the concentration of the glass spheres is high enough, phase separation is observed (Figure 1c). As expected by theory,[14] the free volume of a suspension composed of a binary mixture of hard rods and hard spheres is maximised when the two components phase separate. As a result, the translation entropy of the system increases at the expense of lowering the orientation entropy of mixing. If one of the physical properties of the glass spheres, such as particle size, is different enough, then microphase separation between the glass spheres will occur. Different sized glass spheres repel each other, whereas the similar sized spheres form long chains along the uniform nematic director (Figure 1c). In the chain-like structures, the glass spheres remain separated rather than in contact each other. The chain-like particle association indicates long-range attractive interactions between particles driven by the orientation elasticity of the liquid-crystal host.[2,3] On the other hand, there must exit short-range repulsive interactions, as the particles are separated by a certain distance.

To understand the short-range repulsive interactions in the chain-like structures, we studied systems of a single sphere and two spheres in a nematic polymer solution. The nematic liquid crystal is uniform in its ground state because of the external shear. A spherical particle suspended in liquid crystals tends to distort the long-range ordering of the nematic phase because of the specific interaction at the liquid crystal–particle interface. The features around a single particle is, therefore, determined by the competition between the bulk elastic energy and the surface anchoring energy.[15–17] Strong surface anchoring makes the director field around the particle incompatible with its uniform distribution in the bulk. As a result, a topological defect is born, confined close to the particle. Corresponding to a local minimum, there are two solutions about the director configurations within the strong normal boundary conditions, as

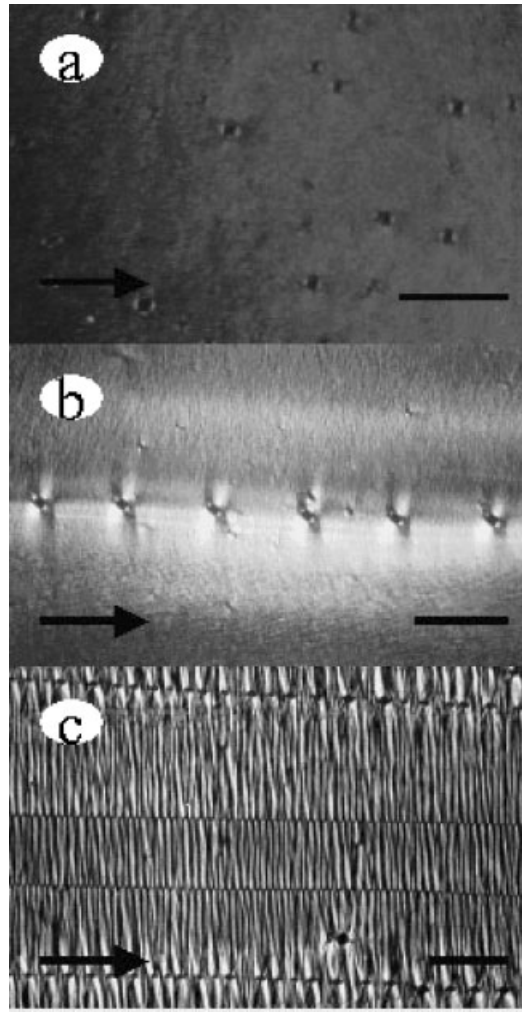

Figure 1. A set of optical micrographs of glass spheres suspended in ethyl cellulose solutions under an external shear force: (a) 0.01 wt.-% glass spheres in an isotropic solution of 10 wt.-% ethyl cellulose in chloroform; (b) 0.01 wt.-% glass spheres in a nematic solution of 40 wt.-% ethyl cellulose in chloroform; (c) 0.2 wt.-% glass spheres in a nematic solution of 40 wt.-% ethyl cellulose in chloroform. The arrows show the shear direction and scale bars are 50 μm.

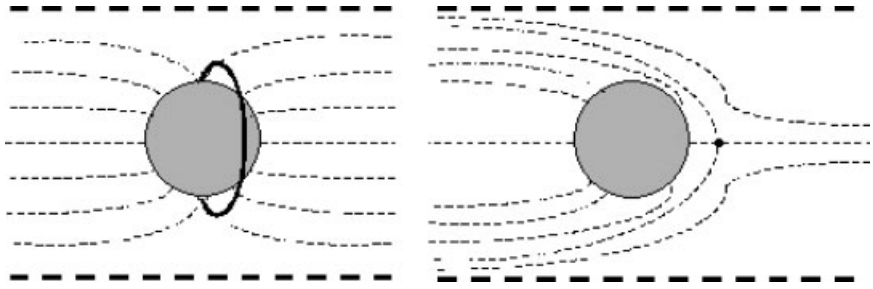

Figure 2. Schematics of possible director fields around a spherical particle with a preferred homeotropic anchoring at its surface that is placed into a uniformly aligned nematic liquid crystal: the Saturn-ring configuration where the particle is surrounded by two $-1/2$ disclinations (left) and the dipole configuration where a particle is accompanied by a hyperbolic hedgehog with charge $N = -1$ (right).

shown in Figure 2. One is a line disclination loop, the so-called Saturn-ring with linear strength $N = -½$ around the particle. The overall point charge in the equatorial plane of the particle is $N = -1$. The other solution is a dipolar configuration with a satellite point defect so-called hyperbolic hedgehog with charge $N = -1$ near one of the particle poles. Both configurations have been observed experimentally in small molecular liquid crystals.[1,3,7,8] In this work, we observed similar configurations in sheared liquid-crystalline polymers. Figure 3 shows a typical optical micrograph of a single glass sphere in the nematic polymer solution. One can immediately see two ''earring'' defects around the particle. The dark earrings are regions where the local optic axis is perpendicular to the plane of polarisation of the incident light. In the other region, the plane of polarisation could be parallel to the local director. In our system, the particle favours the director alignment normal to their surfaces and thus, it will nucleate a topological defect, a so-called radial hedgehog with a charge $N = +1$.[1] Since the overall sample has to be topologically neutral, the charge produced by the particle surface must be balanced by an associated opposite charge, as shown in Figure 2.[15–17] The earring defect is assumed to be a $-½$ disclination and overall topological charge of two earrings is thus -1. As described by theory,[15] the dimensionless parameter WR/K, where K is the average elastic constant, R is the particle size, and W is a surface energy term, measures the relative effect of the particle surface (characteristic surface anchoring energy $\sim WR^2$) and the bulk director distortions (Frank elastic energy $\sim KR$). When $WR/K \ll 1$, the anchoring should be considered weak and not capable of producing a large distortion in the nematic alignment. In contrast, when $WR/K > 1$, the strong normal anchoring creates topological defects around the particle, as shown in Figure 2. For typical values of $K \sim 10^{-11}$ N and $W \sim 10^{-5}$ J $\cdot$ m^{-2},[18] the particles of $R \sim 5$ μm in this work represents a strong normal condition.

Figure 4 shows typical optical micrographs of two different cases for two-particle interactions. When two spheres move towards each other via a shoulder-by-shoulder approach of the earrings, upon contact, the earrings will open and a new dark cross forms (Figure 4a). The new dark cross between the two spheres represents a hyperbolic hedgehog disclination with charge $N = -1$,[19] which is induced in the liquid-crystal host to allow the net topological charge to be conserved. When two spheres move towards each other by a face-by-face approach of the earrings, upon contact, the earrings will open and new dark strings form (Figure 4b). It is assumed that the strings represent localised distortion of the director, which begin as earrings and then transform to form the strings observed. Obviously, the strings also represent a defect with a charge $N = -1$ and may be an escaped form of a hyperbolic hedgehog disclination.[16,19] Whether a cross or strings, the physical origin of the short-range repulsive interactions between the two particles is simple and general. The presence of a topological defect as a repulsive barrier between two neighbouring particles induces a short-range repulsion that prevents the particles from contacting each other.

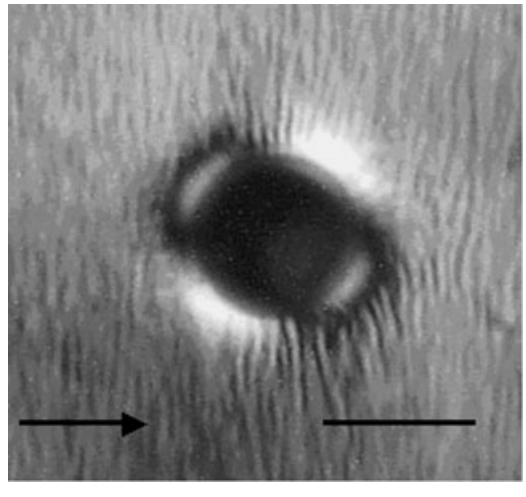

Figure 3. Optical micrograph of a single glass sphere suspended in a nematic phase of 40 wt.-% ethyl cellulose in chloroform. The arrow shows the shear direction and the scale bar is 10 μm.

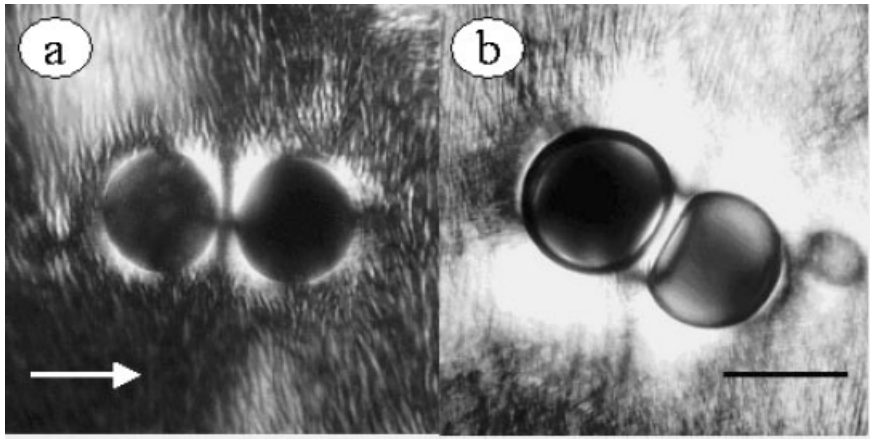

Figure 4. A set of optical micrographs of two glass spheres in a nematic phase of 40 wt.-% ethyl cellulose in chloroform: (a) a cross defect between spheres; (b) a strings defect between spheres. The arrow shows the shear direction and the scale bar is 10 μm.

Conclusion

Phase separation and the ordered association of spherical particles suspended in sheared lyotropic liquid-crystalline polymer solution are observed. The orientation elasticity of the liquid crystals generates long-range attractive interactions between particles, whereas the topological defect between neighbour particles creates short-range repulsions that prevent the particles from contacting each other. The physical picture described here could be helpful for scientists and engineers to modify the experimental parameters during the moulding process of filled liquid-crystalline polymers in order to control the physical properties of the final products.

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