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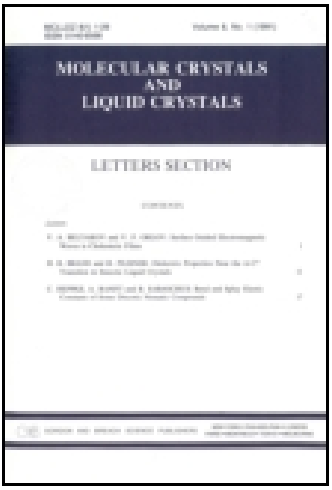

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Liquid Crystals Nanocomposites for Photovoltaic Applications: Structural Properties

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Nanocomposites consisting of liquid crystals and nanoparticles have been studied for their applications in devices, such as photovoltaics and to model biological devices. Understanding the structure the liquid crystal assumes in the vicinity of the nanoparticles, and how it compares to the bulk structure of the liquid crystals gives us an idea of how light, and electrons are transmitted from the liquid crystal to the nanoparticle and how sharp is this transmission. The structure depends on the functionalization (or lack of it) that the nanoparticle has and seems to reflect the faceting or the arrangement of the nanoparticle.

Keywords Liquid crystal nanocomposites; X-ray scattering; photovoltaics; polarized microscopy

1. Introduction

Organic photovoltaic devices are inexpensive to manufacture and process. Crystallinity is one of the ways to improve the current produced in organic photovoltaics [1–3], since it helps to break up the exciton created when light is absorbed. The ability of liquid crystals to self-align combined with their relatively high photoconductivity [4–5] makes them ideal materials for photovoltaic applications as shown in references [1–3] and [6–7] and by our previous work [8]. We have previously shown that in a nanocomposite consisting of a smectic liquid crystal (8CB) and nanoparticles of ZnO an enhancement of the order in the components of the device leads to an increase in current of at least two orders of magnitude [8]. This happens when the concentration of the nanoparticles is around 30% wt, and for nanorods this concentration is approximately 35% [9]. One aspect that has not been studied much in the literature is how the liquid crystals align in the vicinity of the nanoparticles, and how that alignment is dependent on the functionalization compound or lack of it [10].

We have studied the alignment imposed on a smectic liquid crystal, 8CB, in the vicinity of a nanoparticle in a liquid crystal–nanoparticle nanocomposite, in a 30% wt. nanoparticle

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mixture. Close to the nanoparticles, the smectic liquid crystals exhibit a disordered structure, which is still smectic, with a correlation length of one or two molecular lengths.

2. Experimental

The nanoparticles are fabricated with a very narrow size distribution. We have used FeCo and ZnO nanoparticles. The FeCo particles are covered with a variety of functionalizations, and the ZnO particles are covered with Oleic Acid. The FeCo nanoparticles are prepared from a mix of metal salt precursors and dissolved in glycol, which is heated to its boiling point. This mixture is refluxed for about 2 hours. The ZnO nanoparticles are prepared following the process described in reference [8]. Dynamic Light Scattering shows a very narrow size distribution for the particles, with a clustered component which is about eight orders of magnitude smaller than the individual particles [10].

We add 8CB to the isolated nanoparticles to achieve the desired concentration for the sample being made. The sample must be thick enough to intersect the x-ray beam, but it must be homogeneous. We sonicate the mixture at 50°C for five hours. When sonication is complete, a small amount of the mixture is transferred to the substrate [10]. The transition temperatures are measured using the texture change observed with polarized microscopy and compared to the results of Cordoyiannis *et al.* [11] on similar samples.

The nanoparticles introduced into the liquid crystal create a dislocated or defected state that can be analyzed by optical polarized microscopy and x-rays. In order to distinguish the structure surrounding the nanoparticle, we deposited the nanocomposite in a substrate that on average aligns the liquid crystals homeotropically. This substrate is not ideal for photovoltaics but it is ideal to make the studies we are performing here. We can then study the sample when it is deposited in a substrate that on average aligns the liquid crystals homogeneously by examining the differences in the peaks.

The study done on the nanocomposite using polarized microcopy is performed by looking in the direction perpendicular to the substrate. We use the in-plane X-ray scattering geometry to be able to distinguish the effects of the nanoparticle alone for the homeotropically aligned liquid crystal, since the bulk of the sample is not observed in this geometry [8,10,12]. This geometry is similar to the grazing incidence geometry, but it is not since a large range of angles is accepted when the beam hits the sample [12].

3. Results and Discussion

The study done on the nanocomposite using polarized microscopy shows a microscopic structure where both the nanoparticles [10,12] and the dislocations are ordered. The nanoparticles covered with APTS (aminopropyl tri-ethoxy silane), 20% wt in 8CB as seen by the optical polarized microscope, are shown in Figure 1. Note that the ring in the middle of the bright spots aligns in the horizontal direction in this case. The bright spots can be due to a single nanoparticle, according to the sample preparation [10] or a small group of nanoparticles, ordered according to references [13] and [14]. The bulk liquid crystal appears as a black background because its long axis is perpendicular to the field of view and to the substrate.

We show an X-ray scan taken at 26.67 ± 0.05°C for a PEG covered nanoparticle in 8CB in Figure 2. The signal is noisier for the MHDA (mercapto headacanoic acid, not shown) because it is a shorter functionalization. Note that the peak corresponding to the liquid crystal parallel to the surface at $q = 0.2\text{Å}^{-1}$ is absent in this graph. We attribute this to the fact that the PEG is a very long functionalization that introduces a large amount of

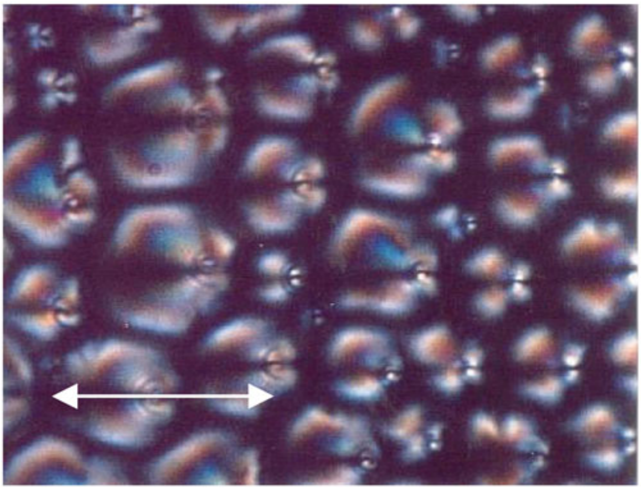

Figure 1. Polarized optical microscope picture of a 20% wt FeCo nanoparticles in 8CB. Note the black background corresponding to the bulk liquid crystal. The marker corresponds to 5 μm.

defects in the parallel direction. All the peaks have been fitted to a Gaussian, implying an ordered structure. The signal is therefore "quantized" [10].

One possible explanation for the "quantization" of the peaks can be the faceting of the nanoparticle, which exists for all nanoparticles studied, and for sizes in the range of 3 nm and up. It can also be due to the grouping of the nanoparticles [13,14]. The FeCo nanoparticles exhibit faceting according to a cubic structure [15]. An analysis of the position of the peaks show that they follow closely the angles between the different directions of a

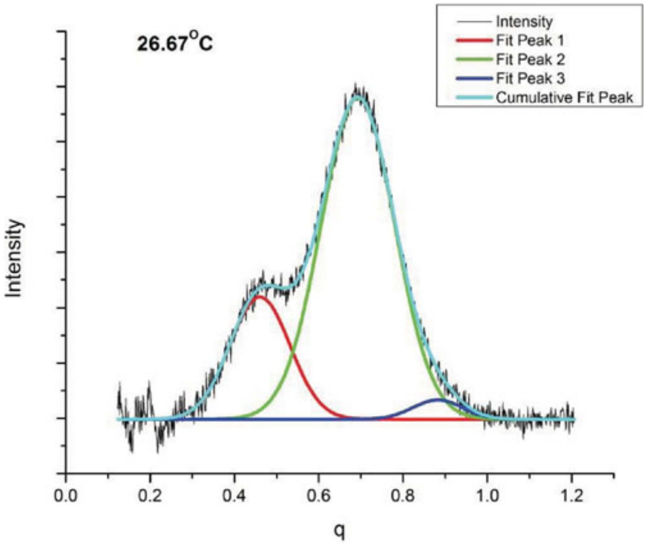

Figure 2. X-ray scan taken at 26.67 ± 0.05°C on a PEG covered FeCo nanoparticle in 8CB at 30% wt. Note the absence of the peak at q = 0.2Å^{-1}.

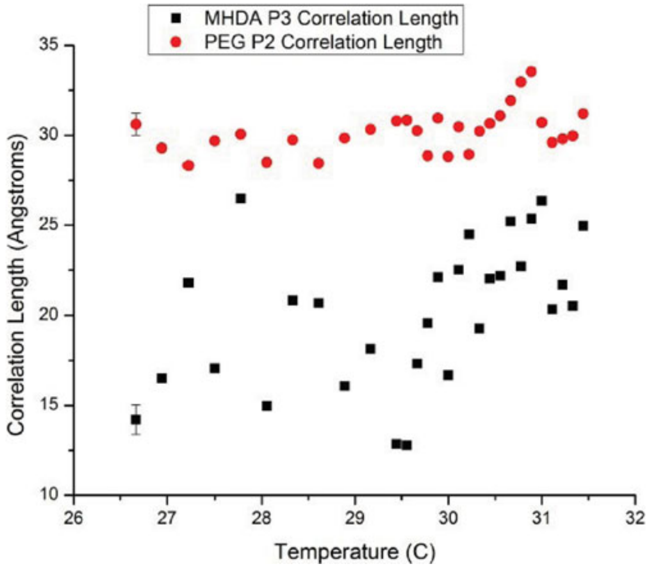

Figure 3. Comparison of the correlation lengths given in angstroms of the MHDA covered nanoparticle and the PEG covered nanoparticle for the peak at q ∼ $0.4Å^{-1}$. Compare with the third column in Table I.

cube, such as the angle between the <001> and the <110>, the <001> and the <111> and the <110> and <111> crystallographic directions [10].

An analysis of the correlation length, associated with the full width at half maximum (FWHM) of the X-ray peaks, and the extent with which the order projects into the sample, shows that this correlation length oscillates between one and two molecular lengths over the entire temperature range studied, into the nematic phase as seen in Figure 3. Figure 3 is a comparison between the correlation peaks obtained for the PEG and the MHDA covered nanoparticles at q ∼ $0.4Å^{-1}$, given in angstroms. The size obtained implies that the structure is disordered but it is smectic in nature, since it can be analyzed with a Gaussian [10].

The smectic nature of the liquid crystal close to the vicinity of the nanoparticle implies the presence of a somewhat ordered phase between the bulk liquid crystal and the nanoparticles. Liquid crystals with ZnO nanoparticles [8] or nanorods [9] show an increase in the correlation length of the bulk liquid crystal, while still keeping the disordered smectic nature in the peaks corresponding to the region close to the more ordered liquid crystal,

Table 1. Weight percent of ZnO and the corresponding correlation length given in nanometers for the ZnO nanorods for the bulk liquid crystal and the disordered signal at q = $0.8Å^{-1}$.

% wt of ZnO nanorod	Correlation length bulk liquid crystal (nm)	Correlation length nano-liquid crystal region (nm)
30	17.5 ± 1.7	2.7 ± 0.3
35	77.6 ± 8.0	3.2 ± 0.3
40	28.1 ± 2.8	2.4 ± 0.2

which for nanorods corresponds to 35% wt [9], and for nanoparticles, corresponds to 30% wt [8]. This can be seen in Table 1. A comparison between Figure 3 and the third column on Table 1 shows that the correlation lengths are almost equal for both FeCo and ZnO and for the different percentage weights measured for ZnO. The electrical current for the more ordered liquid crystal is larger than for the more disordered liquid crystal [8, 9]. The disordered smectic does not interfere with this process and may in fact aid it. We are in the process of studying how this transfer occurs and if the variation of functionalization compound influences it.

4. Conclusions

We have presented evidence of a disordered smectic region close to the nanoparticle in liquid crystals nanocomposites. This region exists independent of the nanoparticle or the functionalization used, however the nature of it depends on the functionalization. It does not interfere with the transfer of charges in the system.

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