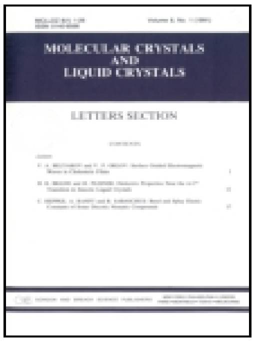

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Stability and Orientational Order of Gold Nanorods in Nematic Suspensions: A Small Angle X-ray Scattering Study

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Stable suspensions of gold nanorods in 4-cyano-4′-pentylbiphenyl (5CB) have been prepared by capping the nanoparticles with polyethylene glycol (PEG). Small angle X-ray scattering has been used to characterize the orientational order of the gold nanorods and the properties of any aggregates. It was found that the nanorods had a very high degree of orientational order with respect to the director of the 5CB matrix and this could be redirected by an applied electric field at 2kHz. Two different PEG molecular weights were investigated and it was found that the lower (1.9kDa) gave exceptionally high order parameters, above 0.9.

Keywords Liquid Crystals, Gold Nanorods, Polymers, Orientational Control, Small Angle X-Ray Scattering

Introduction

The orientation dependent properties of anisotropic nanoparticles could be the basis for many useful new materials [1–6]. However, an important challenge is to develop methods to manipulate particles in this size-regime. The use of liquid crystals as mediators for the placement or orientation of anisotropic nanoparticles holds the promise of precise control of particles at the nanoscale [7,8]. In suspensions consisting of anisotropic particles in small molecule liquid crystals, the particles are susceptible to long-range directional interactions in the liquid crystal host. External electrical or magnetic fields [6] or flow [9,10] can enable control of the particle orientation both directly, through electrical polarization or hydrodynamic torque, and indirectly, through field or flow alignment of the liquid crystal director (preferred molecular orientation), and subsequent minimization of director

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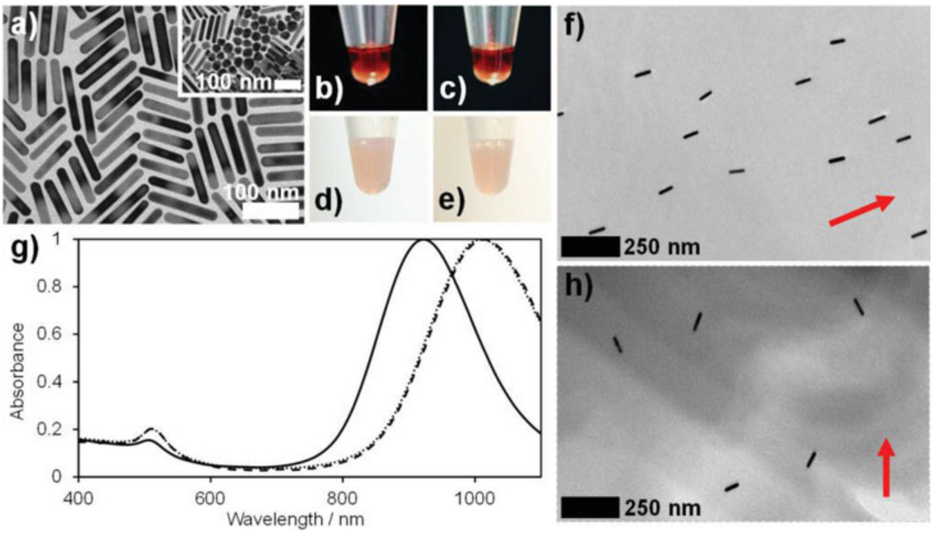

Figure 1. (a) Transmission Electron Microscopy micrograph of as synthesized GNRs of aspect ratio 5.2 where the inset shows a spherical (20 nm) fraction present amounting to 20% by number. Parts (b) and (c) are photographs of isotropic suspensions of GNR(1900) and GNR(5400) with a gold content of 0.02 wt% in 5CB but with 10 v% acetone to keep the sample isotropic. Parts (d) and (e) are the nematic suspensions of (b) and (c) at 0.002 wt% where the colour change is consistent with the removal of acetone. Part (g) compares UV-vis spectra of the isotropic stocks (b & c) following removal of acetone and the as synthesized aqueous suspension (solid black trace) showing the distinct transverse and longitudinal absorption bands. The positions of these bands are consistent with well dispersed GNRs of GNR(1900) (dotted black trace) and GNR(5400) (dashed black trace). (f) and (h) are cryo-TEM micrographs of GNR(1900) and GNR(5400) dispersed in the glassy-nematic phase of 5CB respectively, showing a reduced degree of orientational ordering for GNR(5400) with respect to the direction of sample wicking (red arrow).

distortion *induced* by the particles [11]. In previous work, we have shown that hexagonally packed clusters of gold nanorods (GNRs), modified with short alkyl thiol coatings, can be remarkably well directed by nematic liquid crystal hosts. [12]. Recently, Liu *et al.* [13] achieved orientational control of GNRs as single particles which allowed control of the anisotropic plasmon resonance absorption to be demonstrated. Although initially investigated by Torgova *et al.* [14] and found to yield assembled composites, Liu *et al.* were able to prepare individually dispersed suspensions of polyethylene glycol modified gold nanorods in a nematic host which responded to surface and electric field alignment. In this paper, we detail our work on this system focusing on the effect of the capping-polymer molecular weight on the orientational order within electric-field aligned nematic liquid crystal 4-cyano-4′-pentylbiphenyl (5CB).

Experimental

Polymer modified GNRs of aspect ratio 5.2 (14 × 75 nm) (Figure 1a) were prepared using covalently bound methyl-terminated mercapto-polyethylene glycol (PEG-SH) of molecular weight 1900 g mol^{-1} and 5400 g mol^{-1}. Composites of these particles in 5CB were prepared by rapid dilution of 0.02 wt% (Au) isotropic suspensions of GNRs with well-defined plasmon resonance peaks consistent with freely-dispersed particles (Figure 1b,c,g) into significantly larger volumes of nematic liquid crystal (see Experimental in SI). This yielded stable, 0.002 wt% GNR suspensions with a significant individually dispersed fraction (Figure 1 d,e) which are referred to herein as GNR(1900) and GNR(5400) respectively. In both systems, a dense grafting of the polymer was confirmed by thermogravimetric analysis (see SI, TGA). The PEG-SH packing density was found to be 0.56 PEG/nm^2 and 0.15 PEG/nm^2 for GNR(1900) and GNR(5400) respectively. This coverage was particularly high for GNRs compared to previously studied systems yielding well-stabilized particles [15,16].

Cryo-TEM has been found to be a useful tool in assessing the presentation of GNRs dispersed in nematic 5CB and frozen in a glassy-nematic state (see SI) [17]. Figure 1 (f,h) shows the typical configurations of freely dispersed GNRs in 5CB following drop casting onto carbon coated copper grids. The alignment of the GNR long axis was found to be coincident with the wicking off direction used to prepare the TEM samples in all cases. This can be rationalized if the action of wicking off surplus composite shear aligns the LC host which, with anchoring planar to the carbon surface [18], would lead to a nematic director parallel to the shear-flow direction.

Results and Discussion

Small Angle X-ray Scattering (SAXS) experiments provided a quantitative investigation of the voltage and frequency response of the GNR-nematic composites at standard temperature and pressure. The SAXS data from GNR suspensions prepared using the two different polymer molecular weights revealed a strong directional response to high frequency fields. This alignment is evident in Figures 2a-b, which show the highly anisotropic scattered X-ray intensity. The dominant features in these plots are the single particle form factors for the GNRs where the long axes of the GNRs tend to align parallel to the horizontal applied field. Notably, there was a significant correlation between polymer molecular weight and the order imposed by the electric field consistent with the trends observed in Cryo-TEM experiments. GNR(1900) exhibited a much higher degree of GNR orientational ordering (Figure 2a) compared to the longer polymer modified GNR(5400) system which exhibited a broader azimuthal distribution of scattered intensity (Figure 2b), indicative of a lower orientational anisotropy. The nanorod ordering within the nematic phase was quite distinct from the highly disordered suspensions in the isotropic phase (kept at 45 °C) shown in Figure 2 (c) and (d).

The SAXS data was analysed by comparison with calculations of intensity as a function of Q_{z} and Q_{y} for a model of the suspensions. The model consists of free nanorods, aggregated nanorods and some spherical impurities. The nanorod dimensions were defined by the TEM results. Various other model parameters such as the relative amounts of each component, the aggregate dimensions and lattice parameters, and the orientational order parameters of the free nanorods and the aggregates were adjusted to get a good fit (see SI). This allowed the orientational order parameter of the free nanorods ($\overline{P}_{2GNR}$) to be determined quantitatively. $\overline{P}_{2GNR}$ has been defined to take values between 0 and 1, with 0 indicating an isotropic orientational distribution of GNRs and 1 for a perfect uniaxial alignment with respect to a director. Figure 2(e) reveals how the individually dispersed fraction of GNRs typically reached an optimal alignment ($\overline{P}_{2GNR}$ tending towards 1) for fields in the region of 0.1 Vμm^{-1} at 2 kHz. The efficacy of the alignment was far in excess of that predicted for comparable GNRs in isotropic solvents, calculated as described elsewhere[12]. Indeed, for both samples, a 300-fold enhancement in $\overline{P}_{2GNR}$ was observed at an applied field strength of 0.1 Vμm^{-1} (2 kHz). This is likely to be an underestimate since even in the presence of the 1.4 Vμm^{-1}, 2 kHz field, the scattering of isotropic suspensions (Figure 2c,d) of the two GNR samples changed negligibly, consistent with a $\overline{P}_{2GNR}$ of approximately 0.03.

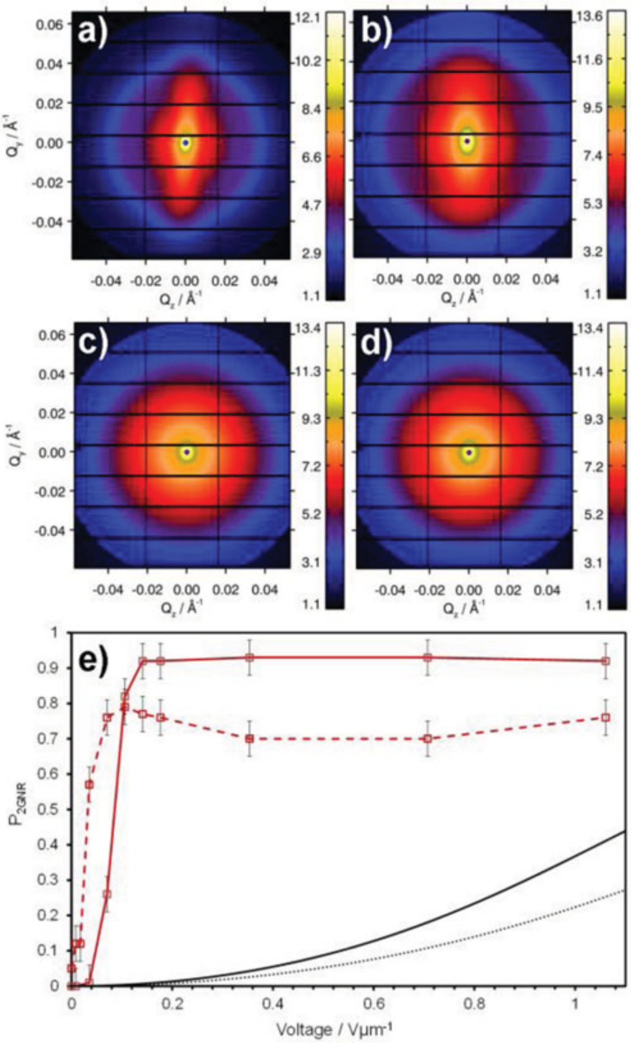

Figure 2. Small angle X-ray scattered intensity as a function of the scattering vectors Q_z and Q_y (parallel and perpendicular to the applied field) for nematic suspensions in a 0.18 Vμm^{-1} (RMS) 2 kHz field for GNR(1900) (a) and GNR(5400) (b). Parts (c) and (d) show the scattered intensity following at 1.4 Vμm^{-1} bias at 2 kHz for samples (a) and (b) respectively heated to 45 °C (above the T_{NI}) in situ where only minor alignment of the GNRs due to induced nanoparticle dipole orientation in electric fields. In part (e) the orientational order parameter, $\overline{P}_{2GNR}$, is shown as a function of applied field strength at 2 kHz for GNR(1900) (solid red) and GNR(5400) (dashed red). The black traces indicate the predicted values of $\overline{P}_{2GNR}$ for GNRs with the same dimensions. The solid and dotted black traces correspond to solvents with relative dielectric constants of 19 and 13.8, selected to represent the value parallel to the applied field for an applied nematic and the isotropic value for 5CB.

At field strengths below 0.14 Vμm^{-1} (2 kHz), $\overline{P}_{2GNR}$values increased rapidly from their initial state with increasing field strength. Above this point, $\overline{P}_{2GNR}$ for the GNR(1900) saturated at approximately 0.9 whereas for the GNR(5400) the order parameter decreased with a further increase in the field strength. The reduction in $\overline{P}_{2GNR}$ could be associated with several mechanisms; electric field induced charges on the GNRs acting to distort the local nematic director, ionic impurities in the 5CB suspensions reducing the effective field strength by ion migration and potentially the resulting ionic flow distorting the nematic director in different regions of the nematic sample (known as electrohydrodynamic instabilities [19]). Below 0.1 Vμm^{-1}, GNR(1900) exhibited a lower alignment compared to its higher molecular weight counterpart. This appears to have been the result of the effective flow alignment of GNR(1900) upon introduction into the capillary tube (parallel to the capillary long axis) requiring that the particle ensemble be rotated from an alignment where the induced torque was at a minimum.

The low frequency response of GNR-liquid crystal composites was explored using the GNR(1900) system. In these experiments, it was observed that when the applied field frequency was reduced below 200 to 300 Hz, the director of the 5CB and the GNRs suspended rotated but a high degree of orientational order was maintained. This effect is shown in Figure 3 where the scattered X-ray intensity from different regions in a capillary sample has been measured for samples aligned by a field of frequency 2, 0.1 and 0.05 kHz, and a strength of 1.4 Vμm^{-1}. The identical measurements at different points in the sample confirm the effect is uniform.

The alignment response of nematics such as 5CB towards electric fields is known to be much stronger at high frequencies because of ionic effects. At low frequencies, surface anchoring, elasticity and possibly electrohydrodynamic effects may determine the orientation of the director, while at high frequencies, the electric field is likely to dominate. Thus it is possible to rationalize the observed rotation of the director away from the horizontal field direction at low frequencies in Figure 3. However, the GNR composite was found to retain an exceptionally high order parameter despite the director deviating up to 70° from the field direction. This confirms that the GNR long axes are strongly anchored to the local 5CB director and are not simply aligned by the electric field.

The SAXS simulations employed have provided a means to quantify the orientational order of the freely-dispersed nanorod fraction in the liquid crystal composites. However, the simulations also showed that there was a fraction of poorly aligned nanorods aggregated in the two samples (between 33% and up to 50%). The aggregates typically had dimensions of about 200 nm where the nanorods had a centre-to-centre distance in the region of 19 nm indicating a thickness of the compacted polymer between them of 5-6nm which represents a significant fraction of the overall aggregate size. The aggregated fraction is likely correlated to the efficacy of PEGylation employed in the particle synthesis. During TGA experiments, it was noted that a substantial fraction of the PEG-SH was lost at low temperatures (up to 90% of the powder weight below 100°C). In part this can be assigned to hydration of the polymer, but it also suggests a significant low molecular weight impurity in the polymers. This lower molecular weight fraction would have reduced the efficacy of the polymer surface modification in preventing close approach under the influence of the Van der Waals attraction. While the particles were highly stable in ethanol-water mixtures, chloroform and THF, their stability in isotropic 5CB was reduced over prolonged storage reflecting this.

The orientational order parameter for the GNR(5400) is similar to the values reported from measurements based on dichroic ratios for similar size GNR also with 5kDa PEG [20]. A calculation based on weak tangential anchoring energy [20] has rationalized the measured order parameters from gold nanoparticles with different aspect ratios, but with the same 5kDa PEG stabilizer, using a single polar anchoring coefficient. The orientational order parameter for the GNR(1900) is exceptionally high. At first sight, it is surprising that

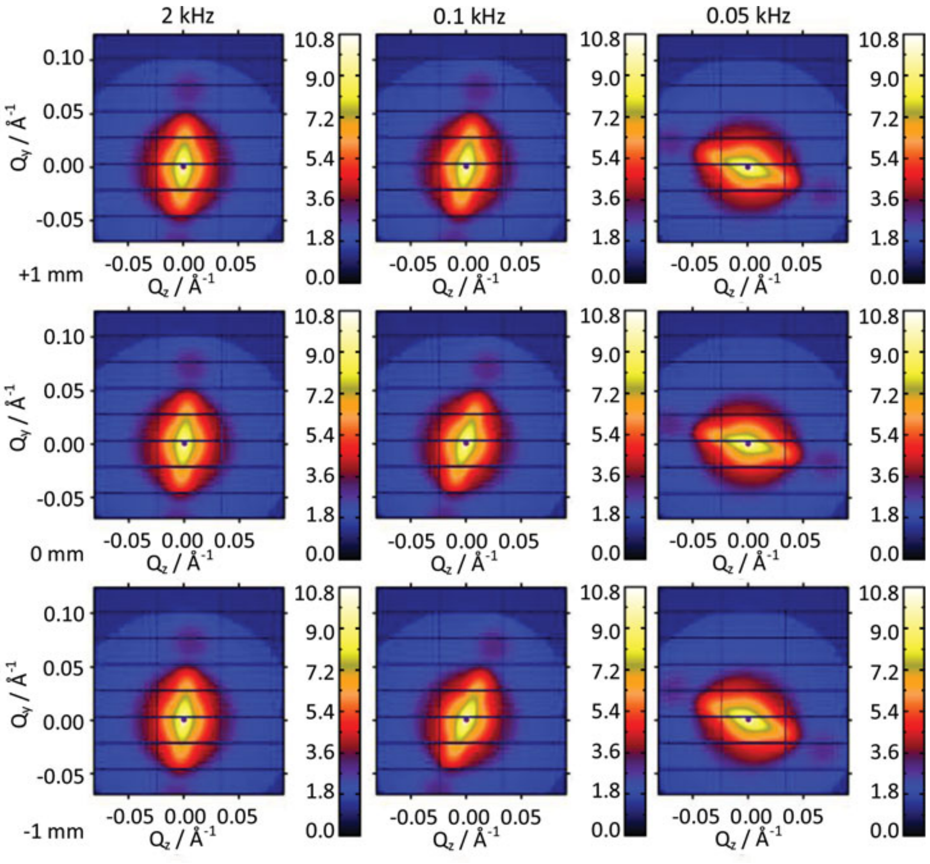

Figure 3. Plots of scattered X-ray intensity for GNR(1900) aligned by a horizontal electric field at three frequencies. The data were obtained by surveying three regions of a sample in a vertical glass capillary along a 3mm vertical line (+1mm (top row), 0mm (middle) and -1mm (bottom)) equidistant from the parallel plate electrodes of the sample holder. The same regions were investigated at 2, 0.1 and 0.05 kHz, 1.4 Vμm^{-1} (RMS) (left to right).

it is higher than the GNR(5400) but this too can be rationalized by assuming a rather larger polar anchoring coefficient. This would be expected for the shorter PEG since it would not reduce the nematic order of the suspension medium over such an extent.

Conclusion

We have demonstrated the use of SAXS for analyzing a nanoparticle in nematic composite in detail. It is sensitive to spherical impurities, aggregate formation, as well as the orientational order and director of the suspended nanoparticles. Stable suspensions of gold nanorods in 5CB have been prepared by capping with PEG where the nanoparticles are well ordered with respect to the director of the nematic matrix and it is possible to redirect the director by an applied electric field at a frequency above a kHz. At lower frequency, we have observed excellent retention of the order parameter where the director is no longer parallel to the applied field but appears to be influenced by the geometry of the capillary. There is scope for achieving very high orientational order parameters for the nanorods using PEG as a surface functionality on GNRs, and it appears that relatively low molecular weight (1.9kDa) PEG is more effective that higher (5.4kD). However, the problems of long term colloidal stability and importantly, the tendency for dense particles to undergo sedimentation will remain limitations for future device applications and should be addressed in upcoming work.

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Supplemental Data

Supplemental data for this article can be accessed at www.tandfonline.com/gmcl.

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