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Electrical conductivity and dielectric constant measurements of liquid crystal–gold nanoparticle composites

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The behaviour of the anisotropic electrical conductivity of liquid crystal–gold nanoparticle (LC-GNP) composites consisting of a commercially available room temperature nematic compound doped with alkylthiol-capped GNPs has been investigated. The nematic–isotropic transition of the composite decreases nearly linearly with increasing X, the concentration of GNP (in weight %) at a rate of about 1°C/weight%. The inclusion of GNPs increases the electrical conductivity of the system with the value increasing by more than two orders of magnitude for X=5%. However, the anisotropy in conductivity, defined as the ratio of the conductivity along ($\sigma_{\|}$) and orthogonal ($\sigma_{\perp}$) to the director shows a much smaller but definite decrease as X increases.

1. Introduction

Composites based on liquid crystals (LCs) have been extensively investigated owing to their attractive electrical properties as well as interesting effects on different phase transitions [1–3]. The most well studied of these are the polymer dispersed liquid crystals in which the LC molecules are contained in a polymer matrix; by matching the refractive index of the polymer with one of the refractive indices of the LC, devices which have been referred to as smart windows are realized [1]. Other classes of materials in which interesting electrical, optical and structural properties have recently been observed are LC systems doped with metal nanoparticles [4], carbon in different forms [5, 6] and carbon nanotubes [7]. The assembly of gold nanoparticles (GNPs) into superstructures has been a very actively pursued topic in recent times [8]. Specifically, some attempts have been made to combine the features of the self-assembling nature of a LC and the electrical/optical properties of a GNP. These include orientationally ordering gold nanorods [9], electric field tuning of plasmonic response [10], a light-driven molecular motor [11] and electrically controlled light scattering [12]. When GNPs were attached to rod-like ligands, LC properties were observed [13], whereas with disc-like ligands liquid crystallinity was lost [14].

2. Experimental

2.1. *Preparation of nanoparticles and composites*

The Brust procedure [15], in which GNPs are prepared and capped with alkanethiols in a non-polar organic phase is a popular method and we have used the same procedure in the present studies. The starting materials, hydrogen tetrachloroaurate(III) trihydrate, sodium borohydride, tetraoctylammonium bromide and 1-dodecanethiol were obtained from Aldrich Chemical Company and used as received. Ethanol and toluene obtained from a local source were purified following standard procedures. Purified and deionozed water was purchased from Millipore company. The deep brown dodecylthio-capped GNPs realized from the Brust procedure were repeatedly (5 times) washed with ethanol. The crude product collected by filtration was quickly dissolved in toluene and again precipitated with ethanol. This process was repeated several times and the pure GNPs were collected by filtration. The IR and UV-Vis spectral data of the prepared material were found to be consistent with the literature reports [16]. GNPs were preserved in the form of a solution in toluene (30%). The liquid crystalline host molecule employed here is 4-pentyl-4′-cyanobiphenyl (5CB), a room temperature liquid crystal available from E. Merck. This compound exhibits only one liquid crystalline phase, the nematic (N) phase, which undergoes a transition to the isotropic (Iso) phase at a temperature of 35°C. To prepare the composites, a colloidal solution of GNP in toluene was

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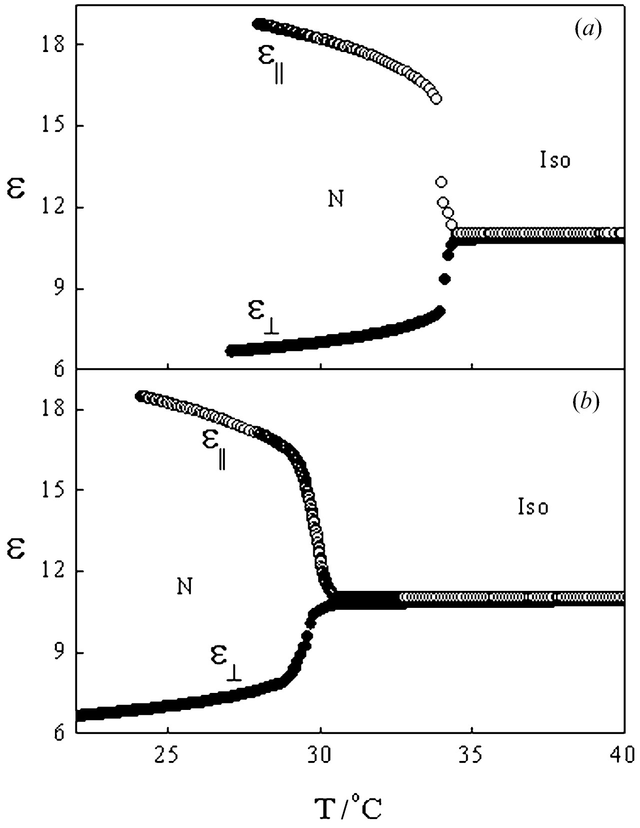

Figure 1. Temperature dependence of the principal dielectric constants $\varepsilon_{\|}$ (open symbols) and $\varepsilon_{\perp}$ (filled symbols) in the nematic and isotropic phases of (*a*) the pure compound and (*b*) 5% GNP composite.

added to a previously weighed sample of 5CB placed in a 5 ml vial. This mixture was sonicated for a fixed duration and evaporated to dryness under reduced pressure. The composite obtained was used for the measurements.

2.2. *Measurements*

Differential scanning calorimetry was performed with the DSC 7 system of Perkin-Elmer. The electrical data were obtained with samples sandwiched between two indium tin oxide-coated glass plates pre-treated with a silane or a unidirectionally rubbed polyimide layer to realize homeotropic or planar alignment of the molecules. Thin Mylar strips, placed outside the electrically active area, defined the thickness of the cell. The sample cells were placed inside a programmable temperature hot stage (FP 84 and controller FP 90 from Mettler). The measurements of the dielectric constant and electrical conductivity were carried out using an impedance analyser (HP 4194A) at different fixed frequencies in the range 10^2–10^5 Hz, but we shall limit the presentation here to the data collected at 10^4 Hz.

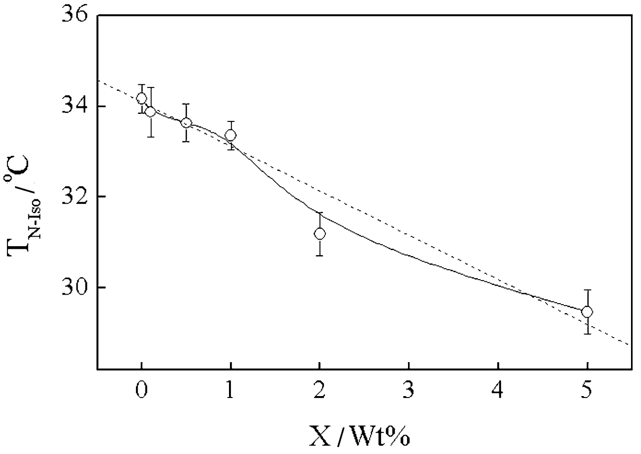

Figure 2. Variation of the nematic–isotropic transition temperature $T_{N\text{–}I}$ on the concentration of GNPs in the composite. The solid line is a guide to the eye.

3. Results and discussion

3.1. *Dielectric constant*

Figures 1 (*a*) and 1 (*b*) show the temperature dependence of the dielectric constants along (homeotropic geometry, $\varepsilon_{\|}$) and orthogonal (planar geometry, $\varepsilon_{\perp}$) to the nematic director for pure 5CB and a representative composite $X=5\%$, (X indicates the concentration, by weight, of GNP in the composite). In both the samples, as well as the two geometries the nematic–isotropic (N–Iso) transition is clearly marked by a significant change in the value of the dielectric constant. The interesting features seen are (1) the transition remains quite sharp even for the composite that has the highest concentration of GNP used in this study ($X=5\%$), pointing to a homogeneous dispersion of GNP in the liquid crystal medium; (2) the surface-determined orientational anchoring of the liquid crystal molecules is still dominant for the composites; (3) there is a substantial decrease in the transition temperature ($T_{N\text{–}Iso}$) for the composite. In fact, the decrease in $T_{N\text{–}Iso}$ is monotonic but is not exactly linear with the GNP concentration (see figure 2). This type of behaviour, of uniformly dispersed non-meosgenic impurities depressing the N–I transition temperature, is quite well known [17].

From the temperature dependence of the dielectric constants, we have calculated the dielectric anisotropy (ε_a) for composites having different concentrations of GNP, at a reduced temperature ($T_{N\text{–}Iso}-T$) of 3°C; ε_a as well as ε_I (the value in the isotropic phase) are essentially independent of X (figure 3). The detailed

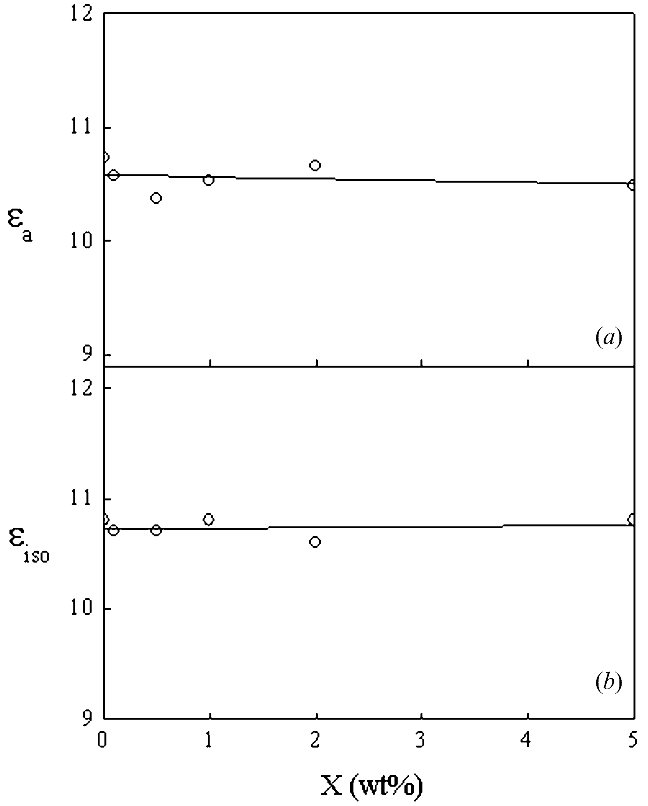

Figure 3. Diagram showing that the dielectric anisotropy ε_a and the dielectric constant ε_{Iso} in the isotropic phase have a negligible dependence on the concentration of GNP in the composite.

temperature dependence of the dielectric constant for the $X=2\%$ composite shows that there are two abrupt changes in the vicinity of the N–Iso transition, see figure 4(*a*). The DSC scan for the $X=2\%$ composite taken in the cooling mode corroborates this result, showing two thermal anomalies at temperatures corresponding to the steps seen in the dielectric data, see figure 4(*b*). It may be argued that the two peaks could be due to the composite and the pure material having independent transitions. But the fact that the transition temperature corresponding to either of the peaks is well below that for the pure compound rules out such a possibility.

It may be recalled that in the aerosil–liquid crystal system, for a concentration of 2% aerosil in the LC material, the nematic–isotropic transition has double-peak behaviour in the calorimetric scans and also that the lower temperature peak is much weaker in strength. Such a feature has been explained as due to a crossover from the random-direction to random-field regime [18]. However, it must be remembered that in the case of the aerosil-LC system, the aerosil particles form a weak hydrogen bond network owing to the presence of hydroxyl groups present on their outer surface. This fragile network leads to the formation of 'pores' in which the LC molecules become confined. Due to the interaction of the LC molecules with the aerosil surfaces the orientation of the molecules is random between the pores and is responsible for the likely crossover between the two regimes mentioned above, causing a double-peak profile in the calorimetric scans.

In the present case, GNPs form no such network, but still show the double-peak behaviour. A possible explanation is that the anchoring of the LC molecules due to the alkyl chains present on the GNP surface extends to substantial distances into the bulk of the LC. Perhaps, then, arguments similar to those that have been put forward for the aerosil systems play a role here causing the double-peak calorimetric profile and the two-step change in the dielectric data.

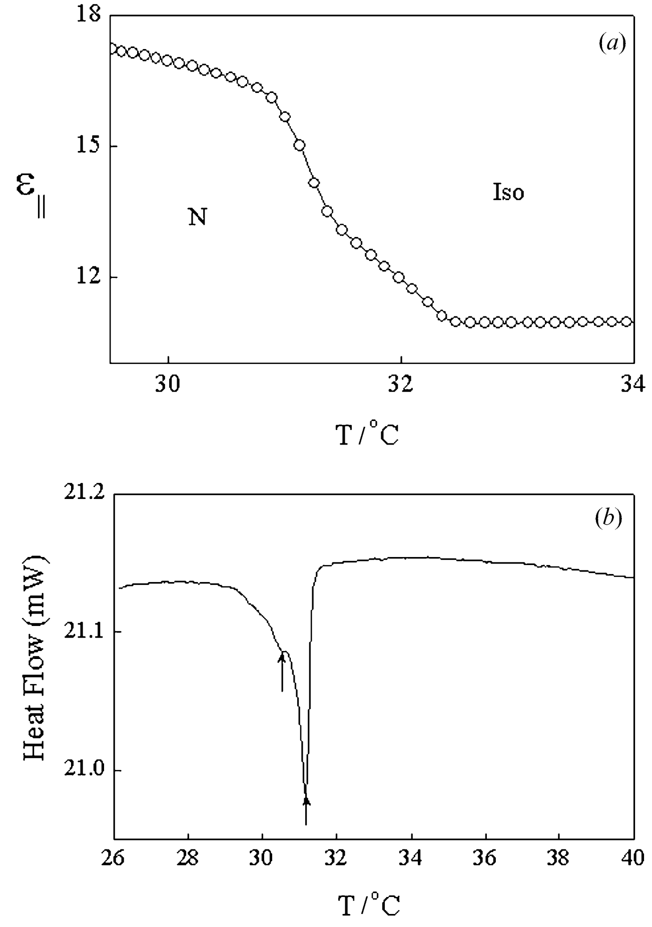

Figure 4. (*a*) Thermal variation of $\varepsilon_{\parallel}$ across the nematic–isotropic transition for the composite with $X=2\%$. Note that the overall change across the transition occurs in two steps. (*b*) DSC scan taken in the cooling mode for the $X=2\%$ composite, showing two thermal anomalies indicated by arrows.

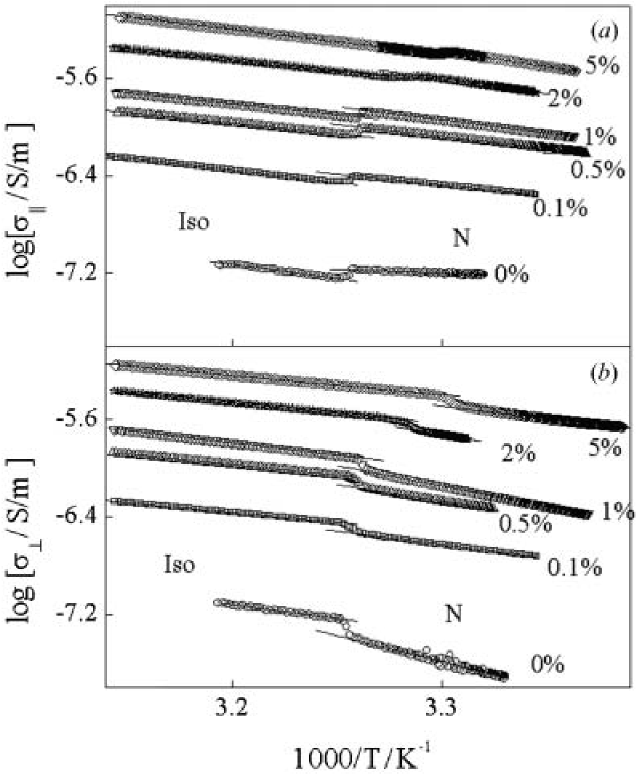

Figure 5. Semi-logarithmic plot of the temperature dependence of electrical conductivity in the nematic and isotropic phases (*a*) along ($\sigma_{||}$) and (*b*) perpendicular ($\sigma_\perp$) to the director, for the pure compound and the different composites. The numbers to the right of each data set indicate the concentration X of GNPs in the composite. The linear variation of the data shown by the straight line fits suggests the Arrhenius behaviour of the conductivity.

3.2. *Electrical conductivity*

The temperature dependence of the conductivity of the pure LC material, as well as the composites with various concentrations of GNPs, both along ($\sigma_{||}$) and perpendicular ($\sigma_\perp$) to the director direction are shown in figures 5(*a*) and 5(*b*), respectively. There is a difference in the isotropic values obtained in the two configurations. After geometrical factors are properly accounted for, the dielectric constant data for the two sets (in isotropic) agree very well for lower concentrations. For X=5% the data at best shows <2% difference. However, the conductivity data differ by more than this factor, a feature that is repeatable. Since the geometry cannot play a role here, we feel that the interaction of the two surface-orienting agents used, especially silane, may have some influence on the behaviour seen. In deed, the interaction between the GNP and the silane layer can be quite strong [19].

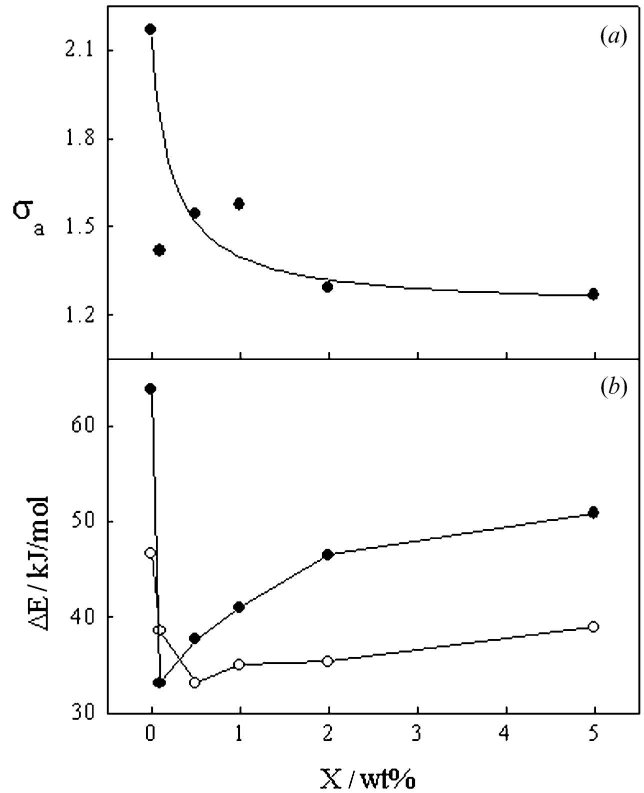

Figure 6. Concentration dependence of (*a*) the conductivity anisotropy and (*b*) activation energy in the nematic (filled symbols) and isotropic (open symbols) phases.

The salient features observed in the data of figure 5 are: (1) a large increase is seen in both $\sigma_{||}$ and $\sigma_\perp$ as the concentration of GNPs is increased—there is an increase of nearly two orders of magnitude for the X=5% composite; (2) in each case the onset of the N–I transition is marked by a clear change in the magnitude of the conductivity; (3) at the transition, while $\sigma_{||}$ shows a small increase, $\sigma_\perp$ shows a decrease, a trait commonly observed in LC materials having a positive conductivity anisotropy ($\sigma_{||} > \sigma_\perp$). It is interesting to note that such a feature is retained even after adding 5% GNP [Measurements were also carried out by dissolving 1-dodecanethiol in 5CB. The clearing temperature does become affected. For example, for ~1% thiol in 5CB, the transition temperature is lowered by ~3.5°C; for a similar concentration of the GNP system the shift is less than 1°C. In contrast, the conductivity hardly changes on adding the simple thiol material, whereas it increases by more than an order of magnitude for the composite with GNP. Thus we believe that the results obtained are dominated by the presence of GNP rather than simply the influence of the thiol material.].

The conductivity anisotropy σ_a, defined as the ratio of $\sigma_{||}$ to $\sigma_\perp$, decreases with increasing X, approaching a value of 1 for higher concentrations, see figure 6 (*a*). However, as mentioned earlier, the absolute values of the individual conductivities in the N phase as well as that in the I phase exhibit a monotonic increase as the GNPs concentration is increased. Thus the effect of adding GNPs is not only to increase the overall conductivity of the system, but also slightly to diminish the nematic characteristic of anisotropic transport.

In the two phases, except near the transition, the logarithm of the conductivity has a linear variation with inverse temperature and can be described by the Arrhenius equation,

$$\sigma=\sigma_o \exp(-\Delta E/kT) \qquad (1)$$

where σ_o is the pre-exponential factor, k is the Boltzmann constant and ΔE is the activation energy. The solid lines in figures 5 (*a*) and 5 (*b*) show that equation (1) describes the data well in the two phases (away from the transition). Figure 6 (*b*) shows that in both the phases the activation energy values determined are lower for the composites than for the pure compound. This is particularly significant in the isotropic phase indicating that the presence of GNPs enhances the electronic jumps between atomic sites. Thus, as far as conductivity is concerned, GNP behaves like an ionic additive to the LC system. Note that the appearance of the LC phase results in no drastic change in the conductivity suggesting that the orientational order has little influence on its magnitude. However, we do expect that the introduction of positionally ordered phases (1D ordered smectics or 3D ordered crystal B phase) should change the scenario. Experiments are underway in this regard.

4. Summary

The behaviour of the dielectric constant and electrical conductivity of liquid crystal–gold nanoparticle composites, consisting of a commercially available room temperature nematic compound doped with alkylthio-capped GNP has been investigated. The nematic–isotropic transition temperature is observed to have a monotonic dependence on X, the concentration of GNP. Both the dielectric constants and the conductivities measured parallel and perpendicular to the director show abrupt changes at the transition, even for $X=5\%$. The inclusion of GNPs increases the electrical conductivity of the system with the value increasing by more than two orders of magnitude for $X=5\%$.

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