

Carbon nanotube-induced chirality in an achiral liquid crystal

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A small quantity of carbon nanotubes was dispersed in an achiral liquid crystal (LC), and the mixture was found to exhibit a weak degree of chirality. The induced chirality in the LC was probed by means of the electroclinic effect in the LC's smectic-A phase, which showed significant pretransitional behavior on approaching the smectic-A–smectic-C transition temperature from above. The results suggest that there is a net chirality associated with the carbon nanotubes, which is transmitted into the LC. © 2010 American Institute of Physics. [doi:10.1063/1.3492844]

Liquid crystals (LCs) are able to impart their long range orientational order onto dispersed nanomaterials such as carbon nanotubes (CNTs).^{1–6} Experiments have shown that a low concentration of CNTs can be organized in a nematic matrix over macroscopic dimensions,^{1,2} which can exhibit remarkable physical phenomena, such as improvement in electro-optic response of LCs,⁶ incremental changes in the LC orientational order parameter,⁷ and an electromechanical memory effect.⁸ Recent calculations predict that a strong interaction, due mainly to π – π electron stacking between LC-CNT molecules,^{6,9} is associated with CNT self-alignment along the LC director. Due to this anchoring energy, the CNT induces local short-range orientational order on LC molecules surrounding the CNT-wall, resulting in an average director in the nematic and smectic-A (Sm-A) phases along the tube axis.^{7,8} But, in the isotropic phase, when long-range orientational order vanishes, the short-range domains appear as isolated pseudonematic domains that can respond to an electric field.⁸ Because the CNTs can be chiral,¹⁰ we ask the following question: can the CNT's surface chirality be transmitted into the adjacent LC domains? If so, the resulting CNT-LC mixture could exhibit a spatially averaged bulk chirality. Here we report an experimental observation of chirality in a mixture of multiwall CNTs (MWCNTs) and the achiral LC 4-n-pentylphenylthiol-4'-n-octyloxybenzoate ($\bar{8}S5$) in the smectic-A (Sm-A) phase by means of the electroclinic effect (ECE).

Garoff and Meyer demonstrated an ECE in a bulk chiral Sm-A LC,¹¹ whereby an electric field \vec{E} applied parallel to the smectic layer induces a polar tilt $\theta[\propto E]$ of the director in a plane perpendicular to \vec{E} . The tilt susceptibility $d\theta/dE$, also known as the electroclinic coefficient e_c , diverges on cooling toward the chiral smectic-C* (Sm-C*) phase. The ECE involves the reduced C_2 symmetry of the lower temperature Sm-C* phase and is absent when the system is achiral or racemic. Chiral-based effects at LC/substrate interfaces also have been known for some time.^{12–16} In these systems either the LC or the alignment layer is chiral, and the interface's reduced symmetry gives rise to surface electroclinic behavior. The interface need not be flat, however. CNTs exist as a macromolecule of carbon and can occur both in chiral and achiral forms depending on their wrapping angle.¹⁷

MWCNTs can have diameters of tens of nanometers and lengths of hundreds to thousands of nanometers, much larger than LC dimensions. Thus, an inherently chiral—but curved—CNT surface may transmit its chirality over some distance ξ into the nearby (and otherwise achiral) LC. For an achiral Sm-A phase, the region within a distance ξ from the CNT surface may assume chiral physical characteristics, and thus on application of \vec{E} parallel to the smectic layers, the LC director in this region would undergo a tilt by an angle $\theta(\vec{r})$, which is a function the chiral vector¹⁰ of the CNT and its coupling to the LC, the LC-CNT anchoring strength, the temperature T relative to the Sm-A–Sm-C* phase transition temperature T_{AC^*} , and the position \vec{r} relative to the CNT surface. But since the CNTs are dispersed throughout the LC, the LC-CNT system has a large interfacial area to volume ratio, and thus could exhibit a bulklike spatially averaged ECE that reflects the net chirality of the CNTs. But in the absence of chiral CNTs or for a perfectly racemic mixture of chiral CNTs one would expect behavior associated with an achiral LC, including the absence of an ECE.

The MWCNTs were obtained from Nanostructured & Amorphous Materials, Inc. and had an outer diameter 8–15 nm, inner diameter 3–5 nm, length 500–2000 nm, and a distribution of different chiral strengths.^{10,18} To reduce aggregation, a small amount of MWCNT sample was dispersed in acetone and shaken on a vortex mixer for 15 min, followed by sonication for 2 h. The LC $\bar{8}S5$ then was added to the acetone+CNT mixture and sonicated for 1 h to allow the LC to dissolve completely. Finally, the acetone was evaporated at an elevated temperature, leaving a nearly pure LC-CNT mixture with approximately 0.6 wt % MWCNTs in the LC. We used Instec Research Instrumentation Technology cells [LC3–05.0, planar rubbed, 5×5 mm² semitransparent indium tin oxide (ITO) coated area, and a $d=5$ μ m spacing]. Two cells were filled at temperature $T > 86^\circ$ in the isotropic phase by capillary action, one with LC only and the other with the LC-CNT mixture; from then on both cells always remained in the Sm-C (or higher temperature) phase,¹⁹ where the cooling phase sequence is isotropic— 86° —nematic— 64° —Sm-A— 56° —Sm-C. Note that the small cell spacing tends to filter out any nanotube aggregates larger than d . Before performing any ECE measurements, the LC-CNT cell was examined using a polarizing optical microscope, which revealed uniform nematic, Sm-A, and Sm-C textures like that of the pure LC cell, indi-

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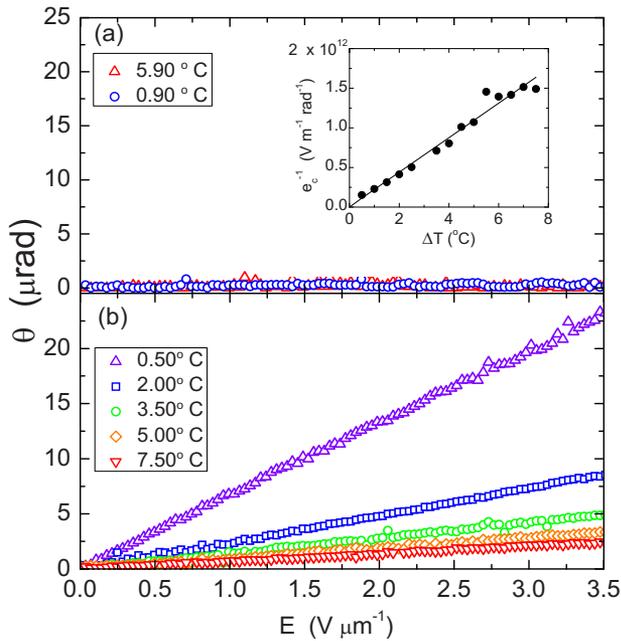


FIG. 1. (Color online) ECE in the Sm-A phase: (a) tilt angle θ vs E ($f=1$ kHz) for bulk $\bar{8}S5$ at two different values of ΔT ($\Delta T \equiv T - T_{AC^*}$), listed in the legend; (b) tilt angle θ vs E ($f=1$ kHz) for $\bar{8}S5 + \text{MWCNTs}$ at five different values of ΔT listed in the legend. Inset: Inverse of electroclinic coefficient e_c^{-1} vs ΔT . A linear fit is shown.

cating a uniform director field. There was no indication of phase separation or agglomerates at any temperature. Thus, at least on visible light length scales, CNT-aggregates (if any) must be small enough to not perturb the director field due to their low concentration.

The optical setup consisted of a beam from a 5 mW He-Ne laser at wavelength 633 nm that passed through a polarizer, the cell, a crossed analyzer and into a detector. The beam was polarized at an angle of $\pi/8$ with respect to the cells' rubbing direction; this is the classical "electroclinic geometry."²⁰ The output of the detector was fed into both a lock-in amplifier that was referenced to the driving frequency f of the applied electric field and to a dc voltmeter, allowing us to measure the ac intensity I_{ac} at frequency f and the dc intensity I_{dc} , respectively. The setup and data acquisition were computer controlled. We obtained using the formula $\theta = I_{ac}/4I_{dc}$ (Ref. 20) the field-induced tilt angle θ , which in mean field theory is $kE/(T - T_{AC^*})$,¹¹ where k is a proportionality constant. k reflects the dielectric properties of the LC and the chiral coupling to the electric field, and vanishes in the absence of chirality.

Figure 1 shows θ as a function of the rms applied field E at $f=1$ kHz for (a) pure $\bar{8}S5$ and for (b) the $\bar{8}S5 + \text{MWCNT}$ mixture. As expected, the LC in the absence of CNTs does not exhibit any ECE in the Sm-A phase, confirming the absence of molecular chirality associated with pure $\bar{8}S5$. On the other hand, the CNT-doped $\bar{8}S5$ clearly shows a bulk ECE that grows on cooling toward T_{AC^*} , demonstrating a net chirality in the Sm-A phase. We also examined the temperature behavior of the ECE mixture above T_{AC^*} , where $e_c = d\theta/dE$ was found to increase rapidly on cooling, with an apparent divergence at T_{AC^*} . In Fig. 1 (inset) we plot e_c^{-1} versus ΔT for the LC-CNT mixture, where $\Delta T \equiv T - T_{AC^*}$, observing an approximately linear variation with T , con-

sistent with mean-field behavior and with previous results on fully chiral LCs.^{21,22} Importantly, e_c diverges at T_{AC^*} , indicating that the observed effect indeed corresponds to coupling between \vec{E} and the CNT-induced chiral LC domains, rather than a direct electric field—CNT coupling. We also performed the experiments at frequencies $f=100$ Hz and 10 kHz, with no significant differences. As an additional verification of the chiral nature of the mixture, we used the method of Raynes,²³ which is sensitive to very long helical pitches. Here the cell's substrates have a 90° easy axis twist and are separated by spacer particles. Straight-line disclinations from one spacer to another would appear when the nematic LC is nonchiral; curved disclinations (favoring one sense of handedness) would appear for a chiral LC. We observed straight disclinations for the pure LC and highly curved disclinations for the LC-CNT mixture, indicating our mixture is chiral.

Under ideal conditions, one might expect that the catalytic chemical vapor deposition method for CNT production would result in equal amounts of left and right handed chiral tubes, i.e., nearly racemic. This raises the question as to whether the observed chirality comes from chiral impurities or is due to an enantiomeric excess of CNTs. Based on energy dispersive x-ray spectroscopy data from the manufacturer, there is no suggestion of chiral impurities. Additionally, we also "washed" the CNTs by mixing them in acetone, centrifuging the CNTs to a pellet, and removing the solvent to extract any possible chiral impurities soluble in acetone. The washed CNTs then were dispersed in the LC and the ECE measurement repeated, with only an approximately 20% decrease in the magnitude of the ECE, due largely to concentration and perhaps aggregation variations from sample to sample. We then repeated the washing process with the aromatic solvent toluene, again with no significant effect. To determine whether any chiral impurity in the acetone may have remained in the LC-CNT mixture, we dissolved the pure LC (without CNTs) in acetone and then evaporated off the acetone. No ECE was observed, indicating the absence of dissolved chiral impurities. Finally, we note that approximately 10^8 CNTs were illuminated by the laser, and therefore statistical fluctuations in enantiomer concentration cannot explain the observed ECE. We thus believe that our sample of CNTs has a nonzero enantiomer excess.

The magnitude of the ECE induced by the CNTs ($e_c \sim 1.5 \times 10^{-12}$ mV⁻¹ at $T = T_{AC^*} + 3.0^\circ\text{C}$) is considerably smaller than that for a typical chiral LC ($e_c \sim 3 \times 10^{-9}$ mV⁻¹) at the same reduced temperature.^{20,24} Much of this difference is due to the low concentration (0.6 wt %) of CNTs. If we assume for simplicity that (i) only a single type of (R) and left (S) handed CNT enantiomer is present, (ii) a CNT enantiomer excess $ee=0.1$, where $ee \equiv \{[R] - [S]\} / \{[R] + [S]\}$ and [...] represents mole fraction, (iii) an average CNT outer diameter of 12 nm and length of 1000 nm, and (iv) the chirality is transmitted a distance $\xi \sim 1$ nm into the LC, then the volume fraction of LC that would exhibit chiral behavior would be $\sim 10^{-3}$. This figure is comparable to the factor between our measured e_c and that of a typical chiral ferroelectric LC, which suggests that there is a moderately large enantiomer excess in our sample of CNTs, that the volume fraction of CNTs is responsible for much of our (small) measured e_c , and that the transmission of chirality into the LC extends a relatively short distance ξ .

To be sure, this is only an order of magnitude estimate, and the combination of issues such as the actual distribution of chiral CNT architectures, the effective ee and ξ , and how the transverse dipole due to the carbonyl group couples to the chirality could have conspired to produce the measured e_c . Specifically, we would have measured the same e_c if both ξ were larger and ee were smaller by, e.g., a factor of 10. Thus, it will be important that enantiomer excess be controlled in MWCNTs, perhaps similar to methods under development for enantiomerically purifying single wall CNTs.²⁵⁻²⁷

The appearance of an ECE for the CNT-doped LC and its absence for the pure LC is an unambiguous signature of induced chirality in an achiral LC, almost certainly arising from the CNTs. We remark that ongoing studies of the ECE dynamics show a clear ECE signature in the nematic phase of the LC-CNT mixture; this work will be published elsewhere. Ultimately the induced chirality may be tailored precisely by dispersing CNTs with well-controlled and known chiral vectors.

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