

## Carbon nanotube-induced macroscopic helical twist in an achiral nematic liquid crystal

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An achiral nematic liquid crystal was doped with a small quantity of carbon nanotubes having a net chirality, and the mixture was found to exhibit an average mechanical twist over macroscopic dimensions. The nanotube-induced chiral pitch length  $P$  was determined as a function of the average nanotube concentration by measuring the radii of curvature of reverse twist disclination lines in  $90^\circ$  nematic twist cells. The results suggest that the nanotubes' spatial concentration can vary significantly across the cell and that at high average concentration, the nanotubes undergo aggregation, resulting in an apparent saturation of  $P^{-1}$  at high concentrations. The macroscopic helical twisting power of the nanotubes has been estimated from the results. © 2011 American Institute of Physics. [doi:10.1063/1.3576101]

### I. INTRODUCTION

Liquid crystals (LCs) have received increasing attention in recent years for their ability to transfer their long range orientational order onto dispersed nanomaterials, such as carbon nanotubes, quantum dots, nanorods, and various shaped colloids.<sup>1–11</sup> Recent experiments have demonstrated that a low concentration of carbon nanotubes (CNTs) can be organized in a nematic medium over macroscopic dimensions,<sup>1,2</sup> providing a fascinating system that involves an anisotropic colloidal dispersion in an anisotropic medium. A dilute CNT suspension in a nematic LC is stable because dispersed CNTs, without large agglomerates, do not perturb the director field significantly. Consequently, the suspended nanotubes share their intrinsic properties with the LC matrix, such as electrical conductivity and dielectric anisotropy.<sup>2,4,12</sup> Recent calculations predict that a strong interaction, due mainly to surface anchoring with a binding energy of about  $-2$  eV for  $\pi-\pi$  electron stacking between LC-CNT molecules,<sup>6,13</sup> is associated with the CNT self-alignment mechanism along the LC director. Due to this anchoring energy, the CNTs induce local short-range orientational order on LC molecules surrounding the CNT wall, resulting in an average director in the nematic phase along the tube axis.<sup>12,14</sup> Recently we demonstrated experimentally<sup>15</sup> that the CNTs share their inherent surface chirality<sup>16</sup> with the adjacent LC domains, and an achiral LC doped with CNTs can exhibit a spatially averaged bulk electroclinic effect<sup>17</sup> in the Smectic-*A* phase above the Smectic-*C* phase transition temperature. Due to the chiral induction by CNTs, we also made the first qualitative observation that the director in the nematic phase undergoes a helical twist with a pitch length  $P$ , where  $P$  is the distance over which the director rotates by an angle of  $2\pi$ .

In this article, we present a detailed experimental measurement of the chiral pitch lengths induced by multiwall carbon nanotubes (MWCNTs) in the achiral nematic LC,

4-cyano-4'-pentylbiphenyl (5CB, Merck, clearing temperature  $35^\circ\text{C}$ ) as a function of CNT average weight fraction  $C_w$ . The chiral pitch lengths and their distributions versus  $C_w$  have been studied by measuring the curvature of reverse twist disclination lines in a  $90^\circ$  twist cell, a technique first demonstrated by Raynes.<sup>18</sup> The concept behind Raynes' method is as follows: In the absence of an inherent nematic twist ( $P^{-1} \rightarrow 0$ ), there are two possible domains in the  $90^\circ$  twist cell, one with right-handed twist and one with left-handed twist. Because both domains are energetically equivalent and therefore equally likely, the disclination lines that run between the cell's spacer particles are linear, that is, straight. However, for a chiral liquid crystal with an intrinsic nonzero  $P^{-1}$ , domains having the same sense of surface-imposed twist grow at the expense of those having the opposite sense of surface-imposed twist, and thus the disclination lines that connect the spacer particles become bowed. The equilibrium shape of the disclination line is determined by the minimization of the total energy, which involves the energy of the disclination and the twist elastic energy, where it is assumed that the LC director is anchored strongly at the two substrates. Thus a measure of the disclination's radius of curvature  $R$  yields the inherent chiral pitch  $P$ .<sup>18</sup> Moreover, if the twist is due to a chiral dopant, the statistical distribution of pitches reflects the concentration distribution of the dopant.

Chiral-based effects at LC/substrate interfaces have been known for some time.<sup>19–25</sup> In these systems, either the LC is chiral or the alignment layer is chiral, and the reduced symmetry at the interface can give rise to a variety of chiral-type phenomena. Propagation of chirality from a chiral surface into an achiral nematic liquid crystal also has been investigated theoretically.<sup>26,27</sup> A computer simulation study has shown that although the surface/LC chiral interaction does not extend beyond the first or second shell of surface neighbors, the induced twist can be more complex: Because it involves an elastic interaction, it can propagate into the bulk, depending on the boundary conditions if there is more than one surface.<sup>26</sup> Carbon nanotubes provide just such a

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surface. Because CNTs are, in effect, a sheet of graphene rolled into a cylinder, they can occur both in chiral and achiral forms depending on their wrapping angle.<sup>28</sup> Multi-walled CNTs can have diameters of tens of nanometers and lengths of hundreds to thousands of nanometers, much larger than LC dimensions. Previously we have shown<sup>15</sup> that an inherently chiral CNT surface may transmit some of its chiral properties in the form of an electroclinic effect<sup>17</sup> over a small distance (approximately a few nanometers) into the nearby—and otherwise achiral—LC. The breaking of mirror symmetry is also a necessary ingredient for the induction of a spontaneous twist in the nematic phase, although the magnitudes of the electroclinic effect and the nematic pitch depend differently on the particulars of LC's molecular structure. Here we examine the CNT-imposed mechanical twist on a bulk LC, including the saturation of the inverse pitch at large average nanotube concentrations and the spatial variation of the helical pitch.

## II. EXPERIMENTAL

The MWCNTs were obtained from Nanostructured & Amorphous Materials, Inc., and have an outer diameter in the range 8–15 nm, inner diameter of 3–5 nm, and length of 500–2000 nm. According to the manufacturer, the sample contains nanotubes having a distribution of different chiral strengths.<sup>16,29,30</sup> A small amount of MWCNT sample was first dispersed in acetone and shaken on a vortex mixer for 15 min, followed by sonication for 2 h. This process reduces the bundling tendency of the MWCNTs. The liquid crystal 5CB then was added to the acetone + CNT mixture and sonicated for 1 h to allow the LC to dissolve completely into the solution. Finally, the acetone was evaporated at an elevated temperature, leaving a nearly pure LC-CNT mixture. The process was repeated to produce several known average concentrations of MWCNTs in the LC. Twisted LC cells were prepared using a pair of glass substrates that were spin-coated with the polyamic acid RN-1175 (Nissan Chemical Industries), baked, and rubbed unidirectionally using a cloth covered rubbing wheel. The two substrates were placed together, separated by randomly dispersed spacer particles of 10  $\mu\text{m}$ , such that their rubbing directions were orientated at 90° with respect to each other. The cells were filled with the pure LC or the LC + CNT mixtures at temperature  $T > 35^\circ\text{C}$  in the isotropic phase by capillary action and cooled to room temperature in the nematic phase, where twisted planar alignment was achieved. Note that the small cell spacing tends to filter out any nanotube aggregates larger than the spacer dimension.

## III. RESULTS AND DISCUSSION

Figure 1 shows a typical polarized micrograph of pure 5CB inside a 90° twist cell. As expected for a pure achiral LC, the disclination lines between the equally likely left- and right-handed substrate-imposed twist domains are very close to straight, minimizing the line tension associated with the disclination. The tiny deviations from linearity likely are due to less-than-perfectly-uniform anchoring conditions at the

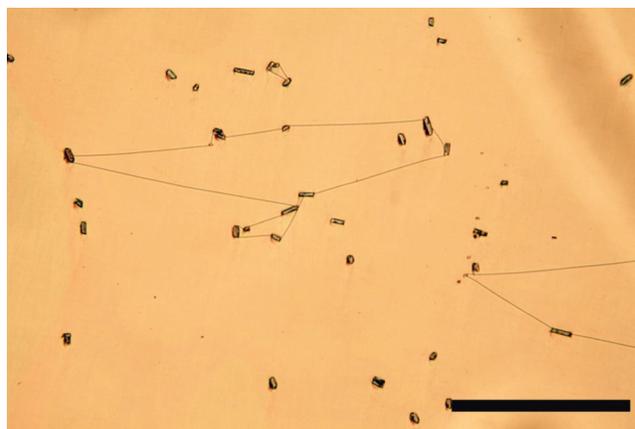


FIG. 1. (Color online) A polarized photo micrograph of a 90° twist nematic cell containing achiral 5CB. The dark spots correspond to 10  $\mu\text{m}$  spacer particles, and the lines are disclinations (domain walls) that separate two twist domains of  $+\pi/2$  and  $-\pi/2$ . The very small deviations of the domain walls from linearity likely are due to nonuniform anchoring conditions. The bar represents 250  $\mu\text{m}$ .

substrates. Thus Fig. 1 indicates that there is no chirality associated with the pure 5CB LC, as expected. The dark spots observed in Fig. 1 are the spacer particles, which pin the disclinations. Under the same conditions, a chiral LC would exhibit highly curved disclination lines in order to minimize the total energy, and the chiral pitch length  $P = 2R$ , where  $R$  is the radius of curvature of the bowed disclination line.<sup>18</sup> Figure 2 shows micrographs of 5CB + CNTs in twist cells for four different CNT concentrations. The clearly visible curved disclination lines between spacer particles confirm that the CNTs induce a significant mechanical twist in the nematic phase. That the sense of curvature, that is, bowing inward or bowing outward, is the same for all segments of the domain wall suggests that the sign of the twist—and therefore the chiral handedness—is the same throughout the cell. Nevertheless, and importantly, the radii of curvature exhibit a nonuniform distribution throughout the cell. Because the radius of curvature varies inversely with the CNT concentration, this behavior suggests a nonuniform density distribution of CNTs in the nematic medium,

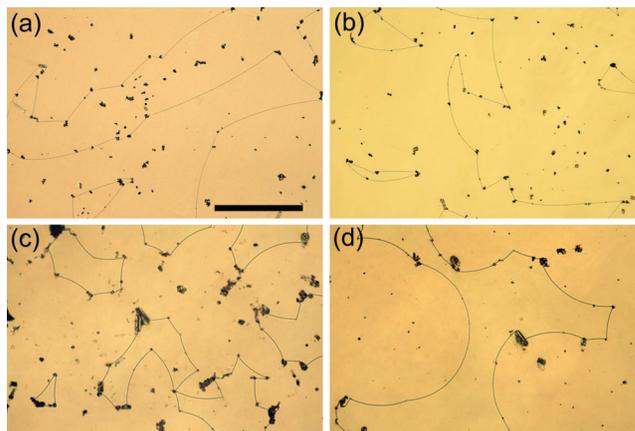


FIG. 2. (Color online) Micrographs showing bowed disclinations of 5CB + MWCNT samples for four different average CNT concentrations  $C_w$ : (a) 0.0001, (b) 0.008, (c) 0.002, and (d) 0.003 weight fraction. The bar in (a) represents 250  $\mu\text{m}$ .

which is discussed in more detail in the following text. By comparison, we examined a mixture of 5CB with a uniformly dispersed low molecular weight chiral dopant CB15 (Merck) having the same weight concentration as the CNTs but a much larger *number* concentration, which we estimate to be more than 5 orders of magnitude larger than that for the CNTs. For the CB15-doped sample, we found that the curvature of the disclination lines is uniform throughout the cell, that is, the distribution of radii or curvature is extremely narrow. A similarly narrow distribution for dopant particles of size comparable to the LC molecules—and thus having a much larger number concentration than that of our CNT-doped sample—also was observed by Raynes.<sup>18</sup>

For each average weight fraction  $C_w$ , the radius of curvature was obtained along several different segments by computer identification and digitization of the disclination lines in Fig. 2, from which we calculated the inverse pitch lengths  $P^{-1}$ ; the results are plotted in Fig. 3. The distribution of  $P^{-1}$  is shown by multiple data points for each sample-averaged concentration  $C_w$ . For consistency, approximately eight to nine disclination lines were chosen for analysis at random from the  $892 \times 595 \mu\text{m}^2$  micrograph at each concentration. In Fig. 3, we see that the relative variation  $\Delta P^{-1}/P^{-1}$  of the inverse pitch, on average, is larger at lower concentrations than at higher concentrations. This suggests that the spatial distribution of CNTs, assuming no aggregation, in a nematic matrix is more uniform when the local number concentration of CNTs is large. We can estimate the expected statistical distribution by taking the average CNT outer diameter to be 12 nm, average length 1000 nm, and density  $2 \text{ gm cm}^{-3}$ , resulting in an average volume  $\sim 10^{-16} \text{ cm}^3$  for a carbon nanotube. For an average weight fraction  $C_w = 0.001$ , one would expect  $N \sim 5 \times 10^3$  tubes in a volume  $\sim 10^{-9} \text{ cm}^3$ . This volume corresponds to a cube of side  $10 \mu\text{m}$ , which is the thickness of the cell and also is approximately the minimum length scale in the plane of the cell over which curva-

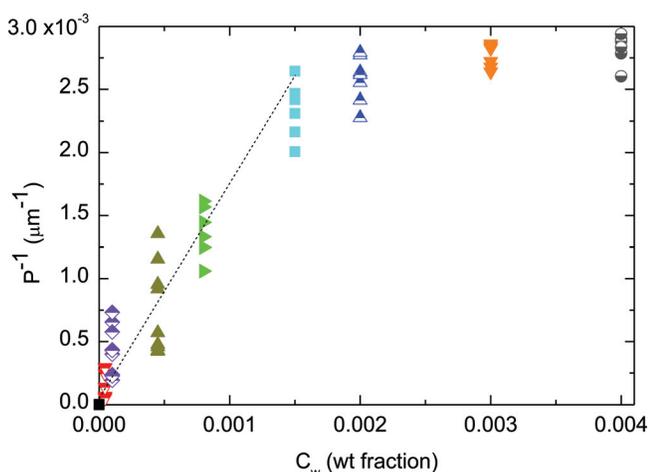


FIG. 3. (Color online) Inverse pitch length  $P^{-1}$  vs average CNT concentration  $C_w$ . Eight or nine different radii of curvature were obtained for each average concentration  $C_w$ , and the resulting inverse pitches  $P^{-1}$  are plotted. Based upon the slope  $dP^{-1}/dC_w$  and the distribution  $\Delta P^{-1}$  of inverse pitches at each value of  $C_w$ , we can estimate the fractional variation of the number of tubes in each volume that contribute to the twist to be  $\Delta P^{-1}/[C_w(dP^{-1}/dC_w)]$ .

ture can be detected. Thus the relative variation  $1/N^{1/2}$  in the local nanotube number could be of order a few percent. But the relative variations  $\Delta P^{-1}/P^{-1}$  observed in Fig. 3 are larger than this estimate, perhaps by a factor of about 10. Based on the slope  $dP^{-1}/dC_w$  in Fig. 3, this suggests that the variation in the number of CNTs that contribute to the twist from one volume of  $10^{-9} \text{ cm}^3$  to another could be as high as 20%. This statistical variation could be due in part to a small degree of aggregation and/or interactions with a not-completely-uniform surface preparation. A much more likely explanation, however, is that the enantiomer excess  $e$  is less than 1, perhaps only  $\sim 0.01$ – $0.1$ <sup>15</sup>, which would have the effect of significantly decreasing the concentration of tubes that contribute to the twist and thereby increasing  $\Delta P^{-1}$ . The enantiomer excess will be discussed again below in the context of helical twisting power.

It is also interesting to note in Fig. 3 that the chiral induction of mechanical twist by CNTs first begins to saturate in the higher concentration regime,  $C_w \geq 0.0015$  and is nearly fully saturated at  $C_w \sim 0.004$ . At lower concentrations, the average inverse pitch  $P^{-1}$  appears to be approximately linear in  $C_w$ , although given the  $P^{-1}$  distribution for each CNT concentration, we cannot state unequivocally whether  $dP^{-1}/dC_w$  is constant for  $C_w < 0.0015$  or whether  $dP^{-1}/dC_w$  is a continuously decreasing function of  $C_w$ .

What is the origin of the apparent saturation of  $P^{-1}$ ? Assuming the same average tube dimensions as used in the preceding text, for a  $C_w = 0.002$  weight fraction sample, the average separation between the CNTs would be of order 500 nm. This distance is much larger than the chiral interaction length scale of at most a few nanometers into the LC (calculated theoretically<sup>26</sup> and estimated experimentally<sup>15</sup>), which suggests that the fundamental chiral interactions should not saturate at this low concentration. Instead we believe that the saturation of  $P^{-1}$  is due to a rapid increase in the number (and perhaps size) of CNT aggregates at weight fractions  $C_w > 0.0015$ – $0.002$ , although the aggregates remain sufficiently small ( $< 0.5 \mu\text{m}$ ) that they are not visible under the optical microscope. Because the CNTs present in the aggregates and/or clusters are not completely exposed to the LC media, they do not contribute substantially to the chiral interactions with the surrounding LC. Thus we believe that the inverse chiral pitch  $P^{-1}$  tends to saturate at higher CNT concentrations due mostly to increasing aggregation. [We remark in passing that we also used a polarizing optical microscope to examine a *non-twist* cell filled with 5CB + CNTs, in which the planar LC director  $\hat{n}$  had a uniform orientation through the cell thickness, that is,  $\hat{n}(z) = \hat{n}_0$ . Because the pitch length of the mixture is much larger than the cell thickness, surface stabilization of the director ensures that the optical micrographs for the mixtures exhibit uniform nematic textures. The micrographs appear similar to that of the pure LC cell, indicating that, at least on the length scales resolvable by visible light, any CNT aggregates must be small enough that they do not perturb the director field on optical length scales.]

An important question is: Why do we see a net chirality at all? One might expect that under ideal conditions the catalytic chemical vapor deposition (CCVD) method would

produce a distribution of chiralities with similar quantities of left- and right-handed chiral nanotubes, leaving the MWCNT sample nearly racemic. This brings up the question as to whether the observed chiral effects—both the electroclinic effect<sup>15</sup> and the chiral twist to be discussed in the following text—come from any trace amount of chiral impurities or are due to an enantiomeric excess of CNTs. We took number of steps, discussed in detail in Ref. 15, to ensure and verify the absence of chiral impurities at every stage of sample preparation. Moreover, we can discount chirality from the 5CB liquid crystal, as we can see from Fig. 1 that our 5CB sample shows no significant twist in the absence of CNTs. Instead we believe that our sample of CNTs has a nonzero enantiomer excess, likely due to their manufacture under nonideal conditions. Although statistical fluctuations in CNT chirality can contribute to a net chiral effect, we believe that such a contribution would be negligible due to the large number ( $>10^{13}$ ) of nanotubes that we prepared for our experiment. Empirically, a nonzero enantiomer excess (as opposed to the presence of chiral impurities) is borne out by two observations: the apparent leveling-off and saturation of  $P^{-1}$  at higher concentrations (Fig. 3), which would not occur if there were chiral impurities in the CNT sample, and the wide distribution  $\Delta P^{-1}$  in locally measured inverse radii of curvature, which is indicative of the chirality arising from a small number—with a concomitant large relative variation of concentration with position—of CNTs in a given volume of sample.

The ability of a dopant to induce mechanical twist in an achiral nematic phase normally is characterized by the macroscopic helical twisting power (HTP),  $\beta_M = (ePC_w)^{-1}$  (Ref. 31), which corresponds to the inverse twist induced on adding a chiral dopant at concentration  $C_w$  and having enantiomer excess  $e$ . For example, the Merck material CB15, which does not have a liquid crystalline phase on its own, can be added in small amounts to an achiral liquid crystal to break the degeneracy between  $+\pi/2$  and  $-\pi/2$  twists in a nematic twist cell. For our experiments, we find that  $(PC_w)^{-1} \sim 1.7 \mu\text{m}^{-1}$  in the low concentration region, as obtained from the initial slope of Fig. 3. If we assume that the CNT sample has an enantiomeric excess  $e = 0.1$ ,<sup>15</sup> then on average only 1/10 of the carbon nanotubes would be contributing to the twist, and the helical twisting power of the CNT dopant would be  $\beta_M = 17 \mu\text{m}^{-1}$ ; if our enantiomer excess  $e$  actually was equal to 0.01, the HTP would correspond to  $\beta_M = 170 \mu\text{m}^{-1}$ . This suggests that the twisting ability of our CNT sample is comparable to that of commercial small-molecule chiral dopants (such as CB15) that possess  $\beta_M$  in a wide range between 8 and  $100 \mu\text{m}^{-1}$  (Ref. 31) and is similar to typical cholesteric liquid crystals that possess pitches in the subwavelength of light range.<sup>32</sup>

#### IV. SUMMARY

To summarize, a small quantity of carbon nanotubes having a net chirality can induce a twist in a nematic liquid crystal. Because the nanotubes are much larger in size than the liquid crystalline molecules, only a small number concentration is required to induce a measurable twist. But owing to the small numbers of nanotubes required, the spa-

tial variation of concentration gives rise to a distribution of helical pitch lengths in the cell. At high concentrations, the inverse pitch was found to saturate, which we believe is due to aggregation of CNTs. Future work will center on experiments using CNTs of controlled chirality.

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