

Liquid crystal–carbon nanotube dispersions

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Parallel alignment of nanotubes can be obtained by dispersion in a self-organizing anisotropic fluid such as a nematic liquid crystal. Exploiting the cooperative reorientation of liquid crystals, the overall direction of the nanotube alignment can be controlled both statically and dynamically by the application of external fields. These can be electric, magnetic, mechanic, or even optic in nature. Employing multiwall as well as single-wall carbon nanotubes, we show their parallel alignment along a uniform liquid crystal director field and electrically verify their reorientation behavior for two complementary geometries. These demonstrate electrically controlled carbon nanotube OFF–ON and ON–OFF switches. Further applicational potential will be outlined. © 2005 American Institute of Physics. [DOI: 10.1063/1.1850606]

I. INTRODUCTION

The extraordinary properties of carbon nanotubes,^{1–3} such as their large mechanical and electrical anisotropy, have triggered enormous interest in these materials over the last decade. The mechanical stiffness along the tube axis, combined with flexibility in a perpendicular direction, is especially interesting for high elastic modulus reinforced fibers and polymer composites in general.⁴ The anisotropy of the electric conductivity, being large (metallic or semiconducting) along the tube axis and small perpendicular to it, has led to proposals of nanotubes being used as molecular wires in nano-scale electronics and transistors,^{5–8} or as field emission sources.^{9,10} Other possible applications include their use as actuators¹¹ or nano-sensors for chemical and biological molecular detection.^{12,13}

Carbon nanotubes occur in two general morphologies, single-wall (SWNT) and multiwall nanotubes (MWNT), and are normally produced by the techniques of arc-discharge,¹⁴ chemical vapor deposition,¹⁵ or laser ablation.¹⁶ All of these methods generally lead to a random orientation of the nanotubes. Furthermore, the high aspect ratio of the tubes together with their flexibility lead to physical entanglement, while attractive van der Waals interactions between individual nanotubes invariably results in their association in bundles. The latter is also responsible for the generally poor solubility of nanotubes in most solvents. For many applications of carbon nanotubes a uniform alignment is essential, and in general the ability of giving nanotubes a predetermined direction is of great importance. Additionally, it is highly desirable to be able to manipulate this direction, for example, by application of external fields, may these be elec-

tric, magnetic, or mechanical in nature. Attempted alignment of nanotubes as polymer composite systems¹⁷ is relatively poor, even after mechanical stretching, further inhibiting the possibility for re-alignment of the dispersed tubes. Remarkable advances have been made over the last years to position individual nanotubes by AFM techniques,^{7,8} but the large-scale post growth alignment of ensembles of nanotubes is still a fundamental problem, despite recent advances to grow very well aligned nanotubes on substrates.¹⁸

Liquid crystals (LC)^{19,20} are anisotropic fluids, thermodynamically located between the isotropic liquid and the three-dimensional positionally ordered solid phase. Due to molecular self-assembly LCs exhibit orientational order of rod-shaped molecules, i.e., anisotropic physical properties, while at the same time maintaining flow properties in their least ordered configuration, the nematic phase. The direction of the average long molecular axis of a nematic liquid crystal, called the director \mathbf{n} , can easily be controlled by suitable alignment layers. In addition, the director can be reoriented by the application of electric or magnetic fields, a process commonly known as the Freedericksz transition.²¹ Variants of the latter are being exploited in all common LCD applications from cheap wrist watches to the highly sophisticated laptop displays. The self-organizing properties of liquid crystals may thus be used to impose alignment on dispersed carbon nanotubes²² and the Freedericksz transition to manipulate the alignment direction²³ through elastic interactions with the liquid crystal director field. This approach opens the possibility to dynamically and collectively change the orientation direction of ensembles of nanotubes and thus their direction of mechanical and especially also electrical anisotropy. In this paper we will demonstrate the realization of electrically controlled carbon nanotube OFF–ON and ON–OFF switches by use of liquid crystal–nanotube dispersions in two different geometries.

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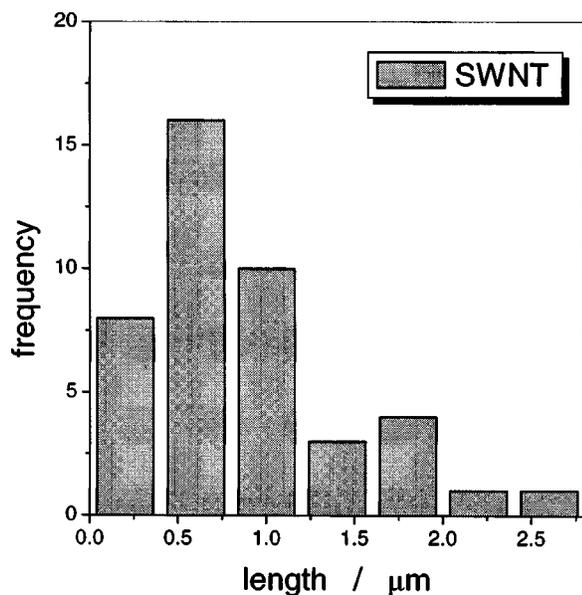


FIG. 1. Length distribution of the dispersed single-wall nanotubes (SWNT) as determined by scanning electron microscopy (SEM). The average length of the nanotubes after chemical treatment was approximately 600 nm.

II. EXPERIMENT

The single-wall nanotubes employed in this study are commercially available materials. They were produced by the laser ablation technique and purchased as purified material. Before use they were further treated to obtain a relatively uniform length distribution by breaking them into shorter segments by oxidative attack and repurifying them by treatment with strong acids and successive cycles of centrifugation, giving tubes of peak length in the range of 400–800 nm. The respective length distribution as determined by scanning electron microscopy (Cambridge Instruments Stereoscan 200) is depicted in Fig. 1. The multiwall nanotubes were kindly provided by E. Campbell, Chalmers University, Gothenburg. They were produced by chemical vapor deposition (CVD), purified by acid treatment and subsequently used as provided. Characterization by SEM showed that the multiwall nanotubes aggregated in large fibers,²³ with impurity residues. Electrical measurements on the liquid crystal–MWNT dispersions are, therefore, only discussed qualitatively. SWNTs were further characterized by atomic force microscopy (AFM, Quesant Nomad) and Raman spectroscopy²³ (Renishaw, laser wavelength 514 nm), the latter giving spectra equivalent to those reported in literature.^{24–26}

Liquid crystal–nanotube dispersions were prepared by adding small amounts of either SWNTs or MWNTs to the respective liquid crystals and sonicating the mixtures at 40 kHz for one hour to promote dispersion. It is presumed that this procedure reduces the bundling of nanotubes and thus enhances their solubility. The liquid crystals used, E7 and ZLI2806, are commercially available mixtures (Merck, Darmstadt) with a nematic phase at room temperature. E7 is a material with positive dielectric anisotropy ($\Delta\epsilon > 0$), whereas ZLI2806 exhibits a negative dielectric anisotropy ($\Delta\epsilon < 0$). The respective liquid crystal–nanotube dispersions

were introduced into sandwich cells of gap $d=6\ \mu\text{m}$ by capillary action in the nematic phase. These cells consist of parallel glass plates, coated with transparent ITO electrodes and a thin polymer layer to promote liquid crystal alignment. For the E7–nanotube dispersions, a planar cell geometry was used, with a rubbed polyimide alignment layer ensuring a uniform director field in the plane of the electrodes. As E7 has a positive dielectric anisotropy, application of an electric field will result in a reorientation of the liquid crystal from planar to homeotropic (perpendicular to the electrode plane) after a certain threshold voltage is exceeded. For the ZLI2806–nanotube dispersions a homeotropic cell geometry was used, with perpendicular anchoring being promoted by an alignment layer of JALS 240-R40, a special polyimide (JSR Electronics, Leuven). Due to the negative dielectric anisotropy of ZLI2806, application of an electric field results in a reorientation from homeotropic to planar. Uniform alignment was in all cases confirmed by polarizing microscopy (Nikon Optiphot-pol), which was also employed in combination with digital image analysis (JVC KY-F1030, image size 1280×960 pixels) for the determination of the orientation distribution function of E7–MWNT, as well as glycerine–MWNT dispersions. The latter were prepared to allow comparison with an isotropic fluid material of comparable viscosity. The reorientation of the nanotubes, induced by the respective Fredericksz transition of the liquid crystals (planar to homeotropic for E7 and homeotropic to planar for ZLI2806 dispersions), was followed by conductivity measurements (Wayne Kerr Precision Component Analyzer) at a frequency of 2 kHz at increasing voltage.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Orientational order

As mentioned above, the multiwall carbon nanotubes used in this study were aggregated in large fibers composed of many individual MWNTs. When filling the sandwich cells with the liquid crystal–nanotube dispersion, the cell gap represented a natural size selection. This is also the reason why we cannot state an exact composition of our dispersions within the cells. Dispersions of E7–MWNT in planar geometry were used to optically determine the orientational order distribution function with respect to the liquid crystal director \mathbf{n} ($\theta=0^\circ$), because their size was sufficiently large to be resolved by polarizing microscopy. The average length of the MWNT bundles (peak of the length distribution) was determined to be $20\ \mu\text{m}$, while the average width was $3\ \mu\text{m}$, the latter obviously being smaller than the cell gap. Figure 2(a) depicts the orientational distribution of the multiwall nanotubes determined from 65 individual MWNT bundles in E7. The distribution is clearly centered around $\theta=0^\circ$, the direction of the uniform liquid crystal director field. For comparison, Fig. 2(b) shows the orientational distribution of MWNTs in the isotropic liquid glycerine, with the direction $\theta=0^\circ$ taken as the edge of the cell. It is clear that in the latter case orientational order of the MWNTs is nearly absent. The fact that the distribution is not completely constant can be accounted for by effects of flow alignment when filling the sandwich cells, which leads to slightly reduced values for

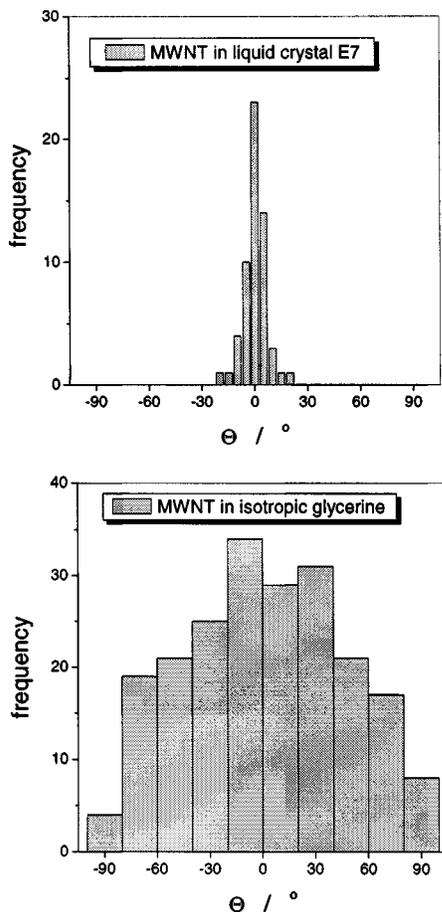


FIG. 2. Orientational order distribution of optically resolvable multiwall nanotubes (MWNT): (a) liquid crystal E7-MWNT dispersion (with respect to the liquid crystal director $\theta=0^\circ$) and (b) isotropic glycerine-MWNT dispersion (with respect to the flow direction $\theta=0^\circ$ during cell filling). From the distributions an order parameter of $S=0.9$ can be derived for the E7-MWNT dispersion and that of $S=0.36$ for the glycerine-MWNT dispersion.

orientation perpendicular and somewhat enhanced values for orientation parallel to the flow direction ($\theta=0^\circ$). Comparison of Fig. 2(a) and Fig. 2(b) unambiguously demonstrates that nanotube alignment is imposed through the liquid crystal. We presume that this alignment is the result of both elastic interactions between the liquid crystal and the MWNTs, as well as flow alignment during cell filling. From the order distribution functions of Fig. 2 the orientational order parameter,^{27,28} $S=\langle P_2 \rangle = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle$, for the nanotubes can be determined to $S=0.9$ for the E7-MWNT and to $S=0.36$ for the glycerine-MWNT dispersion. The latter value represents the contribution from flow alignment, while the former value is larger than that of the nematic order parameter ($S_{\text{nem}} \sim 0.6$). The reason why nanotube order imposed through the liquid crystal is even larger than that of the nematic phase itself lies in the additional contribution from flow alignment and the strongly reduced fluctuations due to temperature, because the nanotube bundles have a length and mass, which are many orders of magnitude larger than those of a liquid crystal molecule.

The dispersed single-wall nanotubes are too small to be resolved by optical microscopy; from the radial breathing mode (RBM=189 cm^{-1}) resolved by Raman spectroscopy,

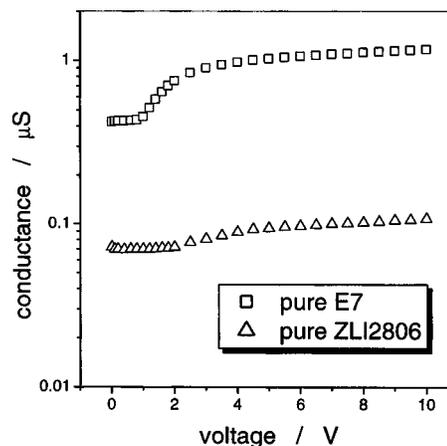


FIG. 3. Conductance as a function of the applied voltage of cells filled with the neat liquid crystal mixtures: E7 (squares) undergoing the Fredericksz transition from planar to homeotropic and ZLI2806 (up triangles), reorienting from homeotropic to planar geometry. The threshold voltage for the E7 planar-homeotropic reorientation is about 0.8 V, that of the ZLI2806 homeotropic-planar reorientation approximately 2 V.

the diameter of individual SWNTs is determined to be 1.2 nm. However, SEM investigations show an average length of 600 nm and an average width of 60 nm. This implies that at least before ultrasonic treatment a part of the dispersed SWNT material is aggregated in bundles, but clearly smaller than those of the MWNTs.

B. Nanotube reorientation

Having established that the nanotube's long axes follow the direction of the uniformly aligned liquid crystal director, we now apply an electric field to the liquid crystal—nanotube dispersions in sandwich cells with differing anchoring geometry. This induces a reorientation of the liquid crystal director, commonly known as the Fredericks transition, and through elastic interactions causes the nanotubes to follow this reorientation. The process can be followed by conductance measurements, because the nanotubes are highly conductive along the tube axis, while being basically insulating across it. Also the liquid crystal director reorientation causes a change in conductance, due to the anisotropy of the LC. This contribution is shown in Fig. 3 for pure E7 (squares) and pure ZLI2806 (triangles) as a function of increasing voltage. In both cases the conductivity slightly increases as the voltage exceeds the threshold for the Fredericksz transition from planar to homeotropic in the case of E7 and homeotropic to planar for ZLI2806.

Figure 4 depicts the voltage dependence of the conductance for the E7-SWNT dispersion. Starting from the planar orientation with the nanotube's long axes in the plane of the electrodes, a low and constant conductance is observed, which is somewhat larger than that of the pure E7 liquid crystal, due to the inevitable introduction of ionic impurities. As the threshold voltage for the transition to the homeotropic orientation is passed at approximately 3 V, the conductance drastically increases by about three orders of magnitude, indicating that the nanotubes follow the director reorientation into the perpendicular orientation with respect to the electrodes. At higher voltages the large conductivity along the

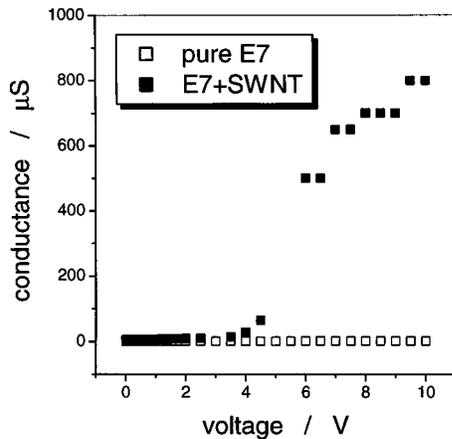


FIG. 4. Conductance as a function of the applied voltage for the E7-SWNT dispersion under planar anchoring geometry (full squares). For comparison also the conductance of the pure liquid crystal is depicted (open squares), which is clearly negligible. At a slightly smeared out and increased threshold voltage the conductance drastically increases as the nanotubes reorient from the nonconducting planar state at small voltages to the conducting homeotropic state at larger applied electric fields.

nanotube's long axes dominates the conductance behavior of the cell. Note that the contribution of the liquid crystal to the overall conductance is negligible, typically in the order of 0.1%. The strongly increased conductance is not due to a simple addition of ionic impurities, because in this case the data of Fig. 4 should scale with that of the square symbols of Fig. 3, which is not the case. It should be noted that a qualitatively similar voltage-conductance behavior is also observed for E7-MWNT dispersions in planar cells.

The counter-experiment with the dielectrically negative ZLI2806-SWNT dispersion unambiguously evidences the nanotube reorientation along with the liquid crystal director field. The respective voltage dependence of the conductance is depicted in Fig. 5. Even at very low voltages the conductance of the respective cell is large, demonstrating that the

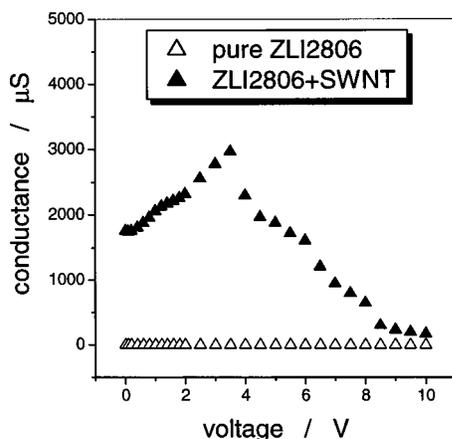


FIG. 5. Conductance as function of applied voltage for the ZLI2806-SWNT dispersion under homeotropic anchoring geometry (full triangles). For comparison also the conductance of the pure liquid crystal is depicted (open triangles), which is clearly negligible. The conductance increases below the slightly higher threshold voltage for the homeotropic (conducting) to planar (nonconducting) transition ($U_{th} \approx 3.5$ V), but as the threshold voltage is exceeded, the conductance decreases due to the reorientation of the nanotubes from the conducting homeotropic to the nonconducting planar orientation.

nanotubes are initially aligned perpendicular to the electrodes, following the homeotropic liquid crystal director field. This conductance increases with increasing voltage below the threshold of the Fredericksz transition to the planar state. At this point it is not entirely clear to which process this initial behavior is related. A possible explanation may be the electric field enhanced ordering or the attraction of nanotubes towards the electrode areas. As the applied voltage exceeds the threshold, the liquid crystal reorients from the homeotropic to the planar orientation. Assuming that the dispersed nanotubes follow the director reorientation through elastic interactions with the LC, a decrease of the conductance would be expected for the increasing voltage above the threshold, because the conducting long axes of the tubes will reorient into the plane of the electrodes. This is indeed the case as depicted in Fig. 5 for the ZLI2806-SWNT dispersion. At high voltages the conductance does not quite exhibit the value of the pure liquid crystal, again because addition of the nanotubes inevitably increases the concentration of ionic impurities. Once more, it should be noted that the conductance behavior of the cell is dominated by the nanotubes, with the liquid crystal contribution being approximately 0.1%.

It is also worthwhile to point out that we could not observe any of the conductance behavior reported for the liquid crystal-nanotube dispersion above by using an isotropic matrix, such as glycerine, chosen because it has a comparable viscosity to a nematic liquid crystal at room temperature. Neither could we observe the reported behavior in the isotropic phase of the liquid crystals at high temperatures. This provides further evidence that the conductance behavior shown in Figs. 4 and 5 is genuinely related to the nanotube interaction with the liquid crystal host.

We have thus unambiguously demonstrated that nanotubes cannot only be aligned through the self-organization of the liquid crystal, but that in fact the direction of the alignment can be pre-selected and even dynamically changed. In the present investigations the latter is accomplished via the application of electric fields. For illustration the respective reorientation processes are schematically summarized in Fig. 6, together with images of their texture appearance.

IV. CONCLUSIONS

We have demonstrated that the self-organizing properties of liquid crystals can be employed to unidirectionally orient carbon nanotubes of the single wall, as well as those of the multiwall type and have determined a nanotube orientational order parameter of approximately $S=0.9$ for the MWNTs. By means of quasi-static conductivity measurements as a function of applied electric field, we have furthermore shown that the collective reorientation processes of liquid crystals can be used to selectively determine the orientation direction of the dispersed nanotubes. This was demonstrated for both planar and homeotropic geometry, using a dielectrically positive and negative liquid crystal-SWNT dispersion, respectively. The reported investigations demonstrate an electrically steered OFF-ON (planar geometry) and ON-OFF (homeotropic geometry) switch based on liquid crystal-nanotube

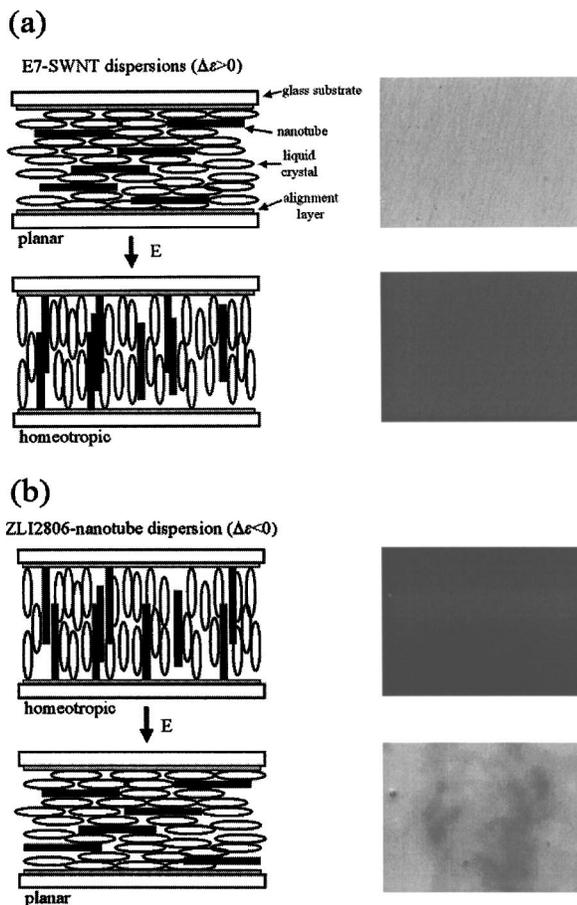


FIG. 6. Schematic illustration of the reorientation processes for (a) the planar to homeotropic transition of the dielectrically positive E7-SWNT dispersion and (b) the homeotropic to planar transition of the dielectrically negative ZLI2806-SWNT dispersion. The optical textures depicted in this figure, taken at an orientation of the liquid crystal optic axis (the director \mathbf{n}) out of the direction of crossed polarizers, confirm the respective reorientations and additionally illustrate that the dispersed nanotubes have no significant influence on the liquid crystal texture, i.e., the optical properties of the dispersion.

dispersions. Similarly, these devices could also be steered by the magnetic fields, exploiting the anisotropy of the magnetic susceptibility of a suitable liquid crystal host. We are currently in the process of investigating dispersions of nanotubes in ferroelectric liquid crystals to achieve an electrically controlled in-plane switch. Further applications can be envisioned by the use of an optically switchable host medium, such as liquid crystals (or respective boundary layers) undergoing cis-trans isomerization on illumination with light. This would result in a planar to homeotropic reorientation depending on the wavelength of the incident light. Possible applications are light steered electric switches and wavelength dependent sensors.

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