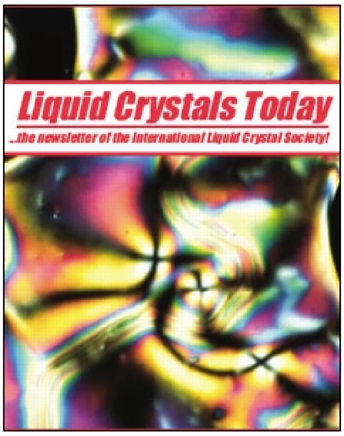

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Carbon nanotubes and liquid crystalline phases

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Carbon nanotubes and liquid crystalline phases

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This paper presents a review of the literature that deals with carbon nanotubes (CNTs) and liquid crystals (LCs) focusing on two main aspects. First, we describe the liquid crystalline behaviour of carbon nanotubes in solution. Via functionalization or absorption of amphiphilic molecules, CNTs can form nematic phases in water for concentrations above a few percents. Second, we explore the work done on the insertion of CNTs into thermotropic or lyotropic LCs. It is shown that it is possible to disperse small quantities of CNTs in various LC matrices and that the CNTs are responding to the LC director field. In some cases the CNTs are also strongly modifying the LC properties. These promising results indicate that carbon nanotubes and liquid crystals will certainly play an important role in the development of future applications and functional materials.

Keywords: carbon nanotubes, liquid crystalline phases, alignment, nematic, columnar, hexagonal, functional materials.

1. Introduction

Carbon nanotubes (CNTs) have been the subject of strong interest since their identification in the nineties [1–3]. These macromolecules are on the nanometer scale in diameter and on the micrometer scale in length. They can be viewed as highly anisometric rigid rod-like particles. Due to their exceptional mechanical, electronic and electromechanical properties, carbon nanotubes are very promising for a wide range of applications [4]. Recent studies have proved that the alignment of CNTs plays a critical role in the properties of nanotube based materials [5]. For example, it is established in classical mechanics of composite materials that the reinforcement by fibers can be improved by a factor up to six when one compares perfectly aligned and randomly distributed fibers. However, processing materials with well-controlled CNT alignment still remains a challenge. When dispersed or dissolved in liquids, CNTs are most of the time very diluted and form isotropic assemblies. In solid forms such as polymer composites, fibers, mats, CNTs are often disordered, or artificially ordered in the presence of an external field: magnetic, electric, shear, spinning or drawing.

Rod or disk-like molecules, rigid polymers, anisotropic colloids, and self-assembled amphiphilic molecules can exhibit liquid crystalline ordering in appropriate conditions of temperature and concentration. Liquid crystals [6, 7] (LCs) are often met in biological media or used for technological applications. For example the functions of electro-optical displays are based on the optical birefringence and dielectric anisotropy of nematic phases of rod-like molecules. Various commercial temperature sensors are made with chiral molecules ordered in cholesteric phases. Rigid polyaramide polymers are processed into extremely strong fibers (Kevlar®) from liquid crystalline phases which can be more effectively aligned. These simple examples demonstrate that new properties can emerge or be enhanced when materials are used in their liquid crystalline states, and strengthen the interest of making liquid crystalline phases of CNTs or inserting CNTs into existing liquid crystalline phases.

This paper is a review of the literature that deals with CNTs and liquid crystalline phases. From 2001, year of a first theoretical work on the liquid crystalline behaviour of carbon nanotubes, a number of advances have been achieved with experimental discoveries of various CNT and LC mixtures and demonstrations of novel properties. The focus of this review is twofold: 1) liquid crystalline behaviour of carbon nanotubes in solution, and 2) inclusion of CNTs in lyotropic or thermotropic LCs. These approaches are different but they both target new materials and emergence or enhancement of properties through the combination of CNT properties and liquid crystalline ordering. Synthesis, characterizations, and potential applications of these new materials are discussed. A conclusion that

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stresses challenge for future developments in the field closes the paper.

2. Liquid-crystalline behaviour of carbon nanotubes

Rod-like colloids, viruses, and rigid polymers form so called lyotropic liquid crystals when they are suspended in a solvent at a sufficiently high concentration. The transition from the isotropic to the nematic phase results from a competition between the rotational and translational entropies of the particles. But the phase behaviour of such systems also strongly depends on the interactions between the particles. This has been studied in depth with model viruses [8], which are monodisperse and perfectly straight rod like particles. In more complex systems, such as nanotube dispersions, not only the interactions between the rods themselves but also the tortuosity and polydispersity of the particles come into play. Even though the physical entropic origin of liquid crystallinity of rod dispersions is well understood, the phase behaviour of CNTs can be particularly complicated. In addition, the chemical stabilization of carbon nanotubes at high concentration is difficult in experiments.

From a theoretical viewpoint, the first studies considered CNTs as model straight, monodisperse and rigid rods. In this frame, Somoza *et al.* predicted in 2001 the phase behaviour of finite-size capped CNTs as a function of their length and diameter [9]. The authors studied the CNT liquid crystal phases with continuum-based density functional theory in two limit cases: the case of nanotubes interacting only via attractive van der Waals forces and the case of purely hard-core repulsive interactions. In the first case, nematic but also columnar phases are expected with increasing CNT concentration. The latter are stable even at high temperatures. According to the authors this is consistent with the structure of ropes or bundles with hexagonal ordering that is commonly observed when single wall carbon nanotubes are synthesised via high temperature techniques [10]. Nevertheless, such ropes are obtained in dried states and do not involve liquid crystalline ordering during their growth at high temperature in extreme conditions. The actual link between the thermodynamic stability of columnar phases and the existence of ropes remains questionable. In addition, it is worth noting that when stabilized by surfactants, CNT ropes do not grow in diameter as one would expect for the coarsening of a phase separation. Nevertheless, the stability of a columnar phase predicted by Somoza can explain why ropes are so stable and CNT unbundling so difficult. Indeed in general CNTs can be unbundled only through strong sonication.

In the case of purely repulsive interactions between tubes, when van der Waals forces are screened out, both nematic and smectic-A phases could be obtained. As expected, the isotropic-nematic transition is dependent on the length of the nanotubes. For a given CNT diameter the transition is reached at lower concentration when the CNTs are longer (i.e., greater aspect ratio). The smectic phase is expected at higher concentration. All these predictions are consistent with previous studies made on liquid-crystal phases, in particular with the behaviour of systems such as TMV, f_d viruses [11], or DNA [12]. While nematic phases have been experimentally reported, no evidence of smectic phases of carbon nanotubes has ever been shown. The observation of a smectic phase of rods necessitates a polydispersity as narrow as possible: the actual polydispersity of carbon nanotubes does not allow the formation of lamellar phases.

To our knowledge, the first experimental liquid crystals made of CNTs were successfully achieved via three different routes that are described below.

The first experimental observation of the existence of a lyotropic liquid-crystal phase of multiwall carbon nanotubes (MWNTs) has been reported by W. Song *et al.* in 2003 [13]. The nanotubes were synthesized by a CVD method. They were then acid treated to become hydrophilic thanks to COOH- surface functionalizations [14]. Such covalently modified CNTs can be dispersed in water without surfactants or other additives. Examination of a series of aqueous dispersions of different nanotube concentrations showed a phase transition from isotropic to nematic above a critical CNT volume fraction of about 1%. In a following paper [15], the same group has explored the isotropic-nematic transition in further details. Using scanning electron microscopy (SEM), the dimensions of the nanotubes were carefully characterised in order to explain the enlargement of the biphasic regime between the isotropic and nematic phase. The biphasic regime typically occurs above 1% concentration of nanotubes, and vanishes above 4%. As shown in figure 1, the system forms a single nematic phase above this concentration. Onsager theory [16] predicts that monodisperse and rigid rods of diameter D and length L form an isotropic phase for concentrations lower than $\phi 1_{the}=3.3D/L$ and a nematic phase above $\phi 2_{the}=4.5D/L$. Here the biphasic domain is wider. The enlargement was attributed by the authors to the polydispersity of the system in terms of length, diameter and straightness of the nanotubes. Such a polydispersity was also expected to yield segregation of the more "mesogenic" CNTs into growing liquid crystalline phase. This last hypothesis is very interesting because it opens the route

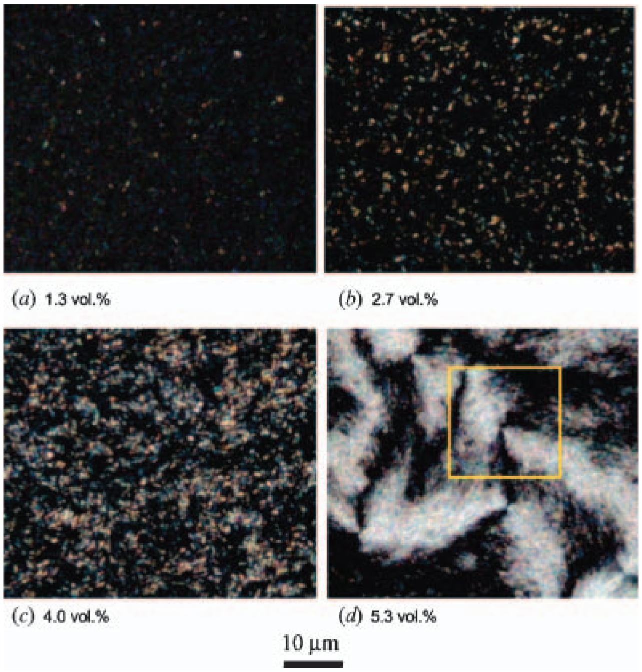


Figure 1. Micrographs of MWNT dispersions at different concentrations, imaged in reflected light with crossed polarisers: (a) 1.3 vol% dispersion, showing weak birefringence from nematic nuclei; (b) 2.7 vol%, where growing nematic nuclei appear; (c) 4.0 vol% dispersion, where the nematic nuclei are beginning to "join up" in some regions; (d) 5.3 vol% dispersion, showing the Schlieren texture of nematic liquid crystals (reprinted with permission from reference [15]).

to a way of sorting nanotubes by their size upon separation of the nematic and isotropic phases. Windle's group has recently experimentally tested this idea [17], thus using the nematic liquid crystal phase to make a separation of the nanotubes as a function of their dimensions. Fractionation was achieved in the isotropic-nematic region of the so-called Flory chimney of the phase diagram. The fractionation was successfully achieved either by accelerating it via centrifugation or by letting the preparation stand. In both cases, in using SEM photographs to quantify sorting of long and small tubes, it was shown that long and straight nanotubes, those with higher mesogenicity, separate preferentially to the nematic phase, whereas smaller nanotubes and impurities remain preferentially in the isotropic one. This method seems efficient to separate nanotubes on the basis of their relative mesogenicity and allows thereby the polydispersity to be decreased.

Parallel to this work made exclusively on MWNT, P. K. Rai in M. Pasquali's group has established the phase diagram of single wall carbon nanotubes (SWNT) in superacids. In this particular system, the nanotubes are solubilised in fuming sulphuric and chlorosulfonic acids [18, 19]. Strong acids protonate the sidewalls of the SWNT, resulting in a delocalized positive charge on the carbon atoms; this induces electrostatic repulsion between tubes and promotes their dispersion. As shown in figure 2, here also the phase diagram is reminiscent of the phase behaviour of other rod-like macromolecule and anisotropic particle suspensions. The phase boundaries are expected to depend on the amount of sulphuric acid and thus on the strength of the superacids [20]. To quantify the maximal amount of nanotubes that can exist in the isotropic phase, the authors have centrifuged the biphasic samples, separating thereby the isotropic phase from the ordered phase. The nanotube concentration was quantified in the isotropic phase by UV-vis-nIR absorbance. This work was done for several dispersions with increasing acid strength. The results show conclusively that the maximum amount of nanotubes in the isotropic phase depends on the acid strength. The isotropic to biphasic transition threshold increases with the acid strength. In other words, the isotropic phase is more stable when the acid strength is high, because the nanotubes are more protonated and experience stronger charge stabilization. By pointing out the effect of the strong interactions of the nanotubes with the solvent, this system has opened the route to the exploration of mechanisms involved in the stabilization of CNT dispersions, where "solvent quality" appears to be a critical parameter. Such kind of rod suspensions escapes the simple Onsager-like hard rods, because first, they involve strong van der Waals interactions between nanotubes and second, because the solvent screens the electrostatic repulsion, much more efficiently than, for

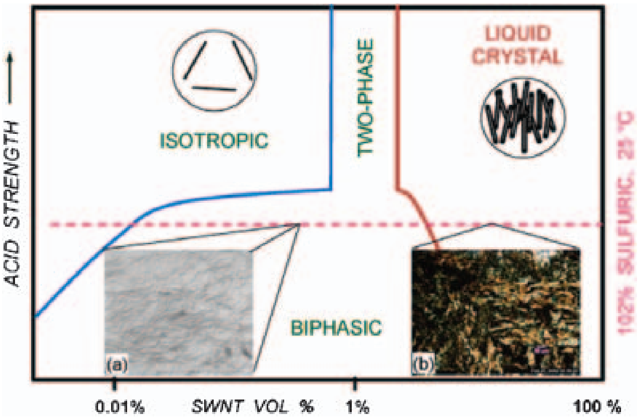


Figure 2. Postulated phase diagram of SWNTs in acids. In 102% sulphuric acid, the biphasic region extends from a concentration of 100 ppm to 8%. The inset (a) shows the domains of ordered SWNT surrounded by the isotropic phase, and the inset (b) shows the birefringence of the pure liquid-crystalline dispersion (reprinted with permission from reference [20]).

example, electrolyte solution in the case of rod-like polyelectrolyte.

Another piece of experimental evidence for the existence of a liquid crystalline phase of carbon nanotubes has been shown in 2005 by Badaire *et al.* [21]. The particularity of this work, compared to the previous ones, consists in using non-functionalized nanotubes dispersed in water. It has the advantage of keeping the nanotubes unmodified while still using a solvent that is easy to handle. According to the authors, surfactants, which are commonly used as efficient agents to disperse nanotubes in water, cannot be easily used to obtain CNTs homogeneously dispersed at high concentrations. Actually, surfactants form free micelles in the dispersion, which induce aggregation of the nanotubes by depletion phenomena. The aggregates are disordered and form a percolated network which spans the volume of the sample. It is possible that they impose kinetic barriers toward the formation of LC phases. This still needs further studies to be clarified [22–24]. Denatured DNA was used as dispersant to avoid depletion induced CNT aggregation. Denatured single stranded DNA is a charged amphiphilic polymer that strongly adsorbs on nanotubes, thus effectively dispersing them into water via electrostatic repulsions. The phase diagram [SWNT/DNA] is very simple and exhibits two domains separated by a line which goes through the origin and which has a slope close to one [25]. Above the line the nanotube bundles are homogeneously dispersed after sufficient sonication. Below the line, at low DNA concentration, nanotube aggregates are still observed even after strong sonication because of insufficient coating of the nanotubes by the stabilizing polymers. This behaviour simply reflects that a well defined minimum amount of DNA has to be adsorbed onto the nanotubes to stabilize them and to overcome van der Waals attraction. By gently evaporating water, Badaire *et al.* could increase the nanotubes concentration up to 5 wt%. They observed the formation of a SWNT lyotropic nematic phase, with a biphasic regime in between 2 wt% and 4 wt%, as shown in figure 3.

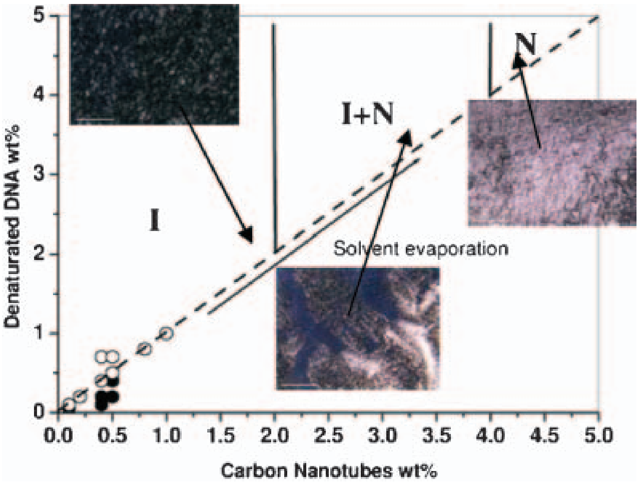


Figure 3. Phase diagram of DNA stabilized SWNT dispersions. The dashed line indicates the limit above which carbon nanotubes are homogeneously dispersed after sonication (white circles). Below the line, aggregates are still observable (black circles). The systems are concentrated to levels greater than 4 wt% by solvent evaporation. This method allows the concentration of DNA and nanotubes to increase proportionally. In the domain of homogeneously stabilized nanotubes, the system forms an isotropic (I) phase at concentrations below 2 wt%, and a nematic (N) phase above 4 wt%. Coexistence (I+N) is observed in between these boundaries. Insets: optical micrographs between crossed polarizers. (a) 2 wt% birefringent domains are visible. (b) 3.4 wt% the proportion of birefringent domains increases. (c) Above 4 wt%, the all sample is birefringent. (Scale bar 200 μm) (reprinted with permission from reference [21]).

The boundaries of the biphasic domain are wider than those predicted for monodisperse rods. Like in [13] the authors explained this widening by considering the polydispersity of the nanotubes. Comparing the boundaries of the experimental phase diagram to that predicted by the Onsager model, they estimated limits for the aspect ratio of the nanotubes. The obtained values are consistent with those obtained via dynamic light scattering measurements [26].

In 2004, Islam *et al.* [27] proposed an elegant approach to circumvent the difficulty of using surfactant to reach concentrated dispersions of CNTs, by embedding surfactant stabilized CNTs [28] in a *N*-isopropyl acrylamide gel which prevents the aggregation of the bundles and which can be used to order them upon thermal deswelling. This system differs from previously studied materials because the CNTs are not freely dispersed in dispersion. With increasing the temperature up to 323 K, the CNT gel, which is initially isotropic, expels water and compresses of a volumic factor close to 8. This compression induces an increase of the SWNT concentration and the system becomes liquid-crystalline. Optical polarised microscopy is performed on different gels containing increasing concentrations of CNTs. Observations reveal that the isotropic-nematic critical concentration is 3.3 mg/ml, e.g., almost 0.33 wt% in the initial gel before swelling. A simple multiplication by the compression factor leads to a concentration of almost 2.4 wt% in the compressed gel. This is close to the fractions in other systems described above. In spite of the constrained Brownian motion of the CNTs in the gel, this similarity suggests that the transition is still driven by a comparable effect which is the competition between rotational and translational entropies.

Since 2001, several experimental contributions have been reported, all of them describing different ways of making liquid-crystalline phases of carbon nanotubes in solution. Via functionalization or absorption of amphiphilic molecules, these systems form nematic phases most of the time for concentrations above a few weight percent. This is consistent in the frame of the Onsager model with aspect ratios typically on the order of 100. Nevertheless, the biphasic domains are somewhat larger than that expected for monodisperse rods. This is explained by the actual polydispersity of currently available CNTs. It thus seems that the physics of CNT liquid crystals is quite well understood on the basis of our previous knowledge of lyotropic nematics. Nevertheless, some challenges are still faced for future developments and potential applications. Indeed, in all these studies, the nematic monodomains are not larger than a few micrometers. This limitation in size is probably related to the fact that nanotubes are not perfect rigid rod-like particles and that they contain impurities. They exhibit structural defects and some tortuosity. As pointed out by the previous authors, they are also very polydisperse. Nevertheless, it seems possible to go towards straighter and more uniform particles. Fractionation as proposed by Windle *et al.* is an exciting and promising route. It has also been shown that CNT dispersions sonicated for long durations at high power contain CNTs which are cut into shorter and more uniform fragments [26]. Investigating the effect of the CNT morphology on the phase diagrams of their dispersions is of great importance to advance the field. Better control and understanding of the long range alignment are critical for the macroscopic ordering of CNT liquid crystals and for properties such as responses to shear, electric or magnetic fields. Even if CNT liquid crystals could be useful as novel field responsive fluids their most exciting properties will probably arise from solid materials derived from liquid crystal ordering. Indeed, composites or films made of homogeneously aligned CNTs are expected to exhibit improved mechanical and transport properties compared to materials where CNTs are isotropically distributed. Aligned CNT films are also expected to exhibit anisotropic optical properties such as luminescence and transmittance. This could be useful for anisotropic optical filters, sensors or wave guides.

3. Insertion of carbon nanotubes into thermotropic or lyotropic liquid-crystalline phases

From a general point of view, there are few examples of experimental studies of anisotropic nanosized particles inserted in LC phases. Depending on the type of liquid crystals used, various phenomena can be expected. In a thermotropic liquid crystal where the molecules are small compared to the inclusions, the medium can be considered as continuous. It is theoretically predicted in this frame that the LC distortions around the particles and induced elastic interactions should vary as the size and shape of the particles are modified [29–38]. If the size of the inclusions becomes comparable to the characteristic size of the liquid crystalline medium such as for nanosized inclusions in lyotropic liquid crystals other effects can dominate. In this case the ordering of the particles can result from their confinement in the layers of lamellar phases or in the columns of hexagonal phases. CNTs meet the criteria to enter in both categories. They are substantially larger than small molecules of conventional thermotropic liquid crystal and their diameter is on the order of the characteristic size of surfactant based lyotropic liquid crystals. This opens the route to a broad variety of materials where CNTs can be ordered in response to the ordering of the liquid crystal host. Examples of systems already studied in these two limits are described in the two following chapters.

From an applied point of view, such systems are of potential importance for the development of new functional composites and devices, where the concentration, dispersion and orientation of the loading particles necessitate a strict control and where the use of a LC matrix could be an effective way to steer the alignment of the particles. Novel properties and potential applications are described in sections 2 and 3.

In this context, inclusion of carbon nanotubes into liquid crystal phases is particularly promising. Nanotubes are highly anisotropic particles on the nanoscale, exhibiting fascinating properties that could lead to new composites or devices with enhanced optical, electrical or mechanical properties.

3.1 *Dispersion of carbon nanotubes into thermotropic liquid crystals*

Experimentally, anisotropic particles have been studied in the context of ferronematic fluids (solutions of small magnetic particles in nematic solvents) [39–41]. It was shown in these studies that the presence of anisotropic particles allows enhancement of the response of the LC to magnetic fields. But these particles are most of the time on the micrometric scale and the studies do not throw light on what happens when the particles are at the same times anisotropic and nanometric. 2D simulations of the behaviour of anisotropic particles embedded in a LC matrix have been proposed by

Andrienko *et al.* in 2002. More recently, 3D predictions have been reported by de Pablo *et al.* [42]. The main expected effect for an isolated particle is the alignment of the rods parallel or perpendicular to the nematic director. If the anchoring at the surface of CNTs is parallel the CNTs will experience an elastic torque when their orientation deviates from the director alignment. If the anchoring is homeotropic, the CNTs are expected to align perpendicular to the director and to experience a torque when they deviate from this preferred alignment. But in addition to simple elastic torques, elastic distortions are also expected to induce anisotropic interactions between the particles and specific ordering. While several examples of preferentially aligned particles have been reported, the consequences of elastic inter-particle interactions are still elusive from an experimental point of view.

The first experimental paper dealing with the inclusion of carbon nanotubes into a LC phase was published in 2002 by Lynch and Patrick [43]. The authors explored two thermotropic LC systems, one being 5CB (4'-pentyl-4-cyanobiphenyl), the other being E7 (a mixture of alkyl and alkoxycyanobiphenyls). Both are well-known for exhibiting a nematic phase at room temperature. The nanotubes used are either MWNTs or SWNTs. The dispersion was realised by sonicating a mixture of pristine CNTs and LC. No indication of the amount of dispersed nanotubes was given. The mixture was deposited onto a grooved polycarbonate membrane (the grooves promote unidirectional alignment of the LC) and drawn slowly through the pores in order to remove the LC solvent, thus leaving a CNT film on the substrate. Observations by AFM were performed to characterize the orientational ordering of the CNTs. Nevertheless, the authors confess that the AFM images had to be done soon after deposition, otherwise nanotubes flocculated in the liquid crystal solution. This is clearly related to the fact that the CNTs are not functionalised and are not chemically compatible with the liquid crystals. This results in a poor stability of the CNT/LC mixture. Nevertheless, once the deposition was achieved, this study showed that either MWNTs or SWNTs responded to the liquid crystal ordering, whatever the thickness of the film.

The technique allowed getting ordered films of CNTs with very high degrees of alignment along the nematic director field. The reported order parameters S is typically between 0.7 and 0.9. The alignment along the director suggested that the anchoring is parallel to the long axis of the nanotubes in both 5CB and E7. As pointed out by the authors, nanotube functionalization should be a way to tune the orientational behaviour of the particles in the LC phase.

In the same year, Da Cruz *et al.* [44] have made dispersions of single-walled carbon nanotubes in 5CB. The mixture was prepared by crushing 2 wt% SWNT and the LC in a mortar. The materials were studied by X-ray scattering and revealed unusual responses to magnetic fields. But the origin of the observed phenomena remained unclear mainly because of the poor stability of the CNTs dispersions and of the presence of large aggregates.

More recently, Kumar *et al.* have published a work in which, very interestingly, they covalently functionalize the nanotubes before including them into a discotic LC phase [45]. This functionalization was performed to make CNTs and LC chemically compatible. The SWNTs were first converted into SWNT-COCl and then mixed with hydroxy-terminated triphenylene. The resulting nanotubes were carefully analysed by different methods, all of them proving the covalent grafting of the triphenylene units on the tubes, even if the functionalization stoichiometry is not indicated. Mixtures of these discotic-functionalized CNTs and triphenylene-based discotic LC (H4TP) were then produced. The authors included up to 10 wt% CNTs in some mixtures, which is very high compared to previous studies. Via polarised optical microscopy (figure 4a) and differential scanning calorimetry, they deduced that the mixtures are columnar mesophases at low temperature. The insertion of CNTs seems to decrease the isotropic to mesophase transition temperatures from 146°C for the pure H4TP to 135°C for the 10 wt% CNT-H4TP composite. Moreover, compared to the pure H4TP phase, which exhibits a hexagonal columnar mesophase, the CNT-H4TP only exhibits a columnar plastic phase, which is less ordered than the

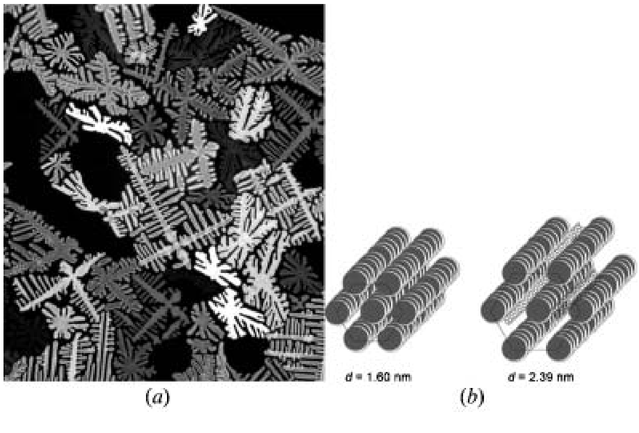


Figure 4. (a) Polarised optical microscopy image of the columnar phase of a mixture containing 10 wt% of functionalised carbon nanotubes and H4TP. (b) Scheme of the insertion of the nanotubes in the columnar phase (reprinted with permission from reference [45]).

hexagonal one. The authors explained this by considering the presence of nanotubes, which would give a positional freedom to the disks. Lastly, X-ray data suggested that the functionalised CNTs are in the space between the disk columns, as speculated in figure 4b. This is, to the best of our knowledge, one of the rare examples of insertion of stable CNTs at high concentrations into a LC host. These studies suggest the thermodynamic stability of the CNT-LC composites, and the effect of the CNT presence on the transition temperatures.

These different contributions clearly reveal that the chemistry of the nanotube dispersions in the LC matrix is of primary importance. Understanding and control of the interactions between the CNTs and the LC molecules are key points to obtain high quality dispersions. A light has recently been brought on this aspect by Scalia *et al.* [46]. In this paper, the authors have performed Raman spectroscopy of SWNT dispersions in 5CB. They focused on the radial breathing modes (RBMs) of the nanotubes. Compared to pure CNTs, the four RBM peaks of CNTs in 5CB exhibit a shift between 1.6 and 5 wavenumbers (see figure 5). This effect can be explained by a π-stacking interaction involving the phenyl rings of the LC at the CNT surface. In addition, polarised optical microscopy observations revealed that the nanotube bundles act as nucleation sites for the LC organization. This study gives a precise idea of the interface across the LC and the CNTs. We expect that this interface plays an important role in the stability of the mixture, in the anchoring of the nanotubes and thereby in their response to the LC long range ordering.

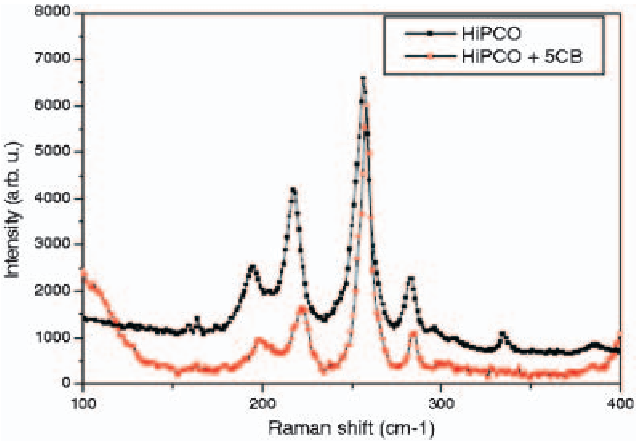


Figure 5. Raman spectra in the RBM (radial breathing mode) of SWNT nanotubes alone (upper curve) and SWNT nanotubes in 5CB liquid crystal (lower curve) (reprinted with permission from reference [46] © 2006).

3.2 *Carbon nanotube inclusion into lyotropic liquid crystals*

There are less examples of inclusion of carbon nanotubes into water-based lyotropic liquid crystals. However, as lyotropic LCs are water-based and common in biological and living systems, it could be very interesting to use CNT/lyotropic LC mixtures for biotechnological applications, like, for instance, templating for cell growth.

The insertion of CNTs into lyotropic liquid crystalline phases was first investigated in 2006 by Weiss *et al.* [47]. The authors demonstrated the inclusion of SWNT in a lyotropic hexagonal phase. 1 wt% of nanotubes was first dispersed in water with either Triton X-100 (non-ionic surfactant) or SDS sodium dodecyl sulphate (anionic surfactant), using sonication. This method is well-known to yield stable and homogeneous suspensions [28, 48]. Then the aqueous dispersion was added to the hexagonal phase of Triton X-100 in water, keeping the amount of Triton close to 50 wt% in the prepared samples. Figure 6 shows micrographs of the hexagonal phase, with and without SWNTs. No phase separation could be observed at the microscopic scale, suggesting a good incorporation of the tubes in the LC phase. The observations are only qualitative, but it seems that the LC matrix imposes a good degree of alignment of the CNTs. In order to better quantify the insertion of CNTs, small angle X-ray scattering (SAXS) and rheological experiments were performed depending on the amount of inserted CNTs. SAXS allows determination of the d-spacing of the hexagonal phase. According to authors, it seems that there is a critical quantity of nanotubes of 0.15 wt%. Below this value, the d-spacing of the hexagonal phase is regularly increasing with the amount of CNTs, indicating a swelling of the phase. Above 0.15 wt%, the distance suddenly decreases and returns to the value of the phase without CNTs. According to the authors this phenomenon is due to the

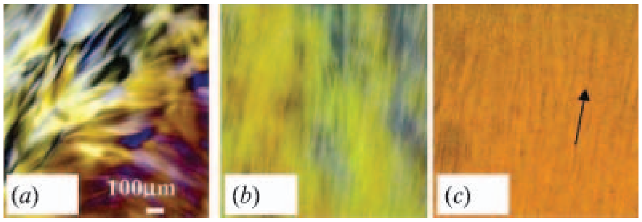


Figure 6. Micrographs of 50 wt% Triton X-100 without and with SWNT (a) without SWNT (under polarized light), showing the texture of the hexagonal phase, and a 0.25 wt% SWNT-doped system imaged using (b) polarized light and (c) unpolarized light. The alignment along the LC director is indicated by an arrow (reprinted with permission from reference [47] © 2006).

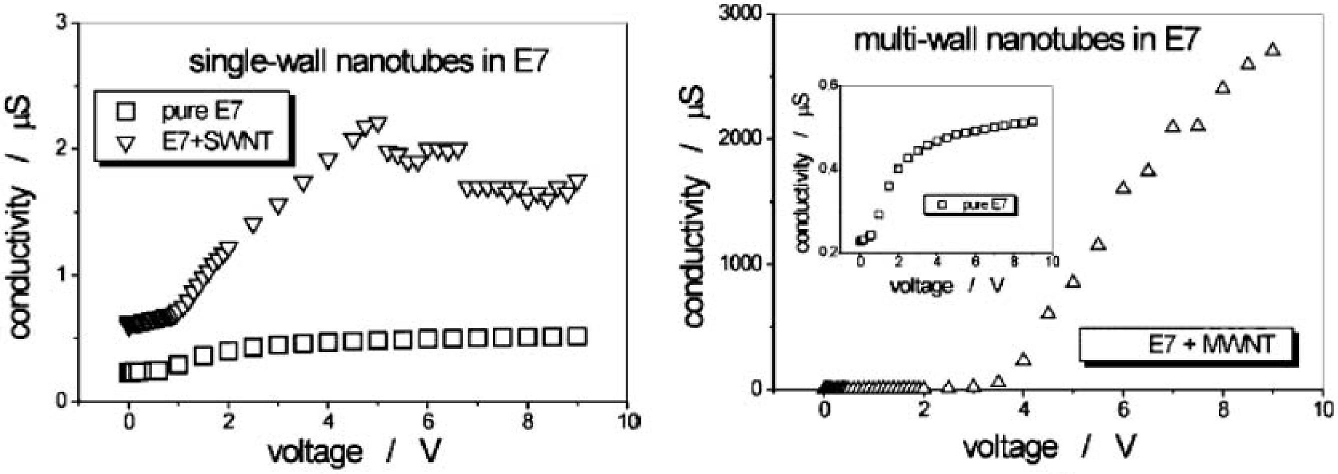
expulsion of the CNTs from the hexagonal phase. But it is not clear why the nanotube doped phase becomes less concentrated (smaller d-spacing) whereas the total nanotube concentration is increased.

Very recently Lagerwall *et al.* have reported another study with the use of nematic lyotropic liquid crystals to align carbon nanotubes [49]. It is, to our knowledge, the only other example of insertion of CNTs into a nematic lyotropic LC. The chosen LC phase is a discotic nematic phase in the ternary SDS-decanol-water system. SWNTs at concentrations up to 0.1 wt% were dispersed in the nematic phase. Even if no visible sedimentation could be detected, optical microscopy revealed small aggregates for concentrations above 0.01 wt%, once again pointing out the difficulty of making stable mixtures of LC and CNTs at high concentration. Under 0.01 wt% of CNTs, the mixture is stable. The order parameter of the stable mixture was evaluated by polarised Raman spectroscopy, which is a technique very sensitive to the degree of alignment of the tubes. For technical reasons described in this paper and in a previous one [50] related to the Raman technique, the addition of a small amount of a chiral dopant was necessary, the LC phase thus becoming cholesteric. The Raman measurements indicated that the nanotubes are aligned along the LC director and allowed the determination of the order parameter S, which is equal to 0.6. In this paper like in the previous one, the authors demonstrated that it is possible to include small quantities of nanotubes into a lyotropic LC and that the CNTs follow the LC director.

3.3 *Novel properties of carbon nanotube modified liquid crystals*

Previously discussed contributions focussed on the inclusion of CNTs into LC matrices with the main attention paid to the structure, chemistry, and quality of the dispersions. A further step is to know how the nanotubes modify the liquid crystal physical properties. Some groups have begun to bring exciting answers to this question. For example, nematic liquid crystals have been doped by carbon nanotubes in order to obtain faster electro-optical responses [51]. Other studies have discussed the effect of CNT addition on the dielectric anisotropy of the doped LC [52, 53], or in the local deformation of the LC director under application of in-plane external field [54].

In 2004 Dierking *et al.* succeeded in dispersing both SWNT and MWNT in E7 [55]. The SWNTs and the MWNTs were dispersed in E7 via sonication. Then the mixture was introduced into sandwich cells with a 6 µm gap. According to the authors, the small cell size realises a size selection, preventing the longer nanotubes from entering the device. This also makes it difficult to determine the exact CNT concentration in the cells. The upper plate of the cell was unidirectionally rubbed to promote planar alignment of the LC along the rubbing direction. Polarised optical microscopic observations realised subsequently indicated that the nanotubes are aligned in the cell with a high order parameter of $S=0.9$. Reorientation experiments were then made on the CNT/E7 mixture. The conductivity of the mixture was measured versus the voltage applied perpendicularly to the cell. First of all, both in case of SWNT and MWNT, the reorientation of nanotubes occurs via the reorientation of the director field of the LC (Freedericksz transition), from planar to homeotropic orientation. Moreover, it is shown that the addition of nanotubes induces a pronounced increase of conductivity above the threshold voltage as compared to pure E7. The mixture probably benefits from the high anisotropy and high conductivity of the nanotubes. This is illustrated in figure 7, where the voltage dependences of the conductivity of the SWNT/E7 and MWNT/E7 mixtures are shown. The global behaviour is the same in both cases, showing that it is possible to reorient the nanotubes in E7 at almost the same threshold voltage. But very interestingly, the conductivity above the transition voltage is much smaller with SWNT than with MWNT, and exhibits fluctuations at large voltages (typically above 4V). According to the authors, this could be attributed to the smaller size of SWNT compared to that of MWNT, the first making network connections which are unstable and subject to fluctuations and the latter reorienting on a whole in a more stable configuration. In any case the increase of conductivity due to the presence of MWNT is very high, as it is 5000 times higher in the MWNT/E7 mixture than in the pure E7 at 8V. In a following article [56], Dierking *et al.* compared the reorientation effect using E7, which has a positive dielectric anisotropy and another LC host, the ZLI2806, with a negative dielectric anisotropy. With ZLI2806, as expected, the conductivity of the mixture decreases once the threshold voltage is passed, the nanotubes following the field-induced homeotropic to planar transition. The two examples, E7 and ZLI2806, unambiguously demonstrate that the alignment of the nanotubes can be pre-controlled via the LC matrix, and then steered using an external field. In another work [57], the authors also demonstrated the efficiency of a magnetic field to reorient the CNT/E7 dispersion and subsequently to increase the systemss overall conductivity. The device is operating at low voltages and its performances increase at high frequencies. These studies demonstrate the advantage of combining CNTs and LC and are the first examples



(*a*) (*b*)

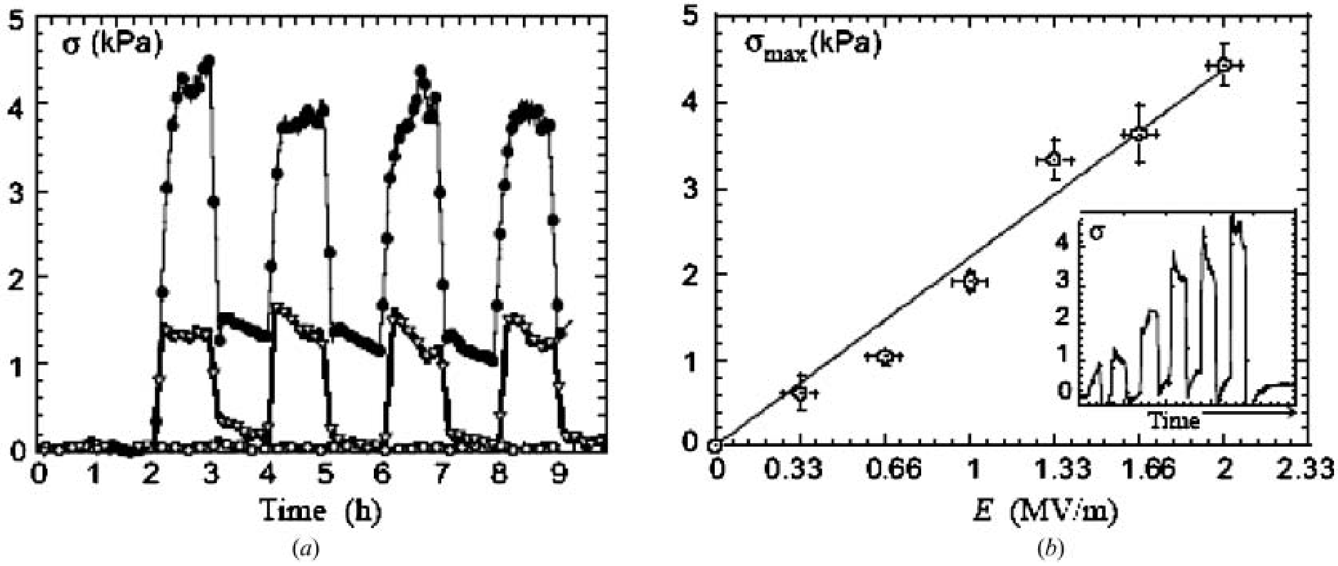
Figure 7. Voltage dependence of the conductivity of a) E7/SWNT mixture (open triangles), and b) E7/MWNT mixture (open triangles). In each graph the data of pure E7 are given (open squares). In both cases, one observes a strong conductivity increase after the threshold voltage is passed, but this increase is much more pronounced in the MWNT/E7 dispersion than in the SWNT/E7 dispersion case (reprinted with permission from reference [55]).

of electrically or magnetically controlled CNT OFF-ON electrical switches. They open the route to devices and applications based on CNT/LC mixtures that would be controlled by various external fields.

Another original application using a mixture of nanotubes and liquid crystal has also been proposed by Courty *et al.* [58]. In this study, the authors filled a nematic elastomer with CNTs at low concentrations (~0.01 wt%). The nanotubes were mixed with toluene via high-power sonication but once again without functionalization and then transferred into the elastomer mixture. This resulted in nanotubes embedded in a rubber elastic medium and aligned along the nematic director at preparation. The alignment was not precisely measured but qualitatively confirmed via tricky SEM experiments. The composite exhibits a very large dielectric anisotropy due to the presence of the CNTs; providing thereby opportunities to achieve extremely high electric energy densities upon application of an electrical field. Actually, when an electric field of the order of 1 MV/m is applied perpendicular to the nematic direction, and thus to the nanotube alignment, the local field-induced torque of the CNT is transmitted to the nematic elastomer and provokes an actuation of the composite with a generated stress of ~1 kPa. The value of this stress is dependent on the field strength but also on the CNT concentration, as shown in figure 8. No electromechanical response can be measured when there are no nanotubes in the structure, evidencing the impact of their insertion in the nematic elastomer. This paper gives an interesting example of a functional composite that can be achieved by mixing carbon nanotubes and a LC matrix. The feasibility of the device is demonstrated, but the authors confess that outstanding problems are remaining. Among them, the difficulty to increase the quantity of CNTs in the matrix, probably related to their poor chemical compatibility.

4. Conclusion

Carbon nanotubes are nano-anisotropic particles of great interest for their intrinsic mechanical, electrical or optical properties. Exploiting these properties on macroscopic scale often requires control of the CNT spatial ordering. It is today well established that such an ordering can be achieved through liquid crystallinity. Several groups have in the recent years succeeded in making either CNT liquid crystals by dispersing CNTs at high concentration in isotropic solvents or by including CNTs in lyotropic or thermotropic LC media. Alignment of the CNTs was successfully obtained. But challenges are still faced in particular to obtain materials aligned on large scale for liquid crystalline CNT dispersions and to stabilize CNTs in thermotropic liquid crystals. This means that research is still needed to improve the chemistry of the investigated and to better understand the morphological factors that govern their ordering. But pioneering studies of the properties of CNT based liquid crystals and CNT liquid crystal mixtures confirm that further and multidisciplinary research efforts are well worth in this field at the boundaries of chemistry, physics and engineering.



(a) (b)

Figure 8. (a)-Field cycles for samples with increasing CNT concentrations: 0% (non filled elastomer) (open circles), 0.0085% (open triangles) and 0.02% (filled circles). (b)-Dependence of the plateau stress $\sigma_{\max}$ on the applied field strength, for the 0.02% composite. The inset shows the elapsed time dependence, with each cycle at increasing constant field E. The linear fit gives a value of $\sigma_{\max}$=2.3E (MV/m) (reprinted with permission from reference [58]).

Indeed, it was already shown that the addition of CNTs to liquid crystals can lead to improved actuator technologies as well as novel electrical switches. Other functional materials and devices can be anticipated based on the intrinsic properties of CNTs such as their electronic properties for photovoltaic applications in discotic liquid crystals, electrochemical actuators and sensors with mats of ordered CNTs with enhanced properties compared to unoriented materials or more simply strong and lightweight composites. There is no doubt that an important part of the future of CNT science and technology will lie in the fourth state of matter.

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