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Effect of carbon nanotubes on phase transitions of nematic liquid crystals

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Phase diagrams of multi-wall carbon nanotube (MWNT)/nematic liquid crystal (E7) and buckminsterfullerene (C_{60} - I_h)/nematic liquid crystal (E7) binary systems have been investigated by means of polarizing optical microscopy and differential scanning calorimetry. It was found that the isotropic–nematic phase transition temperature (T_{NI}) of the liquid crystal component was enhanced by the incorporation of MWNT within a small composition gap. A chimney-type phase diagram can be identified in the MWNT/E7 mixture over a narrow range of ~ 0.1 – 0.2% MWNT concentration. Upon substituting the nanotubes with isotropic fillers such as fullerene, the (C_{60} - I_h)/E7 blend showed no discernible change of T_{NI} in the same concentration range of the chimney of the MWNT/E7 mixture, suggesting a significant contribution of anisotropy (or the aspect ratio) of the nanotubes to the entropy of the system containing liquid crystal molecules. This enhanced T_{NI} phenomenon may be attributed to anisotropic alignment of liquid crystal molecules along the carbon nanotube bundles.

1. Introduction

Since their discovery [1], carbon nanotubes (CNT) have received immense attention across many disciplines by virtue of their unique structure and properties, as well as possible applications as nano-sensors and devices. Applications of interest include electron-emitting panel displays [2], single-molecular transistors in micro-electronics [3], artificial muscles [4], and molecular filtration membranes [5]. An essential prerequisite for realizing the aforementioned applications centres on the fabrication of aligned CNT which has been a focused area of recent research efforts [6–11]. Alignment of nanotubes with the aid of nematic liquid crystals is an alternative approach in which the CNT molecules were found to orient parallel to the director of a nematic solvent [12]. The observed molecular alignment was attributed to liquid crystal-induced alignment of the CNT.

Although phase diagrams of liquid crystal (LC)/polymer mixtures have been of major theoretical and experimental interest [12–19], there is no report in the open literature regarding the phase diagram or miscibility behaviour of CNT/LC or CNT/LC/polymer mixtures. As a scouting study for photolithography of holographic polymer dispersed liquid crystals (HPDLC), a temperature–composition phase diagram

of a multi-wall carbon nanotube (MWNT)/eutectic liquid crystal (E7) mixture has been established in order to determine thermodynamic stability and to identify various coexistence regions. A chimney-type temperature–composition phase diagram was discerned in a narrow composition range of the MWNT/E7 mixture. The enhanced nematic–isotropic nature of liquid crystal in the narrow chimney region may be attributed to an alignment-induced effect of the MWNT. To the best of our knowledge, the present finding of a chimney-type phase diagram is probably the first in the MWNT/E7 system, although such a phase diagram has been theoretically predicted in rigid rod and liquid crystalline polymer solutions [20–23].

2. Experimental

2.1. Materials

The dispersing liquid crystal is a eutectic mixture of nematic liquid crystals, commercially known as E7 (EM Industries). E7 consists of various cyanobiphenyl (CB), oxycyanobiphenyl (OCB), and cyanoterphenyl (CT) derivatives in the following proportion: 5CB (51%), 7CB (21%), 8OCB (16%) and 5CT (12%) by weight. The preference of choosing E7 is due to the broad nematic range (-30 to 61°C) as opposed to a gap of a few degrees for a single component liquid crystal, e.g. $\sim 5^\circ\text{C}$ between the crystal–nematic transition and the

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nematic–isotropic transition (T_{NI}) for 5CB. The nematic–isotropic transition of E7 occurs at $T_{\text{NI}}=61^{\circ}\text{C}$ with $\Delta H_{\text{NI}}=4.5\text{ J g}^{-1}$ [24, 25].

Multi-wall carbon nanotube (MWNT) was obtained through the courtesy of Dr L. Dai; it was synthesized by pyrolysis of $\text{Fe}(\text{CO})_5$ in a quartz tube at 900°C under a gas flow of 85% Ar and 15% H_2 . The hollow nanotubes that resulted from the vapor phase pyrolysis were in a black powder form. MWNT sizes ranged from 30–40 nm in diameter and 10–100 μm in length. The $\text{C}_{60}\text{-I}_h$ buckminsterfullerene (BU-604) was purchased from BuckyUSA with a reported purity of 99%. The average diameter was 7–15 Å. All materials were used as received without further chemical treatment.

2.2. Methods

One of the most challenging tasks is to disperse the MWNT, which has a tendency for aggregation. These MWNT aggregates generally form micrometer scale agglomerates that can be seen under atomic force microscopy [12]. Mechanical agitation was necessary to disrupt the large agglomerates, but it is evidently insufficient to disperse the MWNT on a finer scale. To achieve a finer dispersion of MWNT, sonication was applied to the CNT mixture, although molecular level dispersion was hard to realize. We employed a combination of turbulent agitation for 3 days at ambient temperature, followed by 2 h of sonication of the MWNT/E7 mixtures. The same methodology was applied to the mixture of fullerenes ($\text{C}_{60}\text{-I}_h$) and E7 in order to make a valid comparison with the results from the MWNT/E7 mixture. In establishing the T_{NI} versus

composition phase diagram, various MWNT/E7 concentrations were prepared by mixing appropriate amounts of MWNT or ($\text{C}_{60}\text{-I}_h$) with E7. Since the amount of the fillers in the anisotropic liquid crystal solvent was very small, the concentration of nanotubes (or fullerene) was diluted to approximately half in each step by adding E7. Repeating this dilution procedure gives reasonably accurate concentrations of the fillers. The MWNT/E7 mixtures were then sandwiched between slide glass and micro glass cover, giving a sample thickness range of 20–50 μm .

For the optical microscopy experiment, a Nikon Optipot 2-POL microscope equipped with a filtered Halogen light source (12 V, 100 W) was utilized. Various magnifications of 100–500 \times were employed and digital pictures were acquired using the Snappy interface and software. A sample hot stage (Linkam Scientific Instruments, Model TS1500) connected to a programmable temperature controller (Linkam, Model TMS93) and a cooling unit (Model LNP93/2) was utilized. Samples sandwiched between glass slides and cover glasses were heated at elevated temperature ($\sim 120^{\circ}\text{C}$) until the films became optically isotropic, and then were cooled slowly at a natural rate. The samples were reheated to their isotropic states for 2 min to ensure that the samples received the same thermal history. The heating and cooling rate was $0.5^{\circ}\text{C min}^{-1}$ unless indicated otherwise. A temperature scan experiment was carried out for each composition from the isotropic temperature of the mixture by cooling the mixture to ambient temperature. The structural evolution of the nematic domains was monitored by optical microscopy. Since the nematic–isotropic phase transition is

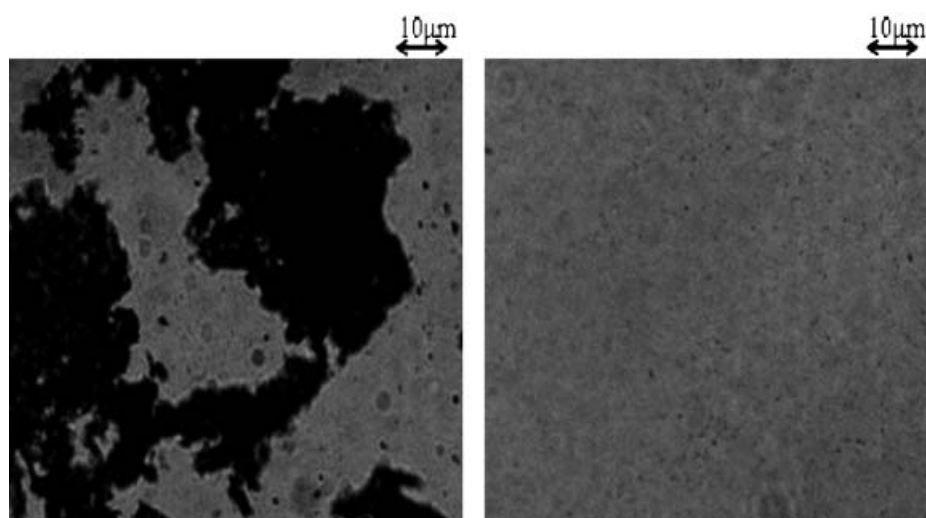


Figure 1. Unpolared optical micrographs (a) before agitation, and (b) after mechanical agitation for 3 days followed by 2 h of sonication. The MWNT concentration was 2 wt% in anisotropic solvent E7.

thermally reversible, the T_{NI} was determined by repeated heating and cooling cycles near the transition point. In some cases where the microscopy technique was inconclusive, fast Fourier transform (FFT) was carried out on the non-isothermal runs to determine light scattering patterns. The concentration fluctuation can be determined by FFT (or light scattering) under unpolarized conditions to probe the cloud points, whereas the orientation fluctuation under crossed polarizers affords determination of the NI transition temperature.

Differential scanning calorimetry (DSC) experiments were undertaken using a Thermal Analyzer (TA Instruments, Model Q1000) equipped with a liquid nitrogen chamber for cooling, and dry nitrogen gas was used for purging the sample. The heating and cooling rates were $10^{\circ}\text{C min}^{-1}$ unless indicated otherwise. Samples in the recommended amount of 5–10 mg were sealed in hermetic pans. DSC experiments were performed in the temperature range 20–120°C to determine the nematic–isotropic transitions of neat E7 and of its blends with MWNT as well as with C_{60} - I_h .

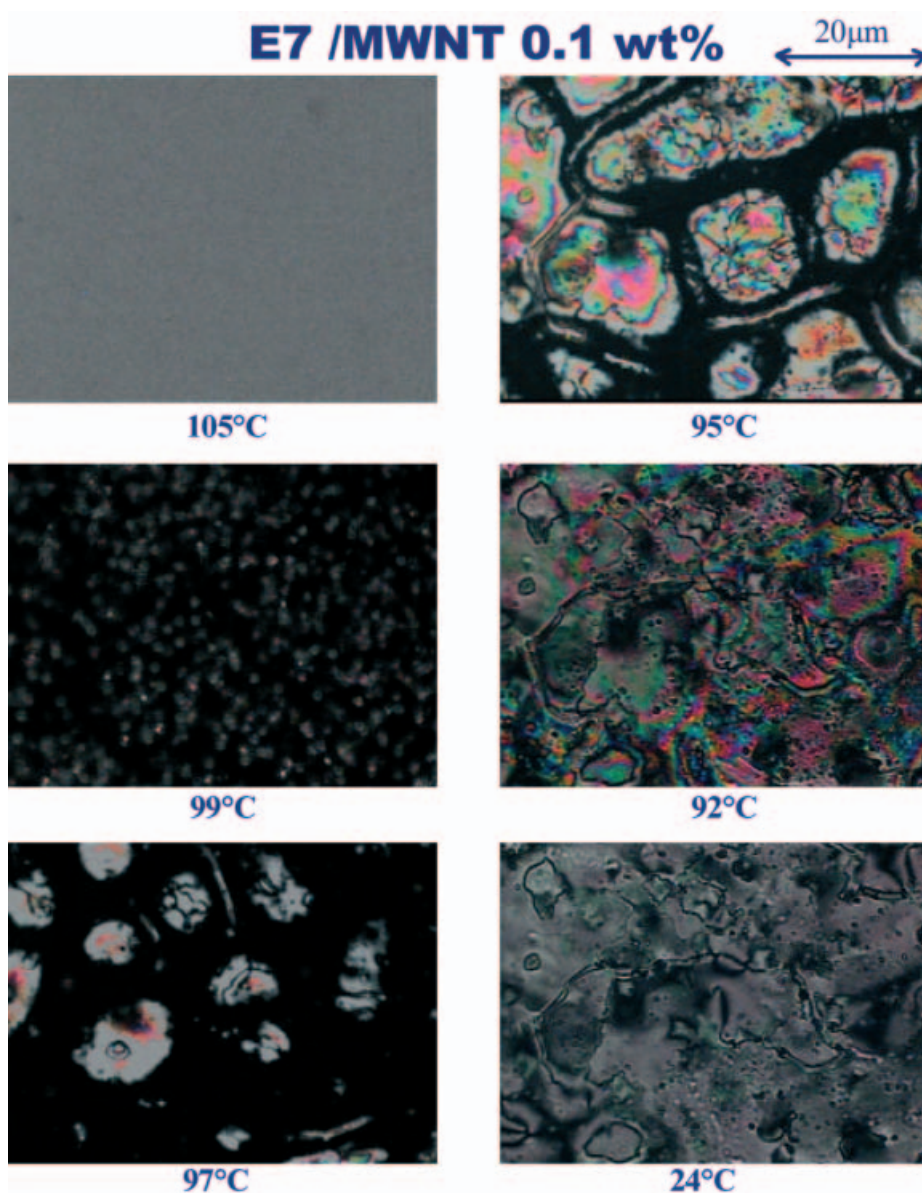


Figure 2. Optical micrographs showing structural evolution during cooling from the isotropic state at 120°C to ambient temperature. The emergence of liquid crystal domains exhibiting schlieren textures with strength ± 1 suggests that the LC is in the nematic phase.

3. Results and discussion

Figure 1 (a) shows optical micrographs exhibiting large MWNT aggregates in the continuum of E7 prepared by simply shaking. Mechanical agitation was necessary to disintegrate such large agglomerates, but the mechanical mixing alone was inadequate to achieve a finer dispersion. We therefore employed a combination of turbulence agitation for 3 days followed by 2 h of sonication of the MWNT/E7 mixtures. At an elevated temperature of 120°C, well above the nematic–isotropic transition temperature of E7, the sample appears optically clear to the naked eye, suggestive of a finer dispersion of MWNT, figure 1 (b). As can be seen, there remain a few agglomerates which suggests that the MWNT concentration may still be too high to achieve a molecular dispersion. The concentration of the MWNT was diluted by half at a time by adding more E7 and the dilution procedure was repeated to achieve very dilute solutions down to 0.05%.

Figure 2 shows micrographs of a 0.1% MWNT concentration obtained under crossed polarizers at an elevated temperature appreciably above the nematic–isotropic transition temperature (T_{NI}) of neat E7. The picture at 105°C is very dark, suggesting that the MWNT/E7 is in the isotropic state. To our surprise, birefringent domain structures appear at 99°C, which is significantly higher than the T_{NI} of neat E7. The structure continues to grow at the expense of the smaller domains through Oswald ripening (see the picture at 97°C). The structure further evolves to larger nematic domains with schlieren textures showing line disclinations (95°C). The growing nematic domains eventually

coalesce (92°C) and the interface disappears, exhibiting nematic disclinations with a strength of ± 1 at ambient temperature. Returning to an elevated temperature confirms that the nematic–isotropic transition temperature of the mixed MWNT/E7 is located about 100°C. This enhanced T_{NI} in the MWNT/E7 mixture may be attributed to the anisotropic alignment of E7 induced by the MWNT bundles. The entropy loss due to the mutual alignment of E7 and MWNT may be counterbalanced by enhanced interaction between the constituents; because the parallel alignment between the nanotube and liquid crystal molecules will increase the number of intermolecular contacts relative to the centre-of-mass to centre-of-mass interaction in the case of random orientation. A similar enhanced T_{NI} behaviour can be confirmed in the 0.2% MWNT concentration (data not shown). On increasing to $\sim 0.23\%$, the T_{NI} decreases to 63°C. This transition eventually approaches to that of the neat E7 with further increase of the nanotube concentration to 0.3% and higher. Also, the T_{NI} declines to 65°C on reducing the concentration to $\sim 0.05\%$ and then declines further to 60°C at 0% MWNT (i.e. neat E7).

It is important to confirm the above observation of enhanced nematic–isotropic transition in the MWNT/E7 composites by other independent methods such as DSC. In figure 3 are shown DSC scans for neat E7 and various MWNT/E7 mixtures ranging from $\sim 1\%$ to $\sim 0.05\%$ MWNT. When the MWNT content increased slowly from 0 to 0.083%, there was little enhancement (4–5°C) in T_{NI} of the liquid crystal component. However, a pronounced enhancement of T_{NI} was observed for a very narrow range (0.098–0.2%) of

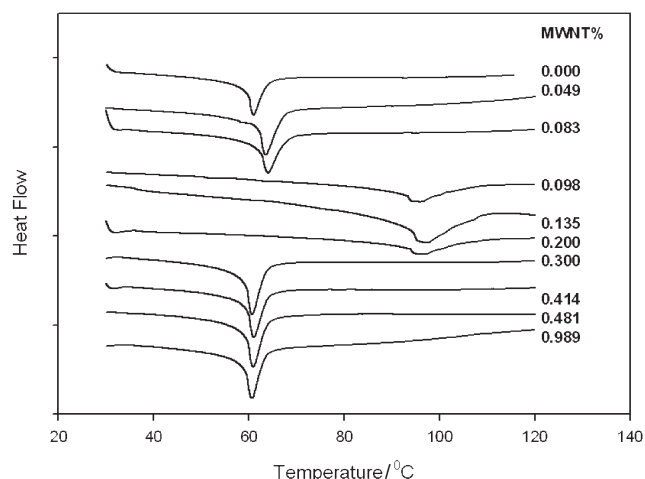


Figure 3. DSC thermograms of MWNT/E7 mixtures ranging from ~ 0.05 to $\sim 1\%$ MWNT together with that of neat E7. In a narrow concentration range (~ 0.1 to 0.2% MWNT), the T_{NI} enhancement can be discerned.

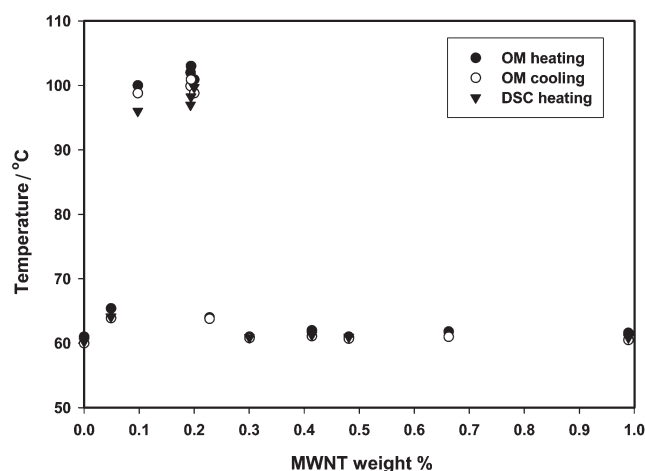


Figure 4. Nematic–isotropic transition temperature versus weight percent of MWNT, giving a chimney-type phase diagram.

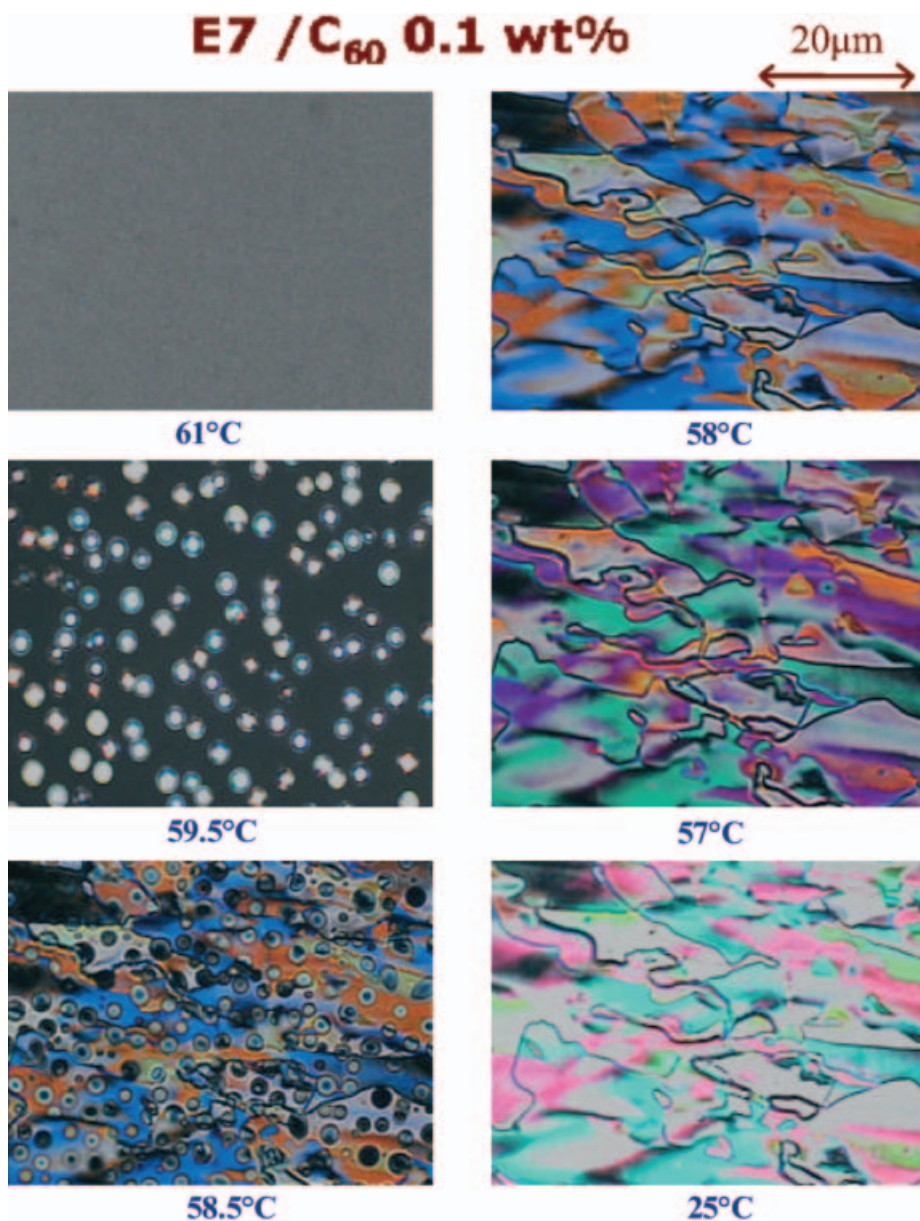


Figure 5. Optical micrographs displaying the evolution of nematic domains transforming to line disclinations during cooling from the isotropic phase. There is no improvement in the T_{NI} of E7 due to the incorporation of C_{60} - I_h .

MWNT. When the MWNT concentration falls below 0.084%, the T_{NI} transition peak drops back to 65°C, and continues to decline gradually with further reduction of MWNT concentration.

The T_{NI} data are plotted against concentration of the MWNT in figure 4, strikingly showing a chimney-type phase diagram in the MWNT/E7 composite. To the best of our knowledge, this work is the first to establish a chimney-type phase diagram in a carbon nanotube/liquid crystal mixture. Moreover, in the examination of

the MWNT dispersion by SEM [26], there is some aggregation of the nanotubes, but the aspect ratio remains fairly large, so that the liquid crystals may align along the nanotube bundles. Depending on the extent of the nanotube aggregation, it is possible that the position of the chimney might move to a different concentration range.

Although such a chimney in the MWNT/E7 mixture might be elusive, a similar chimney type phase diagram has been predicted theoretically by Ballauff [20] using

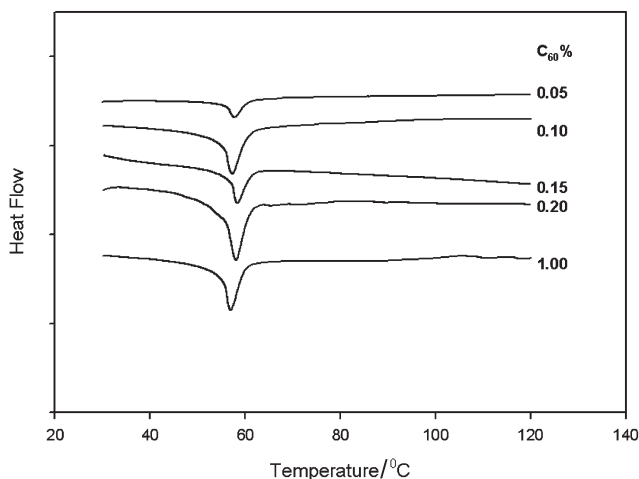


Figure 6. DSC thermograms showing the nematic–isotropic transitions at various concentrations of MWNT (wt %). There is no change in the transition temperature with the addition of fullerenes.

Flory and Ronca [21] treatment for a rigid-rod solution, and also by Dorgan and Ballauff [22] for a liquid crystalline polymer solution. However, the major difference is that the induced transition occurs in the anisotropic solvent induced by the MWNT. Very recently, a temperature versus packing fraction chimney-type phase diagram for capped carbon nanotubes has been predicted theoretically by Somoza *et al.* [23], who pointed out the importance of the aspect ratio on the phase behaviour of the carbon nanotube mixture exhibiting a nematic – columnar spinodal transition. The present enhanced T_{NI} is seemingly driven by anisotropic alignment of liquid crystal molecules on MWNT. The mutual alignment of MWNT and E7 would not only reduce the entropy, but also increase the intermolecular contacts and thus the enthalpy, i.e. an entropy-driven enthalpy change. In order to confirm whether the enhanced N–I transition arises from anisotropic alignment between E7 and MWNT, fullerene (C_{60} -I_h), was utilized instead of the nanotubes. Since the fullerene is isotropic, there would be no mutual alignment with liquid crystal molecules. If fullerene were to interact strongly with E7, the effect would be the disruption of nematic ordering (or plasticization) by C_{60} -I_h, lowering the T_{NI} , which would be contrary to the enhanced T_{NI} observed in the MWNT/E7 case.

Figure 5 shows the evolution of nematic structure at the 0.1% MWNT concentration during cooling from the isotropic phase. At 61°C the picture is featureless. However, multiple nematic droplets develop at 59.5°C, some of the nematic droplets showing a bipolar topology. At 58.5°C the nematic droplets coexist with

line disclinations in the matrix. On cooling to 58°C, the whole field is dominated by the line disclinations. The birefringent structure persists all the way to ambient temperature. A similar trend of phase transformation can be identified in all other concentrations investigated, thereby confirming that there is no discernible change of the T_{NI} of E7 on inclusion of fullerene.

Support for this observation comes from the DSC studies. As shown in figure 6, the DSC curves of the (C_{60} -I_h)/E7 system show a minor decline, say 1°C or less, which is within the error range. It is fair to infer that there is little or no effect of fullerene on T_{NI} in the temperature range where the chimney-type phase diagram was found in the MWNT/E7. The fact that the (C_{60} -I_h)/E7 showed no improvement in the T_{NI} of the liquid crystalline component suggests that the anisotropy of the nanotube plays a critical role. These findings support our claim that the pronounced T_{NI} enhancement might be attributed to mutual alignment of LC and MWNT molecules in their mixtures. To the best of our knowledge, this is the first experimental observation of a chimney-type phase diagram for a MWNT and nematic liquid crystal system, although such a phase diagram has been predicted theoretically for the capped CNT system by Somoza *et al.* [23]. These authors pointed out the important role of the aspect ratio in the phase diagram of a carbon nanotube system exhibiting nematic, smectic, and discotic liquid crystal phases. It appears that the present MWNT molecules, despite the strong tendency of aggregation of the nanotube, have a sufficiently high aspect ratio (>300) for observation of the chimney at 0.1–0.2 wt % MWNT concentration range in the mixture with E7.

4. Conclusion

In summary, phase diagrams of the mixtures MWNT/E7 and (C_{60} -I_h)/E7 have been established for the first time, based on observations by polarized and unpolarized optical microscopy, and by DSC. The nematic–isotropic transition temperature versus composition phase diagram of the MWNT/E7 blend is a chimney-type. The incorporation of MWNT exerted profound enhancement of the liquid crystal T_{NI} in a very narrow range of MWNT concentration (0.1–0.2%). The (C_{60} -I_h)/E7 phase diagram showed no indication of any change in the T_{NI} of E7, which is not surprising in view of the fact that fullerene is an isotropic molecule. It may be hypothesized that the enhanced T_{NI} of the liquid crystal is probably entropic in origin, driven by the mutual alignment of carbon nanotube and liquid crystal molecules.

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