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Carbon nanotubes in triphenylene and rufigallol-based room temperature monomeric and polymeric discotic liquid crystals†

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In this article, after a brief account of the work carried out in the area of dispersion of carbon nanotubes in liquid crystals, we present the dispersion of functionalized single-wall carbon nanotubes in novel room temperature liquid crystalline discotic monomers and polymers. The effect of nanotubes on phase behavior of electron-rich triphenylene derivatives and electron-deficient anthraquinone derivatives has been investigated. Mesophase behavior of the composites with nanotubes has been studied by polarizing optical microscopy, differential scanning calorimetry and X-ray diffractometry. Inclusion of carbon nanotubes into the columnar matrix does not destroy the mesophase of the host compounds but the columnar to isotropic transition temperatures decrease with increase in the quantity of carbon nanotubes in both monomeric and polymeric discotic liquid crystals.

Introduction

The serendipitous discovery of carbon nanotubes (CNTs) by Iijima[1] in 1991 generated tremendous activity in most areas of science and technology as a result of their unprecedented physical and chemical properties. CNTs, one-dimensional carbon allotropes, are well ordered all-carbon hollow cylinders of graphite with a high aspect ratio. CNTs can be either metallic or semiconducting depending on the sheet direction about which the graphite sheet is rolled to form a nanotube cylinder.[2] The combination of superlative mechanical, thermal and electronic properties displayed by CNTs makes them ideal for a wide range of applications, such as conductive and high-strength composites, catalyst supports in heterogeneous catalysis, energy-storage and energy-conversion devices, field emitters, transistors, sensors, gas storage media, tips for scanning probe microscopy and molecular wires. Synthesis, characterization, physical properties and applications of CNTs have been extensively covered in several reviews.[2] Despite the extraordinary promise of CNTs, their realistic application as one-dimensional conductors or semiconductors has been restricted because of difficulties in aligning them in the desired direction. Recent studies have proved that the alignment of CNTs plays a critical role in the properties of nanotube based materials.[3] However, processing materials with well-controlled CNT alignment still remains a challenge.

There has been growing interest in the field of dispersion of CNTs in both thermotropic and lyotropic liquid crystal (LC) phases[4] besides mesophase behavior of CNTs themselves and synthesis of CNTs from discotic liquid crystals (DLCs). Mixing CNTs into LC hosts has become one of the attempted approaches to modify the physical properties of LCs important for optoelectronic applications.[4] Lee and Chiu initiated the work on doping of CNTs in LCs in 2001. They observed self-diffraction by gratings in nematic LCs doped with multiwalled CNTs.[5] In the same year, on the basis of continuum-based density functional theory, Somoza *et al.* proposed that CNTs should form a columnar phase or lyotropic LC phase in the presence and absence of van der Waals interactions.[6] Lynch and Patrick achieved a high degree of CNT alignment along the nematic director field by taking advantage of the self-assembly properties of nematic LCs.[7] Later the electro-optically induced photorefractive effect,[8] reduction of the dc driving voltage,[9] voltage-dependent transmittance and capacitance under ac and dc electric field[10] of LC-CNT mixtures were studied. Similarly the electrooptical characteristics of TN-LCD cells filled with positive and negative dielectric anisotropy LCs and CNTs were investigated.[11] Dierking *et al.* have studied the alignment and reorientation of doped CNTs in LC cells under both electric and magnetic fields along with the change in the conductivity of the LC cell upon reorientation of the CNTs with the LC director field.[12] In contrast to alignment of CNTs with LCs, the alignment of LCs has also been achieved by CNTs.[13] There are a few examples of inclusion of CNTs into lyotropic LCs also.[14]

Preparation of CNTs typically requires high temperature or high pressure. Moreover, the orientation of the graphene layers in the nanotubes is important from their application point of view. To form ordered graphite nanostructures without metal catalysts and with desired graphene layer orientations, one possible approach is carbonization within a discotic columnar mesophase. From this point of view, the columnar structures of DLCs are worthy precursors as the molecules possess a nanographene subunit as the aromatic core and these molecules stack one on top of one another to build up columns which in turn organize themselves in different two-dimensional lattices.[15] Upon carbonization under a controlled heating process the preorganized ordered columnar superstructures can be converted into nanotubes. Mullen *et al.*[16] have produced nanotubes from

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thermotropic DLCs whereas Crawford *et al.*[17] have produced nanotubes from both thermotropic and lyotropic DLCs.

In general, LCs formed by disc-shaped molecules have been attracting growing interest because the supramolecular order of their columnar phases is of fundamental importance not only as models for the study of energy and charge migration in self-organized systems but also as functional materials for many device applications, such as one-dimensional conductors, photoconductors, light emitting diodes, photovoltaic solar cells, field effect transistors and gas sensors. The functional capabilities of these materials are due to their easier processability, spontaneous alignment between electrodes and self-healing of defects owing to their dynamic nature.[15,18]

The insertion (dispersion) of CNTs in the supramolecular order of room-temperature discotic liquid crystalline monomers and polymers may lead to novel materials with interesting properties useful for device applications. With this in mind, we have initiated a research program to disperse functionalized CNTs into the matrix of room-temperature liquid crystalline discotic monomers and polymers. Here, in continuation of our work on dispersion of functionalized nanomaterials in DLCs,[19] we present a study of the mesophase behavior of composites of functionalized single-wall carbon nanotubes (SWNTs) with rufigallol and triphenylene-based room temperature monomeric and polymeric DLCs.

Experimental

General information

Chemicals and solvents (AR quality) were used without any purification. Column chromatographic separation was performed on silica gel (100–200 mesh). ^{1}H NMR spectra and ^{13}C NMR spectra were recorded in $CDCl_3$ on a 400 MHz (Bruker AMX 400) spectrometer. All chemical shifts are reported in δ (ppm) units down field from tetramethylsilane (TMS) and J values are reported in Hz. FT-IR spectra were recorded as KBr discs on a Shimadzu FTIR-8400. Elemental analysis was performed on a Carlo-Erba Flash 1112 analyser. Gel permeation chromatography (GPC; Shimadzu-Japan) analysis of the polymer samples was carried out in THF solution calibrated with a polystyrene standard and having a RI detector. Transition temperatures were observed using a Mettler FP82 HT hot stage and FP90 central processor in conjunction with an OLYMPUS BX51 polarizing optical microscope. Transition temperatures and associated enthalpies were measured by differential scanning calorimetry heating from −30 °C to isotropic temperatures at a scan rate of 5 °C min^{-1} (Perkin-Elmer Model Pyris 1D with Intracooler 2 P cooling system). X-Ray diffraction measurements were carried out using Cu-Kα radiation (λ = 1.54 Å) generated from a 4 kW rotating anode generator (Rigaku Ultrax-18) equipped with a graphite crystal monochromator. Samples were placed in Hampton research capillaries (0.5 mm diameter) from the isotropic phase, sealed and held on a heater. For all the samples, X-ray diffraction was carried out at room temperature (25 °C) and diffraction patterns of the mesophase were recorded on a two-dimensional image plate (Marresearch). Octadecylamine (ODA) functionalized carbon nanotubes were purchased from Carbon Solutions Inc. (P5-SWNT, Batch 05-124).

Synthesis of 1,5-dihydroxy-2,3,6,7-tetrakis(3,7-dimethyloctyloxy)-9,10-anthraquinone, 3

To a solution of rufigallol **2** (1.52 g, 5 mmol), 3,7-dimethyl octylbromide (4.86 g, 22 mmol) in DMSO (10 mL) was added NaOH (0.8 g, 20 mmol) and the mixture was stirred for about 20 h at 90 °C. After cooling the reaction mixture, water was added and the aqueous solution was extracted with chloroform. After solvent evaporation the product was precipitated from chloroform into methanol thrice to obtain the pure product **3** (1.51 g, yield 35%). ^{1}H NMR: δ_H 12.76 (s, 2 H, Ar-OH), 7.4 (s, 2 H, Ar-H), 4.23–4.13 (m, 8 H, ArOCH$_2$), 1.9–1.1 (m, 40 H, aliphatic CH$_2$ and -CH), 0.98 (d, 6 H, J = 6.3 Hz, -CH-CH$_3$), 0.95 (d, 6 H, J = 6.6 Hz, CH$_3$), 0.88 (d, 12 H, J = 4.5 Hz, CH$_3$), 0.85 (d, 12 H, J = 4.5 Hz, CH$_3$); ^{13}C NMR: δ_C 186.4, 158.1, 157.3, 141.2, 128.9, 111.8, 104.8, 72.1, 67.8, 39.3, 37.3, 36.1, 31.1, 29.8, 29.7, 28.8, 28.0, 24.7, 22.6, 19.6; FT-IR: (ν_{max}) 2922, 2854, 1616, 1569, 1506, 1456, 1427, 1365, 1315, 1280, 1226, 1138, 1095, 1045, 950, 864, 802, 723 cm^{-1}. Elemental analysis: Found: C, 75.0; H, 10.71. $C_{54}H_{88}O_8$ requires C, 74.96; H, 10.25%.

Polymerization of 1,5-dihydroxy-2,3,6,7-tetrakis(3,7-dimethyloctyloxy)-9,10-anthraquinone

A solution of tetraalkoxy anthraquinone **3** (0.865 g, 1 mmol), 1,12-dibromododecane (0.328 g, 1 mmol) and caesium carbonate (1.3 g, 4 mmol) in *o*-dichlorobenzene (5 mL) was stirred at 90 °C under argon for 10 days. The reaction mixture was then cooled and 20 mL of chloroform was added to it. The organic layer was separated and washed with water and dried. The solvent was removed under reduced pressure to yield the crude polymer. It was further purified by repeated precipitation from chloroform into methanol. Yield 60%. ^{1}H NMR: δ_H 7.6 (s, 2 H, Ar-H), 4.03–4.18 (m, 12 H, ArOCH$_2$), 1.1–2.0 (m, 60 H, aliphatic -CH$_2$ and -CH), 0.8–1.0 (m, 36 H, -CH$_3$); ^{13}C NMR: δ_C 181.2, 157.4, 153.9, 147.0, 132.6, 120.4, 107.0, 74.7, 72.4, 67.5, 45.2, 39.2, 37.3, 36.1, 32.8, 30.4, 29.7, 27.9, 27.3, 27.1, 26.1, 24.7, 22.7, 22.6, 19.6; FT-IR:(ν_{max}) 2924, 2854, 1666, 1572, 1462, 1377, 1319, 1282, 1132, 1094, 771, 721. Mol. wt. ~ 13691; PDI = 1.44.

Synthesis of 2,6-bis(3,7-dimethyloctyloxy)-3,7,10,11-tetrakis(pentyloxy)-triphenylene, 9

To a solution of 2,6-dihydroxy triphenylene **8** (0.605 g, 1 mmol) in methyl ethyl ketone, MEK (10 mL), 3,7-dimethyloctylbromide (0.885 g, 4 mmol) and caesium carbonate (1.3 g, 4 mmol) was added and the reaction mixture was refluxed overnight. After cooling, the reaction mixture was filtered and solvent evaporated and the product was purified by column chromatography followed by precipitation from dichloromethane into ethanol. Yield 62%. ^{1}H NMR: δ_H 7.8 (s, 6 H, ArH), 4.2–4.3 (m, 12 H, ArOCH$_2$), 1.15–2.0 (m, 44 H, aliphatic CH$_2$ and CH), 1.03 (d, 6 H, J = 6 Hz, CH$_3$), 0.98 (t, 12 H, J = 6 Hz, CH$_3$), 0.87 (d, 12 H, J = 5.6 Hz, CH$_3$); ^{13}C NMR: δ_C 149.0, 123.6, 107.4, 69.7, 68.0, 39.2, 37.4, 36.4, 30.0, 29.1, 28.3, 27.9, 24.7, 22.5, 19.7, 14.0; FT-IR: (ν_{max}) 2922, 2854, 1616, 1514, 1464, 1435, 1379, 1263, 1171, 1053, 976, 870, 837, 771, 729. Elemental Analysis: Found: C, 78.69; H, 11.05, $C_{58}H_{92}O_6$ requires C, 78.68; H, 10.47%.

Polymerization of 2,6-dihydroxy-3,7,10,11-tetrakis(pentyloxy)-triphenylene

A solution of 2,6-dihydroxy triphenylene **8** (0.423 g, 0.7 mmol), 1,12-dibromododecane (0.23 g, 0.7 mmol) and caesium carbonate (0.326 g, 1 mmol) in *N*-methylpyrrolidone, NMP (2 mL), was submerged into a preheated oil bath at 110 °C and stirred for 1 h and cooled. Water was added and the resulting solid repeatedly washed with water and ethanol. Reprecipitation from dichloromethane with ethanol afforded the polymer **10** (295 mg). ^{1}H NMR: δ_H 7.8 (s, 6 H, Ar-H), 4.2 (t, 12 H, $J = 6$ Hz, ArOCH$_2$), 1.94 (m, 12 H, OCH$_2$CH$_2$) 1.3–1.6 (m, 32 H, aliphatic CH$_2$), 0.98 (t, 12 H, $J = 6.8$ Hz, -CH$_3$); ^{13}C NMR: δ_C 149.0, 123.6, 107.4, 69.7, 69.1, 32.8, 29.7, 29.5, 29.1, 28.3, 26.2, 22.5, 14.0; FT-IR: (ν_{max}) 2924, 2852, 1620, 1504, 1456, 1377, 1261, 1169, 1040, 977, 810, 770, 721 cm^{-1}. Mol. wt. ~ 13515; PDI = 1.92.

Preparation of liquid crystalline nanocomposites with ODA functionalized carbon nanotubes

Novel nanocomposites (by weight) of monomeric and polymeric liquid crystalline compounds were prepared as follows: the commercial octadecylamine (ODA) functionalized SWNTs (25 mg) were dissolved in dichloromethane (10 mL) and the insoluble portion was filtered off using a PTFE membrane (0.45 μm). The soluble portion was dried under vacuum to know the exact amount of soluble SWNTs. It was found to be 10 mg. The soluble SWNTs were re-dissolved in 20 mL of dichloromethane. A calculated amount of this solution was added to the liquid crystal monomers (**3** and **9**) and main chain polymers (**4** and **10**). The solution was sonicated for a few minutes followed by removal of solvent and drying under vacuum to make different functionalized SWNT-DLC composites.

Results and discussion

To investigate the effect of carbon nanotubes on the mesophase behavior of electron deficient rufigallol derivatives we have prepared novel room temperature liquid crystalline rufigallol derivatives. The synthesis of electron deficient novel room-temperature liquid crystalline monomer **3** and polymer **4** is outlined in Scheme 1. Commercially available gallic acid **1** was converted to rufigallol **2** as reported.[20] Rufigallol **2** was alkylated with 3,7-dimethyloctylbromide under mild etherification conditions[21] to afford the tetraalkoxy rufigallol **3**. Surprisingly the branched chain substituted tetraalkoxy compound **3** exhibits liquid crystalline behavior at room temperature, in contrast to its straight chain analogues which do not show any liquid crystalline property, this could be because the branched chains fill the necessary space around the core to induce mesomorphism. The thermal behavior of the compound was investigated by polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). This compound shows a columnar hexagonal to isotropic transition at 115.7 °C while heating and an isotropic to columnar hexagonal transition at 114.1 °C while cooling, no other transitions are observed while heating and cooling (scan rate 5 °C min^{-1}) between −30 °C and the isotropic temperature in the DSC thermogram which supports the POM observation. The texture of the columnar phase observed under POM for compound **3** at room temperature is shown in Fig. 1a. The columnar hexagonal mesophase structure of this compound was established by X-ray diffraction studies. The intensity *vs.* θ graph derived from the diffraction pattern of the compound at room

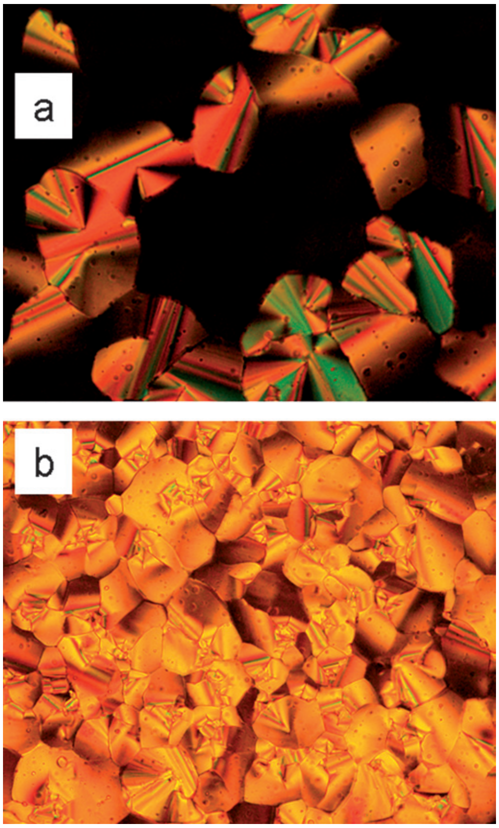
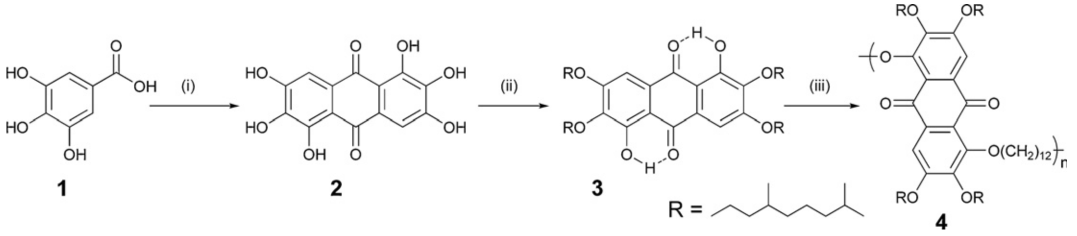


Fig. 1 Optical photomicrographs of (a) **3** and (b) composite **3b** at 25 °C on cooling from the isotropic liquid (crossed polarizers, magnification ×200).



Scheme 1 Synthesis of room-temperature liquid crystalline anthraquinone monomer and polymer. Reaction conditions and reagents: (i) H$_2$SO$_4$, MW, 80%; (ii) 3,7-dimethyloctylbromide, NaOH, DMSO, 90 °C, 35%; (iii) 1,12-dibromododecane, Cs$_2$CO$_3$, *o*-dichlorobenzene, 90 °C, 60%.

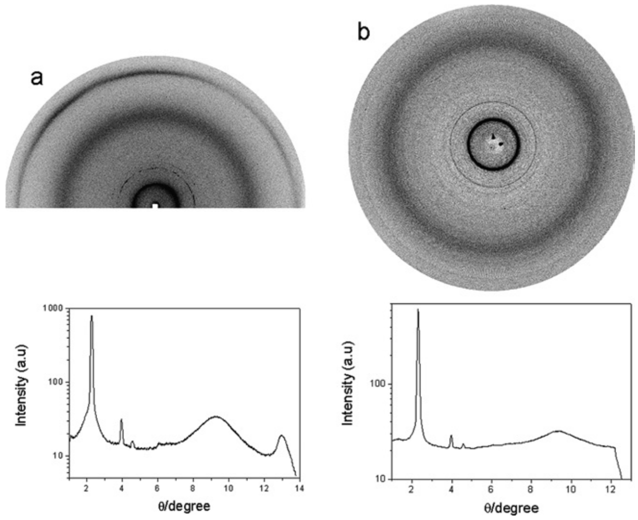


Fig. 2 X-Ray diffraction patterns and the derived one-dimensional intensity *vs.* θ profiles for (a) compound **3** and (b) composite **3b** at 25 °C.

Table 1 Phase transition temperatures (peak °C) and associated enthalpies (J g^{-1}, in parentheses) of novel liquid crystalline compounds and their composites with carbon nanotubes (scan rate 5 °C min^{-1}). Col_h = hexagonal columnar, Col_r = columnar rectangular, I = isotropic, * = from polarized optical microscopy (POM)

Sample	Heating scan	Cooling scan
3	Col_h 115.7 (6.4) I	I 114.1 (6.3) Col_h
3a	Col_h 113.0 (6.0) I	I 110.7 (6.0) Col_h
3b	Col_h 112.0 (6.0) I	I 109.8 (5.9) Col_h
3c	Col_h 109.5 (5.5) I	I 107.6 (5.6) Col_h
4	Col_r 56.3 (3.3) I	—
4a	Col_r 47.7 (1.9) I	—
4b	Col_r 43.3 (2.0) I	—
4c	Col_r 39.2 (1.0) I	—
9	Col_h 69.0 (6.0) I	I 67.0 (6.0) Col_h
9a	Col_h 67.2 (5.1) I	I 65.6 (5.1) Col_h
9b	Col_h 64.4 (3.8) I	I 61.8 (3.7) Col_h
9c	Col_h 63.8 (3.6) I	I 61.7 (3.6) Col_h
10	Col_h 89 I*	—
10a	Col_h 83 I*	—
10b	Col_h 80 I*	—

temperature is shown in Fig. 2a. In the low angle region three sharp peaks, one strong and two weak, are seen, with *d*-spacings in the ratio of 1 : 1/√3 : 1/√4. Identifying the first peak with the Miller index 100, the ratios conform to the expected values for a two-dimensional hexagonal lattice. In the wide angle region two diffused reflections are seen. The broad one centered at about 4.5 Å corresponds to the liquid like order of the aliphatic chains. The relatively sharper one seen at about 3.4 Å and well separated from the broad one is due to the stacking of the molecular cores on top of one another. All the above mentioned features are characteristics of the Col_h phase. Three compositions (by weight) of this compound were made by adding the dichloromethane solution of ODA functionalized carbon nanotubes. Three compositions (**3a**: 0.5%; **3b**: 1%; **3c**: 2%) were prepared and analyzed by DSC, POM and X-ray diffraction. All the composites **3a–c** were also found to be room temperature liquid crystalline like the pure host compound **3**. These composites, under POM, exhibit classical textures of columnar mesophase upon cooling from the isotropic phase as shown in Fig. 1b. Data obtained from the heating and cooling cycles of DSC with a scan rate of 5 °C min^{-1} for these composites are collected in Table 1. The insertion of CNTs decreases the mesophase–isotropic phase transition temperature. With increase in the percentage of the CNTs the mesophase–isotropic transition temperature decreases (Table 1). This is logical as the insertion of CNTs is expected to reduce the ordering of the cores. The X-ray diffraction pattern of composite **3c** at room temperature shows similar features to that of compound **3** confirming the hexagonal columnar mesophase of the composites as shown in Fig. 2b. Since these composites **3a–c** contain very little amounts of functionalized carbon nanotubes we do not observe any significant increase in the intercolumnar distance of the pure compound **3** in these composites. The columnar mesophase structure is not destroyed by the inclusion of functionalized carbon nanotubes, only the columnar to isotropic transition temperature decreases. When we tried to insert more than 2% CNTs in the columnar liquid crystal those composites still exhibited liquid crystalline properties but under the polarizing microscope we could observe small aggregates of CNTs which means the CNTs are not homogeneously dispersed in the liquid crystal matrix of the composites when the CNTs percentage is more.

The dihydroxy functionalized molecule **3** was polymerized to a main chain electron deficient liquid crystalline polyether **4** as shown in Scheme 1 to study the phase behavior of its nanocomposites with carbon nanotubes. The mesophase behavior of this polymer was characterized by polarizing optical microscopy and differential scanning calorimetry. This polymer, which could be deformed at room temperature shows, under the microscope, only one transition on heating. When cooled from the isotropic state it does not exhibit any characteristic texture but a sandy birefringence texture as shown in Fig. 3a appears slowly from the isotropic liquid. The DSC thermogram of the compound shows only one transition at 56.3 °C while heating corresponding to a columnar to isotropic transition but on cooling it does not show any discernible transition. The mesophase structure of the polymer was established to be a rectangular columnar phase with lattice parameters $a = 42.02$ Å and $b = 19.80$ Å. The intensity *vs.* θ graph derived from the X-ray diffraction pattern of the polymer at room temperature shows five reflections in the small angle region as shown in Fig. 4a with two strong reflections at lower angles. Two strong peaks in the small angle region are characteristic of a rectangular columnar phase and the observed other three weak peaks in the small angle region can be indexed for a rectangular lattice. So upon polymerization the columnar hexagonal structure of monomer **3** is transformed to a more ordered columnar rectangular phase as has been observed for main chain polyethers of rufigallol.[21] As in the case of the monomer, we have prepared three different compositions (**4a**: 0.5%; **4b**: 1% and **4c**: 2%) of the polymer by adding functionalized carbon nanotube solution to the polymer followed by sonication and solvent removal. The mesophase behaviors of all these three compositions were characterized by POM, DSC and X-ray diffraction studies. They also exhibit the sandy texture under the polarizing microscope when cooled from the isotropic state as shown in Fig. 3b. Data obtained from the heating cycle of

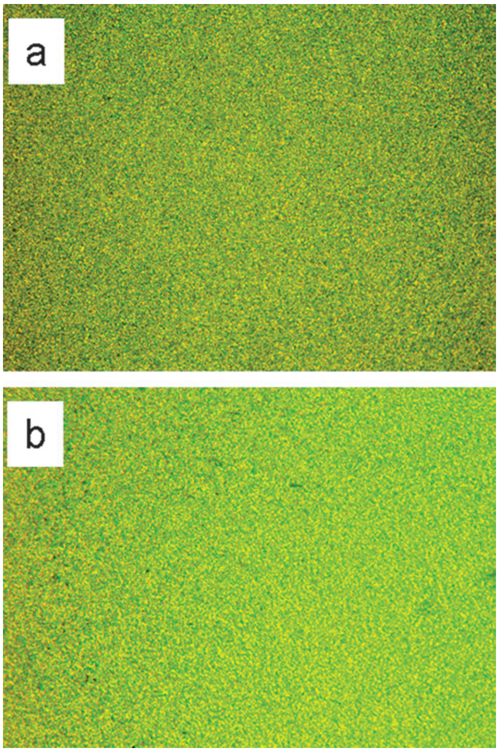


Fig. 3 Optical photomicrograph of (a) polymer **4** and (b) its composite **4b** at 25 °C on cooling from the isotropic liquid (crossed polarizers, magnification ×200).

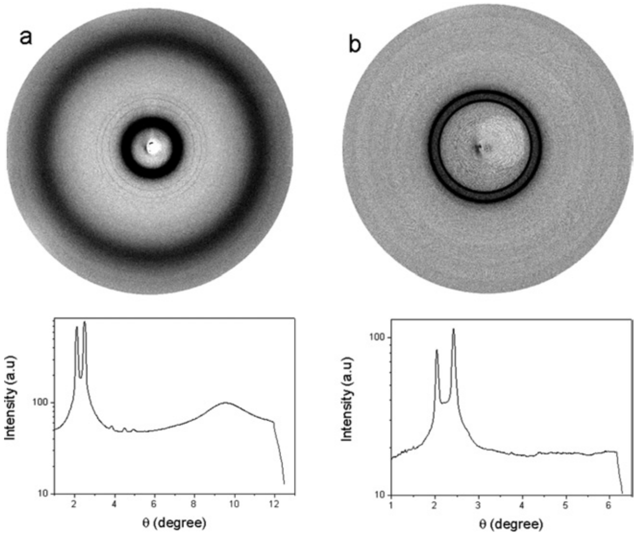
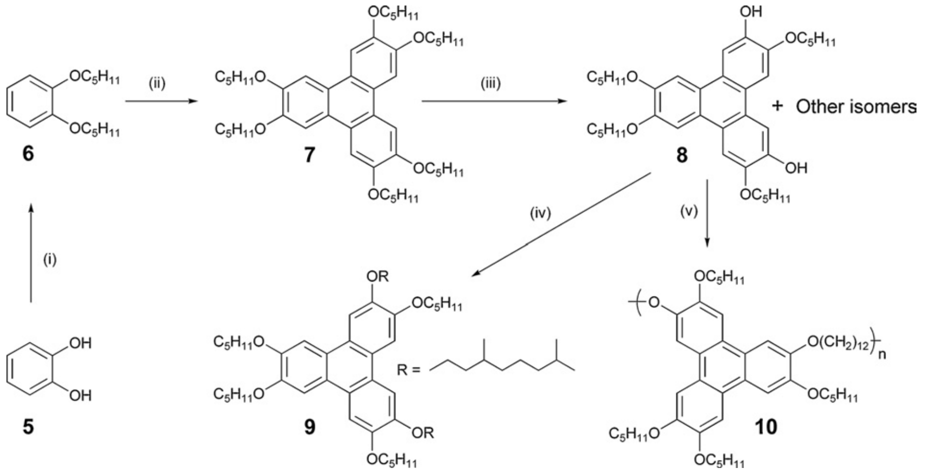


Fig. 4 X-Ray diffraction patterns and the derived one-dimensional intensity *vs.* θ profiles for (a) polymer **4** and (b) for the composite **4c** at 25 °C.

DSC for these composites are collected in Table 1. As expected the isotropic transition temperature of the composites decreases with increase in the CNT quantity. But the mesophase structure of these composites remains rectangular as confirmed by X-ray diffraction of the composites as shown in Fig. 4b.

To investigate the effect of carbon nanotubes on the mesophase behavior of electron rich triphenylene derivatives we have synthesized novel room-temperature liquid crystalline triphenylene derivatives. The synthesis of novel room-temperature liquid crystalline triphenylene monomer **9** and polymer **10** is outlined in Scheme 2. The dihydroxy intermediate **8** was prepared and isolated as reported.[22] Upon replacement of two pentyloxy chains by 3,7-dimethyloctyloxy branched chains compound **9** exhibits liquid crystalline property at room temperature. This could be due to the unsymmetrical substitution of alkoxy chains on the core and stereoheterogeneity introduced by the branched alkoxy chains. Under polarized optical microscopy compound **9** exhibits the classical broken fan texture of a hexagonal columnar phase when cooled from the isotropic phase as shown in Fig. 5a. This compound shows a columnar hexagonal to isotropic transition at 69 °C on heating and an isotropic to columnar hexagonal transition at 67 °C while cooling, no other transitions are observed while heating and cooling between −30 °C and the isotropic temperature in the DSC thermogram as shown in Fig. 6. The mesophase structure of the compound was established with the help of X-ray diffractometry. In the small angle region there are two reflections, one strong and one weak. The ratio of the *d*-spacings of these two peaks is $1 : 1/\sqrt{3}$, which corresponds to a two-dimensional hexagonal lattice. In the wide angle region two reflections are observed: one very broad and another relatively sharp peak. The broad peak centered at about 4.7 Å is due to the liquid like order of the alkyl chains surrounding the aromatic cores; the other peak centered at about 3.6 Å is due to the stacking of the aromatic cores on top of one another which constitute the columns. All these features are characteristic of the columnar hexagonal phase. Three different mixtures of functionalized carbon nanotubes were made with this room temperature liquid crystalline triphenylene derivative. All these compositions (**9a**: 0.2%; **9b**: 1% and **9c**: 2%) were analysed with POM, DSC and X-ray diffraction. Under polarizing optical microscopy these composites develop the classical broken fan textures of a columnar hexagonal phase as shown in Fig. 5b, just like the pure host compound **9**. As with those of anthraquinone derivative composites the columnar to isotropic phase transition temperature decreases with increasing the nanotube quantity and the transitions are broadened. Data collected during the DSC heating and cooling cycles of the pure compound and the composites are collected in Table 1. X-Ray diffraction patterns of the composites show similar features to that of the pure compound confirming the columnar hexagonal phase of the composites as shown in Fig. 7a. In the X-ray diffraction patterns of these composites also we do not observe any significant change in the intercolumnar distance as compared to the pure compound **9**. So the inclusion of CNTs to the columnar matrix destabilizes the phase to a small extent but retains the mesophase structure. In order to see the effect of CNTs on triphenylene based main chain polymers we synthesized polymer **10** as shown in Scheme 2 from the dihydroxy precursor **8**. The liquid crystalline phase behavior of this polymer was studied by POM, DSC and X-ray diffraction. This highly viscous compound does not show any peak during heating and cooling in the DSC thermogram, but it exhibits a birefringence texture like the above mentioned anthraquinone polymer under the polarizing microscope when cooled from isotropic state as shown in Fig. 8a. When heated from room temperature this polymer passes slowly to isotropic state at 89 °C and upon cooling the birefringence texture appears



Scheme 2 Synthesis of room-temperature liquid crystalline triphenylene monomer and polymer. Reaction conditions and reagents: (i) $C_5H_{11}Br$, K_2CO_3, MEK; (ii) $FeCl_3$, CH_2Cl_2; (iii) Cat-B-Br (*B*-bromocatecholborane), CH_2Cl_2; (iv) 3,7-dimethyloctylbromide, Cs_2CO_3, MEK; (v) 1,12-dibromododecane, Cs_2CO_3, NMP, 110 °C, 54%.

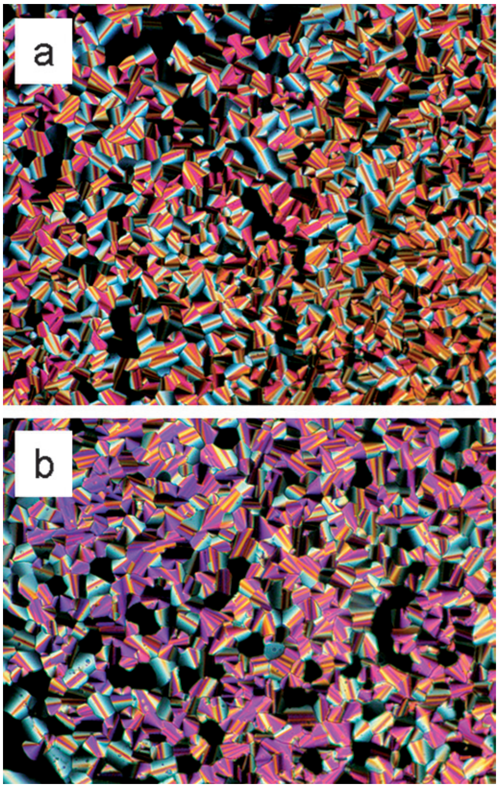


Fig. 5 Optical photomicrographs of (a) compound **9** and (b) its composite **9c** at 25 °C on cooling from the isotropic liquid (crossed polarizers, magnification ×200).

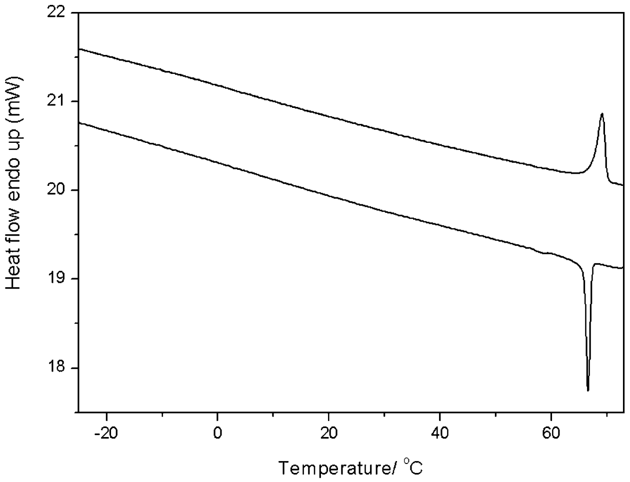


Fig. 6 DSC thermogram for compound **9** on heating and cooling (scan rate of 5 °C min^{-1}).

slowly under the polarizing microscope. In order to confirm the mesophase structure we carried out an X-ray diffraction study of the polymer. Only one strong reflection is observed in the small angle region of the X-ray diffraction pattern; though it is difficult to assign the mesophase structure with only one peak in the small angle region, nevertheless given the general mesophase structure of triphenylene based discotic monomers and polymers[23] we consider this to be a columnar hexagonal phase. Moreover, the miscibility of the mesophase of polymer **10** with the mesophase of compound **9** confirms the columnar hexagonal structure. Two different nanocomposites (**10a**: 0.5%; **10b**: 1%) of the polymer with functionalized carbon nanotubes were prepared and their liquid crystalline properties were studied by POM and X-ray. Like the pure polymer, these composites do not give any peak in their DSC thermograms so the transition temperatures were determined only by POM. The mesophase to isotropic transition temperatures as observed under polarizing optical microscope of these composites are listed in Table 1. Here also the mesophase to isotropic transition temperature decreases and broadens as the amount of carbon nanotubes increases in the matrix. The sandy texture exhibited by the composites when cooled from the isotropic state is shown in Fig. 8b. In all textures some change in the colour was seen upon doping CNTs. This could be because of the disturbed alignment of molecules by the CNTs. X-Ray diffraction patterns of the composites show similar features to

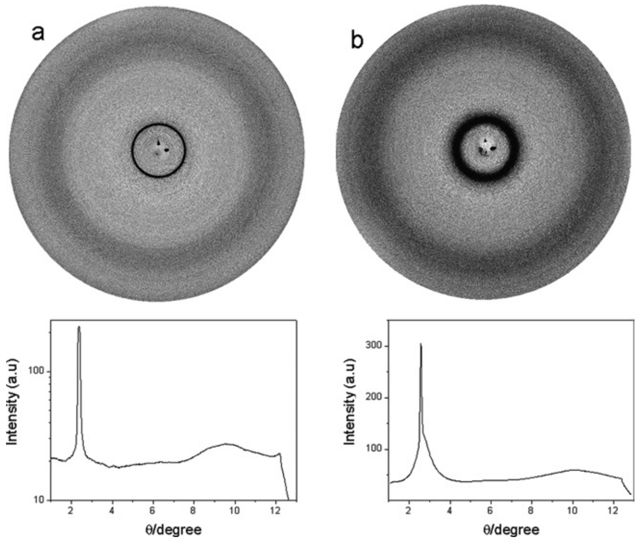


Fig. 7 X-Ray diffraction patterns and the derived one-dimensional intensity *vs.* θ profiles for (a) composite **9c** and (b) composite **10a** at 25 °C.

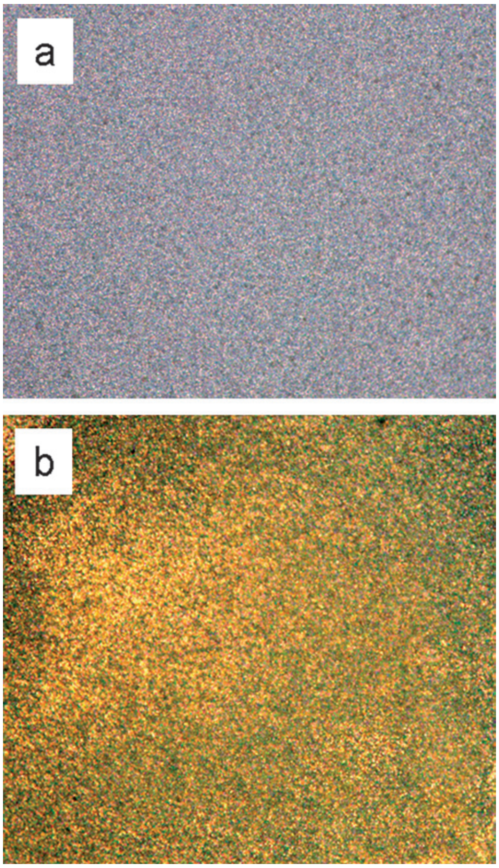


Fig. 8 Optical photomicrographs of (a) polymer **10** and (b) its composite **10a** at 25 °C on cooling from the isotropic liquid (crossed polarizers, magnification ×200).

that of the pure polymer as shown in Fig. 7b which again shows that the mesophase is not destroyed by the inclusion of carbon nanotubes though a large quantity of carbon nanotubes could not be dispersed homogeneously in the matrix.

Conclusions

We have synthesized two novel monomeric and two novel polymeric discotic liquid crystals and studied the effect of inclusion of carbon nanotubes on their mesophase behavior. The insertion of carbon nanotubes in small amounts does not affect the mesophase structure of the pure compounds but brings down the isotropic transition temperatures. With an increase in the amount of carbon nanotubes, the isotropic transition temperature decreases in all the composites. We have previously shown that in discotic liquid crystal–carbon nanotube composites, SWNTs align in the hexagonal columnar phase along the director. These room-temperature liquid crystalline nanocomposites with broad mesophase ranges and different electronic properties may be important for many device applications, such as photoconductors, light-emitting diodes, photovoltaic solar cells, sensors, thin-film transistors, *etc*.

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