Self-assembled ordering of single-walled carbon nanotubes in a lyotropic liquid crystal system

D. Vijayaraghavan *

Raman Research institute, Sadashivanagar, Bangalore 560 080, India

ABSTRACT

We have carried out small angle X-ray scattering (SAXS) studies as a function of temperature on 0.01 wt.% single-walled carbon nanotubes (SWCNTs) dispersed lyotropic liquid crystal (LLC) system consisting of 25 wt.% cetyltrimethylammonium bromide (CTAB) in water. This LLC system exhibits crystalline surfactant + water (Cr), nematic (N), hexagonal (H) and isotropic (I) phases on heating. Our SAXS pattern revealed that in the crystalline + water phase of the LLC, the doped CNTs exhibit 1-D ordering. In the nematic and hexagonal phases of the LLC, the CNTs exhibit 2-D hexagonal ordering. In the isotropic phase, there are domains of CNTs and within each domain, the nanotubes exhibit 1-D ordering. A plot of d-spacing of the CNTs as a function of temperature showed peaks at the phase transition temperatures of the LLC. We have also carried out optical birefringence and electrical conductivity measurements of the composite as a function of temperature. Interestingly, they also showed peaks at the phase transition temperatures. This indicates a correlation between the d-spacing of the CNTs and the anomalous increase in the birefringence and conductivity of the composite at the phase transition temperatures.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Carbon nanotubes (CNTs) possess high aspect ratio and exhibit high tensile strength, anisotropic electrical and thermal conductivities. Due to their unique features, they are expected to find applications in solar cells, sensors and mechanical and electrical nano devices [1–4]. However, to realize most of these applications, uniform alignment of carbon nanotubes is necessary. One way of aligning carbon nanotubes is to disperse them in liquid crystals as it is expected that the liquid crystals impose their orientational order on CNT guests. A uniform nanotube alignment was reported by dispersing CNTs in a thermotropic liquid crystal [5–7]. However, dispersion of individual nanotubes in thermotropic liquid crystals is not straightforward due to the bundling and aggregation of CNTs even for mild concentration of CNTs. On the other hand, in the case of water-based lyotropic liquid crystals (LLC), a considerable amount of SWCNTs (up to 0.2 wt.%) can be dispersed and aligned [8–11]. Efficient dispersal and alignment of CNTs in lyotropic liquid crystals are extensively reported in the literature. Weiss et al. reported the integration of SWCNTs in a hexagonal LLC for various concentrations of SWCNTs and studied the alignment of SWCNTs in the LLC using light microscopy imaging and small-angle X-ray scattering techniques [12]. They find that both the supramolecular (d-spacing) and macroscopic (viscosity) properties show similar trends with varying SWCNT concentration in the composite. Lagerwall et al. have aligned the SWCNTs in the

lyotropic nematic liquid crystals formed both by rod shaped and disc shaped micelles. Their polarized Raman spectroscopy measurements indicated that the nanotubes are aligned along the LC director [9]. Notiv-Roth et al. dispersed SWCNTs in CTAB/water lyotropic liquid crystal system [13]. They carried out SAXS and cryo-TEM studies on the dispersion. Jang et al. reported small angle X-ray scattering studies on SWCNTs dispersed in various concentrations of pluronic F127 block copolymers in water and reported that SWCNTs induced re-entrant lyotropic hexagonal phases [14]. Moussa et al. reported high orientational ordering of SWCNTs when dispersed in a nematic chromonic liquid crystal which is a new class of water-based lyotropic liquid crystal [15].

Interestingly, except in the case of the SWCNTs dispersed in the nematic chromonic LLC [15], the reported studies on SWCNT–LLC dispersions are carried out only at room temperature. The temperature dependence or the dynamics of the CNT alignment in the LLC matrix across different LLC phases and phase transition regions is not investigated in detail so far. We believe that investigating CNT alignment in LLC as a function of temperature in various LLC phases and phase transition regions of the same LLC system will give interesting results. (Incidentally, it is reported that in the case of multi-walled carbon nanotube dispersed thermotropic nematic liquid crystals, the optical transmission of the composite exhibits step-wise change at the nematic–isotropic transition temperature which is attributed to some structural ordering of nanotubes in the composite [16]). Further, it is known that in the case of surfactant/water/CNTs systems, at high surfactant concentration, surfactant micelles induce aggregation of nanotubes due to an attractive

* Tel.: +91 80 9480836191; fax: +91 80 23610492.
  E-mail address: vijay@rri.res.in.

interaction known as depletion attraction [17]. It arises from the osmotic pressure formed by the surfactant micelles. We believe that these attractive interactions can lead to the ordering of the nanotubes in the LLC. Moreover, recently, LLCs have been often utilized for preparation of nanomaterials [18,19]. In this view, we have carried out SAXS, optical birefringence and electrical conductivity measurements as a function of temperature on a LLC–SWCNTs (0.01 wt.%) composite. Our LLC system consists of 25 wt.% cetyltrimethylammonium bromide (CTAB) in water. This LLC system exhibits crystalline surfactant + water (Cr), nematic (N), hexagonal (H) and isotropic (I) phases on heating. Our SAXS studies revealed various self-assembled structures or ordering of SWCNTs depending on the phases of the LLC matrix. The temperature dependence of the d-spacing of the SWCNTs showed peaks in the vicinity of the phase transition temperatures of the LLC. Interestingly, the temperature dependence of the optical birefringence and electrical conductivity of the composite also showed peaks at the phase transition temperatures. This indicates a correlation between the d-spacing of the SWCNTs and the observed anomalous increase in the birefringence and conductivity of the composite at the phase transition temperatures.

2. Experimental

Cetyltrimethylammnium bromide (CTAB) was obtained from Sigma Aldrich and used without further purification. Lyotropic liquid crystal of CTAB was prepared by adding 25 wt.% CTAB in deionised (Millipore) water and sonicating the mixture for 10 min with intermittent stirring. The liquid crystalline phases of the LLC were characterized from their optical textures using a Leitz polarizing microscope (POM) equipped with a Mettler hot stage FP-82. Non-functionalized SWCNTs (P2-SWCNT) and octadecylamine (ODA) functionalized (organic soluble) single-wall carbon nanotubes (P5-SWCNT) were procured from Carbon-Solutions, Inc. (USA). (The individual nanotube lengths range from 0.5 to 3 μm and have an average diameter of 1.4 nm). A homogeneous SWCNT dispersion in the CTAB/water LLC was obtained by adding 0.01 wt.% SWCNTs in the LLC solution and sonicating the mixture for 10 min with intermittent stirring near the isotropic temperature (50 °C) of the LLC. For both the functionalized and non-functionalized CNT samples we followed the same procedure and obtained a uniform black solution indicating a homogenous dispersion of CNTs in the CTAB solution for both the cases. POM observation of our non-functionalized SWCNT/LLC composite showed a small number of CNT aggregates whereas, no such aggregates are seen in the ODA functionalized SWCNT/LLC composite. This indicates that our composites predominantly consist of isolated single-walled carbon nanotubes.

For SAXS studies, the sample was filled in a glass capillary of 1 mm in diameter and flame sealed. The sample was kept in a magnetic field of 1 kilo Gauss. The sample temperature was controlled using a computer controlled temperature controller. The sample was heated slowly to 5 °C above the isotropic temperature and the diffraction data is collected while cooling the sample (0.5 °C/min). The details of the experimental setup for SAXS measurements were given elsewhere [20]. AC electrical conductivity data of the composite was collected while heating the sample from 20 °C at the rate of 1 °C/min. The details of our experimental setup for AC electrical conductivity were given elsewhere [21]. The optical birefringence of the LLC–SWCNT composite was measured using a method available in the literature [22]. The experimental setup consisted of a 1 mW He–Ne laser ((λ = 633 nm), a photoelastic modulator (PEM) and a pair of polarizer and an optical detector. The laser was followed by a polarizer oriented at +45° with respect to the PEM retardation axis (0°). The modulated light passes through the second polarizer oriented at −45° with respect to the PEM axis then to the detector. The detector output was split with one branch going to a lock-in-amplifier (Standford Research System, Model SR 830 DSP) for the detection of the 1f AC signal and the other branch was connected to a DC voltmeter. The sample was placed in a glass cell of dimensions 45 × 10 × 10 mm³ and sealed. This cell was

mounted inside a heater arrangement consisting of an enclosure made of thick aluminum block with a 40 ohm (Minco) heater film affixed on it. In the heater arrangement windows were provided for the light to traverse. A platinum resistance thermometer placed close to the sample cell was used to measure the sample temperature accurately. Birefringence data was collected while cooling the sample from high temperature at the rate of 0.5 °C/min. The temperature of the sample was controlled using a computer controlled temperature controller, the stability being about 0.1 °C.

3. Results and discussion

Our CTAB–water LLC system consists of 25 wt.% CTAB in water. The temperature–composition of CTAB–water binary phase diagram is reported by Hertel et al. [23]. From the phase diagram, for 25 wt.% CTAB, the following phases are seen: crystalline surfactant + water (Cr) phase below 30 °C, nematic phase from 30 to 40 °C and a two phase region (hexagonal/isotropic) above 40 °C. However, from the phase diagram for the CTAB/water system reported by Auvray et al. [24] the high temperature phase above 50 °C is found to be isotropic. From the textural analysis of the LLC phases using our polarized optical microscope (POM) images, we find that 25 wt.% CTAB in the water LLC system exhibits the following phase sequence as a function of temperature: crystalline surfactant + water (Cr) 30 °C nematic (N) 44 °C hexagonal (H) 50 °C isotropic (I).

Fig. 1 shows the SAXS pattern for the LLC–SWCNT composite as a function of temperature in a) crystalline surfactant + water (Cr), b) nematic (N), c) hexagonal (H) and d) isotropic (I) phases of the composite. In all the SAXS patterns, high scattering at low q-values is observed. This pattern is typical for SWCNT dispersion reported in the literature [13]. In addition to this usual SAXS pattern for CNT dispersion as a background, we also find peaks in the scattering curves indicating ordering of the CNTs in our system. In the crystalline phase, for the temperatures from 23.8 to 29 °C, the SAXS pattern exhibits a peak at 0.46 Å⁻¹. We assign this peak to the presence of single-walled carbon nanotube bundles in the system based on the reported (1,0) SAXS peak for CNT bundles [25]. (We believe that the absence of higher order SAXS peaks may be due to the very low concentration of SWCNTs in our system). For temperatures 27 and 29 °C, an additional peak is seen in the SAXS pattern (marked by arrows in the Fig. 1a). We believe that this peak corresponds to some 1-D ordering of some isolated CNTs present in the composite. At 30 °C, the peak at 0.46 Å⁻¹ is absent. This indicates a possible disintegration of bundles into isolated CNTs. From the SAXS pattern, with increasing temperature, we find a considerable shift in the peaks (corresponding to 1-D ordering) toward the low q-region.

In the nematic (N) phase of the composite (Fig. 1b), for all the temperatures studied, two peaks in the ratio 1: √3 are observed indicating a 2-D hexagonal ordering of nanotubes in the composite (for 39 °C, the peaks are indicated by arrows. For the other temperatures (from 31 to 37 °C), the peaks appear very close to the peaks at 39 °C). With increasing temperature (from 31 to 39 °C), peaks shift weakly toward the high q-region. However, at 40 and 42 °C which are very close to the nematic to hexagonal transition temperature (44 °C), the peaks shift considerably toward the low q-region.

In the hexagonal (H) phase of the composite (Fig. 1c), again we find two peaks (indicated by arrows) which are in the ratio 1:√3. This again indicates a 2D-hexagonal ordering of nanotubes in this phase. This hexagonal ordering of nanotubes is present even at temperatures >50 °C (Fig. 1c) in the vicinity of the hexagonal to isotropic phase transition (from 52 to 58 °C). At higher temperatures of the isotropic phase of the composite, at 60 °C, three sharp peaks (as indicated by arrows) are observed without any specific relation between them. We believe that there are three domains of CNTs and within each domain, the nanotubes exhibit 1-D ordering.