# Synthesis and Characterization of Liquid Crystalline Polyester/Graphene and a Study of Their Properties

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A new rod-like thermotropic liquid crystalline polyester (TLCP) material and its nanocomposites based on different concentrations of graphene were synthesized by *in-situ* high-temperature solution polymerization. The resulting nanocomposites were characterized using XRD, microscopic analysis (POM, SEM, and TEM), spectroscopic analysis (FT-IR, UV-Vis, and fluorescence), and thermal analysis (TGA and DSC). The XRD and POM methods showed that the composite materials exhibited only the nematic phase. The TEM images revealed that the graphene were distributed in the polymer with sizes ranging from 100 to 200 nm. The absorption spectroscopy data showed that the electronic properties of graphene were mostly retained without damaging their two-dimensional electronic properties, together with the analysis of the maximum absorption spectrum and concentration of the composites in terms of the Lambert-Beer law. The fluorescence from the TLCP moiety was almost completely quenched and red shifted by graphene, indicating that the linkage mode facilitated effective energy and electron transfer between the rod-like TLCP and the extended  $\pi$ -system of graphene. Therefore, this novel nanocomposite material exhibits excellent thermal properties based on the thermogravimetric analysis.

**Keywords:** Liquid Crystalline Polyester, Graphene,  $\pi$  Conjugation, Thermal Stability, Conductivity.

# **1. INTRODUCTION**

Since the discovery of graphene by Geim et al. in 2004,<sup>1</sup> interest regarding the fundamental properties of graphene has grown especially in recent years. Graphene is a new two-dimensional material composed of a monolayer of carbon atoms.<sup>2</sup> Furthermore, its consists of sp<sup>2</sup> carbon hexagonal networks in which strong covalent bonds are formed between two adjacent carbon atoms.<sup>3</sup> Due to its large specific surface area,<sup>4</sup> thermal conductivity,<sup>5</sup> and good electrical conductivity,<sup>6,7</sup> this twodimensional material is becoming important in various fields such as high-performance nanoelectronic devices,<sup>8</sup> composite materials,<sup>9</sup> biosensors,<sup>10</sup> and energy storage and batteries.<sup>11, 12</sup> These results indicate that graphene has great potential in the fabrication of organic and inorganic materials. People are just now starting to discover this interesting research topic.13

Liquid crystal can be considered as a fourth state of matter following solid, liquid, and gas. Therefore, liquid crystal phases, as the name implies, exist between

crystal solid and isotropic liquid states.<sup>14</sup> Thermotropic liq-A MER uid crystalline polyester (TLCP) has aroused great interest due to its properties as a high-performance engineering material.<sup>15,16</sup> In 2003, Windle et al. first reported the liquid crystalline behavior of an aqueous suspension of acid-oxidized multi-walled carbon nanotubes (MWNTs) and analyzed the phase diagram using the simple rigidrod steric theory.<sup>17</sup> The liquid crystalline behavior of carbon nanotubes has already been reported in several systems.<sup>18-22</sup> However, studies of the covalent or noncovalent incorporation of TLCP with graphene have been limited.<sup>23, 24</sup> Some simple and versatile non-covalent methods through supermolecular interactions such as  $\pi - \pi^*$ stacking, van der Waals, electrostatic interaction, and hydrogen bonding have the advantage of preserving the unique electronic properties of graphene without serious damage.<sup>25</sup> Recently, Novoselov et al.<sup>23</sup> reported a graphene-based liquid crystal device that has excellent performance. More recently, Behabtu et al.24 reported how graphite spontaneously exfoliates into a single-layer graphene in chlorosulphonic acid, dissolves at isotropic concentrations, and spontaneously forms liquid crystalline phases at high concentrations.

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J. Nanosci. Nanotechnol. 2012, Vol. 12, No. 3

In this paper, we report the use of graphene as an excellent additive to polyester matrix. Great efforts have been made to study the thermal, dissolution, and electrical properties of the TLCP/graphene nanocomposites. Our objective is to improve the physical properties of TLCP nanocomposites by incorporating a very small quantity of graphene.

### 2. EXPERIMENTAL DETAILS

#### 2.1. Materials and Preparation

4,4'-Oxybis (benzoic acid) (OBA, 98+%) were purchased from A. Johnson Matthey Company. Resorcinol (99.5%, m.p.: 110–180 °C) was obtained from Tianjin Guangfu Fine Chemical Research Institute, China. Diphenylether (99.5%, b.p.: 256–259 °C) were purchased from Tianjin Chemical Reagent Ltd. Co., China. We used commercially available graphene sheets (Jiansin Scientific and Trading Ltd. Co.) which were produced by the arc-dischargeby method.<sup>26</sup> Main CID is 80

The synthesis of the polyester monomer was shown 80 in Scheme 1 (Part I). The polyester acid chloride Jwas 20 prepared by refluxing 4,4'-Oxybis (benzoic acid) (5.165 g, 20 mmol) with excess thionyl chloride (20 ml) in the presence of a few drop of dry DMF for 8 h. Then excess

thionyl chloride was removed under reduced pressure. It was received the white solid (5.550 g, 94.0%) and dried in a vacuum oven at 60 °C for 24 h, then stored in a desiccator with drying agent. In this study, neat TLCP, TLCP with 0.1 wt.% to 1.0 wt.% of graphene were synthesized according to the method of high-temperature solution polycondensation and *in-situ* polymerization. The neat TLCP chemical formula was shown in Scheme 1 (Part I). A typical procedure was as follow: A mixture consisting of 4,4'-oxydibenzoyl chloride (0.590 g, 2 mmol), resorcinol (0.220 g, 2 mmol) was charged into a round-bottomed three-neck flask, equipped with a spherical adaptor leading to a water-cooled condenser, a nitrogen gas inlet, a heater, and a magnetic stirrer while a solution consisting of diphenylether (15 ml) was added rapidly. The solution was stirred at 180 °C for 6 h and then poured into methanol at 0 °C to coagulate the product. The precipitated polyester was washed with methanol, acetone, and water in sequence. Finally, the white powdery solid was dried in a vacuum oven at 60 °C for 24 h, and then stored in addesiccator with drying agent. The yield was 87.0%. IR (KBr): aromatic ether C–O–C: 1127 and 1060  $\text{cm}^{-1}$ , C=C: 1592, 1499 and 1442 cm<sup>-1</sup>, C=O: 1739 cm<sup>-1</sup>, =C-O-C: 1009 cm<sup>-1</sup>, COO: 1238 cm<sup>-1</sup>.



Scheme 1. Preparation steps and schematic diagram.

The synthesis of nanocomposites based on 0.1 wt.% graphene was given as an example. The same method was adopted for others. Monomers 4,4'-oxydibenzoyl chloride (0.590 g, 2 mmol), resorcinol (0.220 g, 2 mmol) and graphene with 0.1 wt.% were added in diphenylether (15 ml), followed by supersonic treatment for 2 h. Then the mixture was heated to 180 °C for 6 h under nitrogen and anhydrous conditions in a three-necked flask, and then poured into methanol at 0 °C to coagulate the product. The precipitated polymer was washed with methanol, acetone, and water in sequence for several times. The gray powdery solid was dried in a vacuum oven at 60 °C for 24 h, and stored in a desiccator with drying agent. The yield was 85.6 wt.%. IR (KBr): aromatic ether C-O-C: 1128 and 1059 cm<sup>-1</sup>, C=C: 1593 and 1499 cm<sup>-1</sup>, C=O:  $1740 \text{ cm}^{-1}$ , =C-O-C: 1009 cm<sup>-1</sup>, COO: 1238 cm<sup>-1</sup>.

0.5 wt.% graphene: The yield was 80.0 wt.%. IR (KBr): aromatic ether C–O–C: 1128 and 1060 cm<sup>-1</sup>, C=C: 1593, 1499 and 1443 cm<sup>-1</sup>, C=O: 1740 cm<sup>-1</sup>, =C–O–C: 1009 cm<sup>-1</sup>, COO: 1239 cm<sup>-1</sup>. Delivered by

1.0 wt.% graphene: The yield was 84.0 wt.% IR (KBr): aromatic ether C–O–C: 1129 and 1060 cm<sup>-1</sup>, C=C 1593, 8 1499 and 1446 cm<sup>-1</sup>, C=O: 1741 cm<sup>-1</sup>, T=C=O+C: 2 1008 cm<sup>-1</sup>, COO: 1238 cm<sup>-1</sup>.

A typical procedure for preparing TLCP and nanocomposites base on the graphene sheets is given in Scheme 1 (Part I).

#### 2.2. Characterization

The Fourier transform infrared spectrum (FT-IR) of TLCP was recorded on a Nicolet Nexus 670 from 400 to 4000 cm<sup>-1</sup>. X-ray diffraction (XRD) measurement was performed at room temperature on a Rigaku (D/Max-IIIB) X-ray diffractometer using Ni-filter Cu-K<sub> $\alpha$ </sub> radiation. The scanning was 10°/min over a range of 10-50°. and the scanning type was continuous scan. Transmission electron microscopy (TEM) measurements were taken on a Hitachi-600 electron microscope, with an accelerating voltage of 100 kV. The thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of TLCP and nanocomposites were carried out under N2 atmosphere over the temperature range of 25-800 °C at a heating rate of 10 °C/min on TGA/DSC1 equipment (Mettler Toledo Inc.) to investigate the thermal degradation and decomposition. Fluorescence spectra were recorded in the form of thin film on a Hitachi F-4500 fluorescence spectrophotometer. UV-vis spectra were recorded on a Lambda 35 in ethanol solution over a range of 200-500 nm.

# 3. RESULTS AND DISCUSSION

## 3.1. X-Ray Diffraction Analysis

The information obtainable from X-ray diffraction studies includes the degree of crystallinity, crystal lattice, crystal size, molecular orientation, and a variety of structural defects. The intermolecular spacing can be estimated from the radial position of the large angles using the equation  $(2 \cdot d \cdot \sin \theta = 1.117 \cdot \lambda)$ .<sup>14</sup> In this paper, the representative XRD curves are shown in Figure 1. The data showed a diffraction peak at a  $2\theta$  of about 20.5°, indicating an average distance of 4.83 Å between two neighbor TLCP molecules within the layers of the mesophase. The sharp diffraction angles at  $2\theta = 12.7^{\circ}$ ,  $15.2^{\circ}$ ,  $16.5^{\circ}$ , and  $20.5^{\circ}$ , and the amorphous diffuse angle at about  $2\theta$  of  $25.5^{\circ}$ corresponds to the characterization of the semi-crystalline polymer.<sup>27-29</sup> Besides these, the intensity was increased with the increase of graphene. However, there was no sharp peak at the low angle region. This result reveals that TLCP and related nanocomposites exhibited only nematic mesophases, which was consistent with their DSC curves in later analysis. Furthermore, the positions of the diffraction peaks of TLCP and the nanocomposites were similar, indicating that the introduction of graphene in TLCP did not affect the nematic type polymer. As shown in Figure 1, no graphene peaks were detected, presumably because the content of graphene doping was very low and the doped graphene were uniformly distributed into the TLCP matrix.

#### 3.2. Morphological Characterization

The POM and SEM micrographs are shown in Figures 2(A) and (B). As shown in Figure 2(A), a birefringent texture can be observed at the phase transition temperature in neat polyester ( $250 \,^{\circ}$ C), which illustrates that the synthesized polyester exhibits a nematic phase. Meanwhile, the SEM micrographs in Figure 2(B) clearly show the features of the polyester surface. To investigate the degree of dispersion of graphene in the polyester matrix, as an example, Figures 2(a) to (c) shows the morphologies of the samples with different concentrations of graphene observed through TEM. Based on these images, the size



Fig. 1. XRD patterns of TLCP and its nanocomposites based on graphene from 0.1 to 1.0 wt.%.



Fig. 2. The structure morphology of TLCP and its nanocomposites. (A) The POM of pure TLCP in 250 °C. (B) The SEM image of TLCP and the TEM of nanocomposites with different concentration of graphene (a) 0.1 wt.%, (b) 0.5 wt.%, (c) 1.0 wt.%.

of graphene was found to be 100–200 nm. Aside from that, the TLCP/graphene nanocomposites with low densities (0.1 and 0.5 wt.%) were observed to have uniformly distributed graphene in the composite matrix [Figs. 2(a) and (b)]. However, the aggregation of graphene occurred when the graphene content was increased to 1.0 wt.% [Fig. 2(c)], which is consistent because graphene easily forms agglomerates irreversibly due to their strong  $\pi$ stacking tendency.<sup>30, 31</sup>

## 3.3. Thermal Behaviors

Both the curves of TGA and DSC detected thermal and phase behaviors, including weight loss, glass transition, and phase transitions. Figure 3(a) is a representative DSC of samples that has a nematic phase above melting. As shown in Fig. 3(a), the polyester has a melting transition  $(T_m)$  at 211 °C and an isotropic transition  $(T_i)$  at 425 °C, as shown by the jump in the heating curve. When doping with different concentrations of graphene into the TLCP matrix by the *in-situ* method, the  $T_m$  and  $T_i$  of nanocomposites were shifted to higher temperatures. In addition, detailed changes are shown in Table I. The reason for the increase in  $T_m$  and  $T_i$  may be that the polyester with  $\pi - \pi^*$  conjugation near the graphene sheet might be degrading more slowly.<sup>32</sup> Subsequently, the thermal stability properties of

TLCP and its nanocomposites were characterized by TGA and the curves are compared in Figure 3(b). At temperature of 5.0 wt.% mass loss increased after adding graphene in the polyester. This could be explained that dispersed graphene might hinder the flux of degradation product and thereby delay the onset of degradation. The thermal decomposition temperatures were the lowest for the resulting product of the polymerization of TLCP in the presence of little graphene. The thermal decomposition temperatures of the TLCP/graphene nanocomposites increased with increasing amounts of graphene in the experimental range. That is, the results show that the degradation of pure TLCP was faster than that of its hybrids (0.1-1.0 wt.% graphene). Accordingly, the thermal stability of the nanocomposites with the interaction of  $\pi - \pi^*$  conjugation between the graphene and the TLCP matrix are better than the pure TLCP and those without this band. Therefore, the interface properties had been improved with the addition of a coupling agent.

#### 3.4. Optical Spectroscopy

We also investigated the optical spectral properties of TLCP and its nanocomposites. Figure 4 shows the UV-Vis absorption spectra of the TLCP and nanocomposites in the presence of different concentrations of graphene, and





Fig. 3. The curves of thermodynamics. (a) Differential scanning calorimetry (DSC) and (b) Thermo gravimetric analysis (TGA).

samples were characterized by the absorption band of the TLCP (202 nm) and graphene (279 nm). The absorption state.<sup>34</sup> From the inserted figure in Figure 4(a), the fluband maximum ( $\lambda_{max}$ /nm) due to the  $\pi$ - $\pi^*$  transition was in the order 1.0 wt.% >0.5 wt.% >0.1 wt.% >TLCP, which suggests that the sample with 1.0 wt.% had the of a thin film. Upon excitation at the maximal absorpshortest conjugation length due to a twisted linkage at the allene (C=C=C) moiety.33 Otherwise, the addition of graphene to the matrix of TLCP caused not only a red shift in the 202 nm band but also significant diversification of the graphene absorption band at 279 nm. Furthermore, the intensity of the absorption band increased with increasing concentrations of graphene. This result indicates that there was notable electronic communication between the two  $\pi$ -systems of graphene and the TLCP in the ground

Table I. Thermal properties of TLCP/graphene nanocomposites.

Graphene content (wt.%)	$T_{\rm m}$ (°C)	$T_i$ (°C)	$\Delta T$
0	211	425	214
0.1	237	450	213
0.5	245	457	212
1.0	255	470	215
Shifted $(T_{\text{max}} - T_{\text{min}})$	44	45	_

Fig. 4. UV-Vis absorption and fluorescence emission spectra of the pure TLCP and TLCP/graphene nanocomposites for 0.1 to 1.0 wt.%. For UV-Vis: C = 0.02 mg/ml, Fluorescence:  $\lambda_{ex} = 295$  nm.

orescence spectra of the TLCP and the nanocomposites were considered under the same conditions in the form tion wavelength, the pure TLCP showed strong fluorescence emission. However, the fluorescence emission of the 1.0 wt.% graphene in TLCP was 15% that of the pure TLCP, indicating that graphene efficiently quenched the fluorescence of the TLCP moiety. This fluorescence quenching has been attributed to the electron or energy transfer from the fluorophore to the graphene sheet. Nevertheless, the emission peak shifts to longer wavelengths, from 365 to 380 nm, when the concentration of graphene is increased. Namely, this emission peak appeared to the red shift. The red shift proves a strong conjugate interaction between the benzene rings of TLCP and graphene. Otherwise, this longer emission wavelength also corresponds to a higher overlap or closer distance of  $\pi$ -electrons between the TLCP and graphene.<sup>35-37</sup> In order to make comparison, the content of 1.0 wt.% graphene treated in mechanical mixing was employed. The direct mixing sample had a hypsochromic shift to 201 nm shown in Figure 4(b).



Fig. 5. Absorption spectra of (a) to (d) represent TLCP and nanocomposites (0.1 to 0.06 mg/ml, respectively). Shown in the insets are the plots of optical density at 200 nm versus concentration. The straight lines are a linear least-square fit to the data.

This phenomenon illustrated that the polyester wrapped the graphene, which would cause a blue shift of TLCP's lowest energy absorption band because of interruption of the  $\pi$ -conjugation.<sup>38</sup> In the same way, the sample of direct mixing was quenched slightly and blue shift (360 nm) from the inserted in Figure 4(b).

Based on the UV-Vis and fluorescence results, we came up with the following hypothesis: Due to the favorable *in-situ* polymerization, the polyester chain gets closer to the graphene surface, which may promote more efficient  $\pi-\pi^*$  interaction,<sup>35</sup> and such parallel stacking and interaction are quite common in many cases.<sup>39,40</sup>

To investigate the dispersibility of the polymer and the nanocomposites, ethanol was used as a solvent. The TLCP and nanocomposites with 0.1 to 1.0 wt.% graphene exhibited significant solubility in ethanol. The process includes pretreatment with mild sonication for 15 min followed by centrifugation at 3000 rpm for 10 min. There were no obvious precipitates observed after a week, indicating that the dispersions were very stable. To further study their solubility, the UV-Vis absorption spectra for polyester

and its composites in ethanol were measured, which are shown in Figure 5. The curves from 5(a) to 5(d) represent the relationship of sample concentration and the maximum adsorption spectra. For example, for the first curve in Figure 5, a continuously rising absorption was obtained as the concentration increased. Furthermore, a linear relationship exists between the concentration and the maximum adsorption value (200 nm) (inset in Fig. 5(a) with an *R*-value of 0.996). The results demonstrate that polyester dispersions conform to the Lambert-Beer law at low concentrations. As shown in Figures 5(b) to (d), when the graphene content was increased, the nanocomposite concentration and the adsorption value also exhibited a linear relationship.<sup>41</sup>

# 4. CONCLUSIONS

A series of liquid crystalline polyester based on different concentrations of graphene nanocomposite materials have been synthesized by *in-situ* high-temperature polymerization. The result from different analytical techniques suggest that graphene, when added to the polyester matrix, is uniformly distributed and it remarkably improves the thermal stability of the nanocomposites. Improvement on the physical properties of the nanocomposites may be caused by the  $\pi - \pi^*$  conjugation between graphene and the host matrix. Graphene, as a brilliant additive, played an important role in enhancing the physical properties of the polymer. Finally, we also provide a method for preparing the TLCP/graphene nanomaterials and believe that these graphene based TLCPs will be of great value in translating the dispersive, electrical, thermal, and liquid properties of nanocomposites in high performance fibers and structural materials in future studies. Taken together, the nanocomposites can also complement current theoretical studies.

Acknowledgment: We thank Dr. B. D. Wang of College of Chemistry and Chemical Engineering at Lanzhou University for his hearty assistance in acquiring UV-Vis absorption spectra data.

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Received: 3 January 2011. Accepted: 19 May 2011.