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Poly(*N*-vinyl carbazole)-grafted multiwalled carbon nanotubes: Synthesis via direct free radical reaction and optical limiting properties

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Abstract

In this work, samples of poly(*N*-vinyl carbazole) (PVK)-grafted multiwalled carbon nanotubes (MWCNTs) were synthesized via free radical reaction. The ready-made PVK was allowed to react directly with MWCNTs at 70 °C in the presence of azo-bis-isobutyronitrile (AIBN). The purified deep grey products, which can dissolve in common organic solvents such as chloroform and 1,2-dichlorobenzene (DCB), were then characterized by FTIR spectra, TEM, TGA, elemental analysis, XPS, UV–vis spectra and Raman spectra. It was confirmed that PVK chains were grafted onto the surface of the carbon nanotubes (CNTs). The optical limiting properties of these PVK-grafted MWCNTs samples were investigated by open-aperture *z*-scan method. All of the samples of PVK-modified carbon nanotubes in chloroform showed optical limiting behavior better than that of C_{60} in toluene.

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Keywords: Carbon nanotubes; Poly(*N*-vinyl carbazole); Free radical reaction; Optical limiting properties

1. Introduction

Carbon nanotubes (CNTs) are endowed with unique structural and electronic properties, and have extensive applications in many fields [1–5]. However, the manipulation and processing of CNTs have been blocked by their insolubility in most common solvents and tendency to aggregate. It has been identified that one of the most promising approaches to effectively resolve these problems is the covalent functionalization of CNTs with polymers, because the long polymer chains will help the tubes dissolve in good solvents and decrease the aggregation even with a low degree of functionalization.

Up to now, there have been some reports describing the attachment of polymers to CNTs via in situ free radical polymerization [6–12]. People found that CNTs can be activated by free radical initiators to open their π-bonds, and then participate in polymerization, resulting in chemical grafting of some polymer chains onto the surfaces of CNTs [6,8]. Furthermore, oxidation provides more possibilities for the nanotubes to bond to a matrix, due to reactive chemical groups such as COOH, COO^- and C=O, which are found both on the tip and on the wall surface [9]. However, to our knowledge, no attempts were made to carry out the direct radical reaction between ready-made polymers and CNTs.

Some research groups have exposed that polymer derivatives of C_{60} can be obtained by the direct radical reaction between C_{60} and polymers. Tang et al. [13] described their results of direct fullerenation of polycarbonate (PC) by irradiating a solution of PC and C_{60} at room temperature using a UV lamp and by warming up a C_{60}/PC solution to 60 °C in the presence of azo-bis-isobutyronitrile (AIBN). They also carried out the reaction of poly(vinyl chloride) (PVC) and C_{60} in chlorobenzene at 60 °C in the presence of AIBN [13]. Afterwards, Qu et al. [14,15] studied the UV-photoinitiated reactions between low-density polyethylene (LDPE) and C_{60} in the presence or absence of benzophenone (BP) as a photoinitiator under different conditions, producing polymeric

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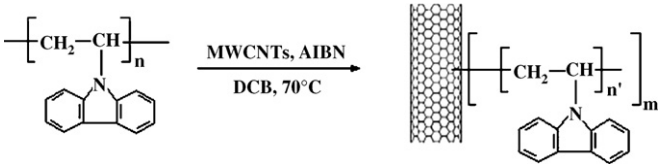

Scheme 1.

alkyl-C_{60} radical adducts. Recently, we [16] reported the synthesis of C_{60}-functionalized polycarbonate by direct reaction of C_{60} and PC in 1,1,2,2-tetrachloroethane using AIBN as radical initiator under microwave irradiation. Nowadays, we also extend our research to carbon nanotubes, whose structure is correlative with C_{60}. The fact that fullerene functionalized polymers can be synthesized via direct reaction of ready-made polymers and C_{60} encourages us to attempt the reaction between ready-made polymers and CNTs in the presence of radical initiator to yield polymer-modified CNTs.

In this article, we prepared poly(*N*-vinyl carbazole)-grafted multiwalled carbon nanotubes (MWCNTs) via the direct reaction of poly(*N*-vinyl carbazole) (PVK) and MWCNTs in the presence of AIBN. The synthetic route was shown in Scheme 1. The optical limiting properties of the PVK-grafted MWCNT products were measured using the open-aperture *z*-scan technique.

2. Experimental

2.1. Reagents and instrumentation

Multiwalled carbon nanotubes, purchased from Shenzhen Nanotech Port Co. Ltd., were heated and refluxed in 100 mL of 20% HNO_3 aqueous solution for 18 h. After cooling to room temperature, they were diluted with 200 mL of deionized water and then vacuum-filtered through a 0.22 μm membrane. The solid was washed with deionized water until neutral pH, and then dried under vacuum. Poly(*N*-vinyl carbazole) ($\overline{M}_n = 6.22 \times 10^4, \overline{M}_w/\overline{M}_n = 2.06$), provided by Department of Macromolecular Science, Fudan University, was further purified before use. AIBN was recrystallized from CH_3OH, and dried at room temperature under vacuum. 1,2-Dichlorobenzene (DCB) was distilled over CaH_2 under vacuum. All other reagents were used as received without further purification.

TEM experiments were conducted on a JEOL2011 microscope operated at 200 kV. The FTIR spectra were recorded on a nicolet FTIR-5DX spectrometer using KBr pellets. Thermogravimetric measurements were made with a Perkin-Elemer Pyris 1 DTA-TGA instrument under nitrogen at a heating rate of 10 °C/min. Elemental analyses for N, C and H were carried out on a vario ELIII elemental analyzer. XPS experiments were carried out on a RBD upgraded PHI-5000C ESCA system (Perkin-Elmer) with Mg Kα radiation ($h\nu = 1253.6$ eV). UV–vis absorption spectra were taken on a HP8452 spectrophotometer. Raman spectroscopy was done with Super LabramΠ Confocal microscopic Raman spectrometer Instrument (Dilor, France).

The optical limiting property measurement was carried out using the open-aperture *z*-scan technique. The light pulse source was the laser beam from a Q-switched Nd:YLF laser with duration of 100 ns, wavelength of 532 nm and repetition rate of 1 kHz. Part of the beam was used to trig the Boxcar integrator. The focal lengths of the focusing lens in front of the sample and the collection lens in front of the detector were 11 and 13 cm, respectively. The sample solution was put in a quartz cell with 1 mm path length, and the measurement was done at room temperature. The data detected by a Boxcar integrator was transferred to a personal computer, which also controlled the step motor driving the sample.

2.2. Preparation of PVK-grafted MWCNTs

All experiments for radical reaction were conducted under purified nitrogen by use of standard Schlenk tubes. The detailed reaction conditions were given in Table 1. First, 100 mg of acid-purified MWCNTs and 10 mL of DCB was introduced into a Schlenk tube, and the mixture was sonicated for 20 min to disperse MWCNTs. Then PVK, AIBN and 10 mL of DCB were charged. After stirring for 2 h at room temperature to form a black suspension, the tube was fitted with a condenser and the mixture was stirred at 70 °C under nitrogen for 52 h. After cooling to room temperature, the reaction mixture was diluted with 100 mL of DCB, bath sonicated for 40 min, and filtered through a 0.22 μm membrane. The solid was repeatedly washed with DCB to remove unreacted PVK. The purified product was dried under vacuum as grey solid.

3. Results and discussion

3.1. The radical reaction of PVK and MWCNTs

In this study, the ready-made PVK was used to functionalize MWCNTs using AIBN as radical initiator and DCB as solvent. The detailed reaction conditions are shown in Table 1. For the sake of sufficiently grafting PVK to MWCNTs, a great deal of PVK was used in the reaction, and the reaction time was prolonged enough (more than 50 h). When the reaction was stopped and allowed to cool to room temperature, the mixture was diluted with 100 mL of DCB, bath sonicated for 40 min, and then filtered though a 0.22 μm membrane. The solid substance left on the membrane was washed repeatedly with DCB until no white cloudy was found when 10 drops of colorless filtrate were dripped into 10 mL of methanol, showing that the free PVK was removed.

The obtained purified grey solid can dissolve in organic solvents such as chloroform and DCB. When they were dispersed in these solvents by sonication, a well-dispersed suspension formed and remained stable for days. The obvious improvement of the solubility for the obtained samples proved that the reaction between ready-made PVK and MWCNTs was successful, and the PVK chains did convalently link to the surface of MWCNTs.