



Synthesis of polyethyleneimines protonated by 1-pyrenesulfonic acid and their usability for solubilization of single-walled carbon nanotube



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ABSTRACT

Reaction of 1-pyrenesulfonic acid (Pyr-SO₃H) with branched polyethyleneimine (PEI) in molar ratios of 1:1, 1:2, 1:3, and 1:4 produced PEIs with sulfopyrenyl pendant groups, denoted as Pyr-PEI(1:1), Pyr-PEI(1:2), Pyr-PEI(1:3), and Pyr-PEI(1:4), respectively; the degrees of protonation depended on the feed ratios of Pyr-SO₃H/PEI. Treatment of single-walled carbon nanotube (SWNT) with Pyr-PEIs caused adhering of the pyrenyl group on the SWNT surface and produced soluble composites, SWNT-Pyr-PEIs. UV-vis and photoluminescence (PL) measurements indicated that the absorbance and PL intensity corresponding to SWNT in SWNT-Pyr-PEIs increased with increasing the content of the PEI unit in the composites. The electrical conductivities of SWNT-Pyr-PEIs were higher than that of pristine SWNT owing to n-doping, based on electron migration from the PEI unit to the SWNT.

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1. Introduction

Chemical modification of SWNT to make it soluble in organic solvents and water leads to many useful applications and has this attracted great research interest [1–5]. Shortened SWNT bearing carboxylic acid chloride groups at the open end is widely used as a starting material to obtain soluble functionalized SWNTs [1–7]. However, the shortened SWNT is damaged by oxidative acid treatment [3]. To avoid damage to SWNTs, noncovalent functionalization has been employed; pyrene derivatives like 1-pyrenecarboxylic acid [8], 1-(trimethylammonium acetyl)pyrene [9], and trimethyl-(2-oxo-2-pyren-1-yl-ethyl) ammonium bromide [10] can adhere on SWNT via π - π stacking interactions between the pyrene moiety and the sidewalls of SWNT. The resulting composites showed improved solubility and dispersibility in organic solvents.

SWNTs can be converted into both p- and n-type conducting materials that find application in molecular electronics [11–13]. Various kinds of p- and n-type dopants have been reported for SWNTs [14–16]. PEI is one of the most widely used polymeric n-dopants for SWNTs. Adherence of PEI on the SWNT surface or introduction of PEI at the open end of SWNT can produce air-stable n-doping states of SWNT based on electron migration from amine groups of PEI [17–19]. However, the SWNT with PEI adhered on its surface is dispersible but insoluble in organic solvents, and SWNT with PEI unit at the open end is damaged. To

the best of our knowledge, there has yet been no report on soluble SWNTs with PEI attached noncovalently to its surface. Such SWNTs can be useful for the development of functional materials. In this study, PEIs protonated by Pyr-SO₃H with several degrees of protonation were synthesized and were used as materials for the preparation of soluble composites with SWNT. Herein the PEI chain should closely approach to the SWNT because the pyrene moieties of the composites can adhere to the SWNT surface.

Herein, we report the synthesis and structural characterization of PEIs protonated by Pyr-SO₃H, their composites with SWNTs, and the optical and electrical properties of the composites.

2. Experimental

2.1. Synthesis of Pry-PEI(1:1)

To an aqueous solution (20 mL) of Pyr-SO₃H (0.14 g, 0.50 mmol; purchased from Tokyo Chemical Industry (TCI) Co.) was added dropwise an aqueous solution (2 mL) of PEI (0.022 g, 0.50 mmol, $M_n \sim 10,000$; purchased from Aldrich-Sigma Co.). After the reaction solution was stirred at room temperature for 1 h, the precipitate was collected by filtration and dried under vacuum to yield Pry-PEI(1:1) (0.052 g, 63%). ¹H NMR (400 MHz, DMSO-*d*₆): 8.09–9.17 (9H), 2.33–2.92 (17H).

Pry-PEI(1:2), Pry-PEI(1:3), and Pry-PEI(1:4) were prepared analogously. Data of Pry-PEI(1:2). Yield = 100%. ¹H NMR (400 MHz, DMSO-*d*₆): 8.06–9.16 (9H), 2.33–2.92 (21H). Data of Pry-PEI(1:3). Yield = 100%. ¹H NMR (400 MHz, DMSO-*d*₆): 8.12–9.17 (9H),

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2.33–2.96 (26H). Data of Pyr-PEI(1:4). Yield = 30%. ^1H NMR (400 MHz, DMSO- d_6): 8.09–8.21 (9H), 2.33–2.67 (30H).

2.2. Preparation of SWNT-Pyr-PEI(1:1)

After SWNT (3 mg, CarboLex AP-grade, 12–15 Å in diameter; purchased from Aldrich-Sigma Co.) was added to a DMSO (purchased from TCI Co.) solution (10 mL) of Pyr-PEI(1:1) (10 mg), the suspension was stirred at room temperature for 24 h. The DMSO solution of SWNT-Pyr-PEI(1:1) was obtained as a supernatant by filtration with a membrane filter and used for the UV-vis and PL measurements. The DMSO solutions of SWNT-Pyr-PEI(1:2), SWNT-Pyr-PEI(1:3), and SWNT-Pyr-PEI(1:4) were prepared by the reaction of SWNT (3 mg) with SWNT-Pyr-PEI(1:2) (6 mg), SWNT-Pyr-PEI(1:3) (4 mg), and SWNT-Pyr-PEI(1:4) (3 mg) with the similar manner that used for the preparation of the DMSO solution of SWNT-Pyr-PEI(1:1), respectively.

3. Results and discussion

3.1. Synthesis

Reaction of Pyr-SO₃H with PEI in water, at molar ratios of 1:1, 1:2, 1:3, and 1:4, yielded Pyr-PEI(1:1), Pyr-PEI(1:2), Pyr-PEI(1:3), and Pyr-PEI(1:4), respectively (Scheme 1). The polymers were soluble in polar organic solvents like *N,N*-dimethylformamide (DMF) and DMSO but insoluble in water.

The degrees of protonation of PEI were estimated titrating the amino groups of PEI with Pyr-SO₃H. The pH changes in the PEI aqueous solution with the addition of Pyr-SO₃H to the solution proceeded normally. The pH of the PEI solution reached 7 when an equimolar amount of Pyr-SO₃H added to the solution, indicating that PEI reacted with Pyr-SO₃H in a 1:1 M ratio. Therefore, the degrees of protonation in Pyr-PEI(1:1), Pyr-PEI(1:2), Pyr-PEI(1:3), and Pyr-PEI(1:4) were almost consistent with the feed ratios of Pyr-SO₃H/PEI. The ^1H NMR data also supported these results, as mentioned below.

3.2. ^1H NMR and IR spectra

The ^1H NMR spectra of the DMSO- d_6 solutions of Pyr-PEI(1:1), Pyr-PEI(1:2), Pyr-PEI(1:3), and Pyr-PEI(1:4) at the same concentration showed the peaks correspond to the protons of the pyrenyl group in the range δ 8.0–7.3. The peak corresponding to the protons of the PEI unit in the polymers is duplicated with respect

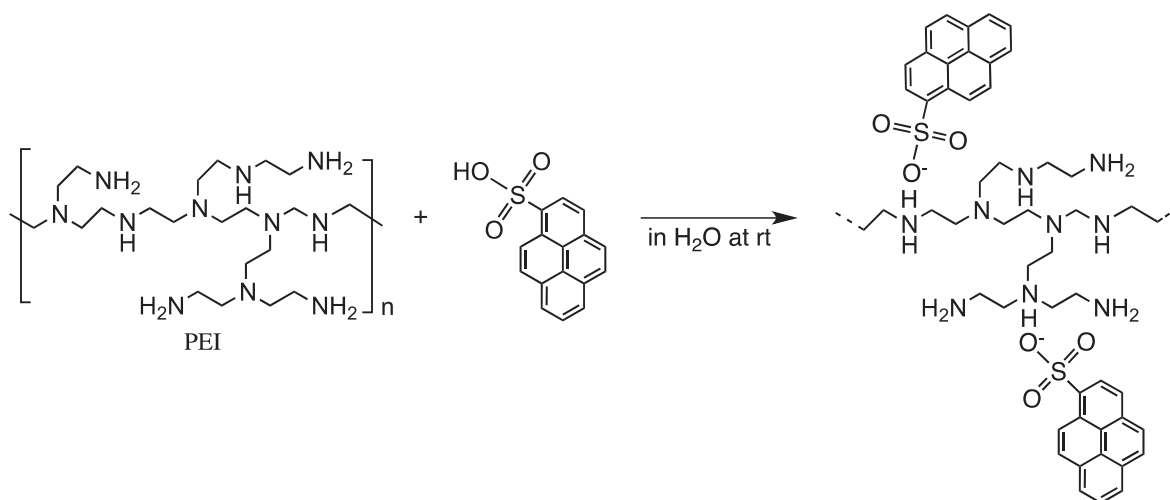
to that of the solvent. However, the relative integrals of the peaks corresponding to the pyrenyl and PEI protons can be estimated from the ^1H NMR spectra because the sample concentrations are identical. The integral ratios of the peaks corresponding to the protons of the pyrenyl group and the PEI unit in Pyr-PEI(1:1), Pyr-PEI(1:2), Pyr-PEI(1:3), and Pyr-PEI(1:4) increased every approximately 4 as 9:17, 9:21, 9:26, and 9:30, respectively. These results indicate that the degree of protonation of PEI could be controlled by the molar ratio of the Pyr-SO₃H/PEI feed.

Fig. 1 shows the IR spectra of Pyr-PEI(1:1), Pyr-PEI(1:2), Pyr-PEI(1:3), and Pyr-PEI(1:4). The main features of the IR spectra are similar, while some of the relative intensities vary appreciably. The peaks at 2920 and 1180 cm⁻¹ were assigned to C–H vibrations of the PEI unit and the S=O stretching vibrations of the SO₃⁻ group, respectively. The peak intensity ratios (I_{2920}/I_{1180}) of Pyr-PEI(1:1), Pyr-PEI(1:2), Pyr-PEI(1:3), and Pyr-PEI(1:4) were 0.52, 0.78, 0.82, and 0.86, respectively. These results are consistent with the above-mentioned ^1H NMR results.

3.3. UV-vis and photoluminescence spectra

The five DMSO solutions of SWNT containing Pyr-PEI(1:1), Pyr-PEI(1:2), Pyr-PEI(1:3), Pyr-PEI(1:4), and PEI, denoted as SWNT-Pyr-PEI(1:1), SWNT-Pyr-PEI(1:2), SWNT-Pyr-PEI(1:3), SWNT-Pyr-PEI(1:4), and SWNT-PEI, respectively, were prepared such that identical SWNT/PEI ratios were maintained. Fig. 2 shows the UV-vis spectra of these solutions. The absorptions in the ranges of 370–380 nm and 450–800 nm were assigned to the π - π^* transitions of the pyrene ring and SWNT, respectively. Pristine SWNT is insoluble in DMSO. The composites of SWNT with the Pyr-PEIs showed absorption corresponding to SWNT, implying improved solubility of SWNT in the solvent. The absorption corresponding to SWNT in the range of 450–800 nm increased with increasing PEI content of the Pyr-PEIs. The absorption of SWNT-Pyr-PEI(1:1) was larger than that of SWNT-PEI in the range of 450–800 nm. These observations confirmed that the pyrenyl group of Pyr-PEIs adhered on the SWNT surface and the PEI unit contributed to the dissolution of SWNT in DMSO.

Fig. 3 shows the PL spectra of SWNT-Pyr-PEI(1:1), SWNT-Pyr-PEI(1:2), SWNT-Pyr-PEI(1:3), and SWNT-Pyr-PEI(1:4) in DMSO. Soluble SWNTs functionalized with alkyl and poly(ethylene glycol) chains have been reported to show PL in solutions, while pristine SWNT does not show any PL [20]. Pyr-PEIs in solution show a PL peak at approximately 510 nm upon excitation with 450 nm light, while PEI itself does not show any PL upon irradiation of the



Scheme 1. Synthesis of Pyr-PEI.

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