Preparation and Characterization of Polystyrene Modified Single-Walled Carbon Nanotube

Guojian Wang, Yue Dong, Lin Liu, Caixia Zhao

Department of Polymer Science, College of Material Science and Engineering, Tongji University, Shanghai 200092, People's Republic of China

ABSTRACT: A halogen atom terminated Polystyrene (PSt) was prepared by means of atom transfer radical polymerization. Then, the halogen atom was converted into -N_3 group and a -N_3 terminated PSt was obtained. Finally PSt was grafted onto the surface of single walled carbon nanotube (SWNT) by the reaction of azide group with SWNT. Comparison of X-ray photoelectron spectrometer of N1s electron belonging to -N_3 and the surface of SWNT demonstrated that three-membered rings were formed by releasing N_2 from -N_3 during the reaction. The structure of PSt modified SWNT was characterized by FTIR, UV, Raman spectrum, and TEM. The experimental results showed that the PSt was connected assuredly to SWNT by the covalent bond. TGA data showed that the amount of PSt on the surface of SWNT firstly increased with growing $\overline{M}_n$ of PSt and then decrease when $\overline{M}_n$ continues to grow. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 1385–1390, 2007

Key words: carbon nanotube; polystyrene; chemical modification; azide; atom transfer radical polymerization

INTRODUCTION

Carbon nanotubes (CNTs) was discovered by S. Iijima in 1991. As a novel kind of nano material, CNTs is endowed with unprecedented mechanical properties such as high strength, modulus, excellent toughness, and low density. Therefore, CNTs shows its unique advantage as fillers to reinforcing polymer. Furthermore, CNTs with certain structure is of high conductance and the electric conductivity of polymer containing these CNTs can be enhanced to great degree. Presently, polymer/CNTs composite is becoming the most popular research field as one of the most valuable application of CNTs.

However, CNTs cannot be dissolved or dispersed stably in water and any common organic solvents, and also are difficult to disperse homogenously in polymer matrix. The defects severely limit fundamental research and further applications based on CNTs.

To deal with this unpleasant phenomenon, researchers are attracted to modify the surface of CNTs with polymer to improve their dissolution and dispersion ability in solvents or polymer matrices. Chemical modification is preferred especially in favor of steady chemical bond between polymer and CNTs and various grafted polymers corresponding to different application. Up to now, reports are mainly focused on the approach introducing carboxyl group to the surface of CNTs. By this approach, polymer chain is grafted to or grated from the surface of CNT based on carboxyl functional.[1–9] Besides this popular approach, some papers also describe modification of CNTs through florene treatment,[10,11] ion polymerization,[12–15] radical polymerization,[16] electric reduction chemistry,[17] electron transfer,[18] and so on.

Early in C_{60} chemistry, azide derivatives are abundantly applied to graft polymer to C_{60} surface and the reaction principle is systematically discussed.[19–21] This paper intends to transfer this approach to single-walled carbon nanotubes (SWNT) chemistry. Previously, the same use of azide derivatives on modification of SWNT was published by Qin[22] and Holzinger.[23] Azide group acts as media to link SWNT and polymer directly, avoiding strong treat with acid which inclines to damage intrinsic structure of carbon wall and meanwhile avoiding multisteps reaction on the surface of SWNT like graft from approach.[8,9]

Polystyrene (PSt) has been grafted to the surface of SWNT via different methods, for example, NMRP[24] and atom transfer radical polymerization (ATRP).[25] In this article, bromine atom at one end of PSt which was synthesized by ATRP was converted into -N_3 group. Then, -N_3 reacted with SWNT via cycloaddition and PSt was grafted to the surface of SWNT. A series of characterization of PSt modified SWNT provided evidences that it was through covalent bond that PSt was grafted to SWNT. Qin's work although described the method to modify SWNTs via addition

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of azide-terminated PSt. But, in our work, the products of each approach were characterized in more detail. As it is well acknowledged, in the research of CNTs chemistry, the evidence for the existence of covalent bonds between polymer and CNTs is especially important and attracting focus from researchers. In this article, more detailed and credible characterization for the approach via addition of azide-terminated PSt was provided. Moreover, the reaction principle of -N$_3$ and the surface of SWNT were explored via X-ray photoelectron spectrometer (XPS) of N1s electron.

EXPERIMENTAL

Materials

Single-walled carbon nanotubes (SWNT, diameter: 1–2 nm, purity $\geq$ 90%) was produced by Chengdu Organic chemicals, Chinese academy of sciences; Styrene(St) was purchased from Shanghai Reagent Company, Chinese Medicine, China; Inhibitor was eliminated by washing with NaOH solution. CuBr was obtained from Shanghai Runjie Reagent Company, China; Ethyl 2-Bromo Propionate (EBP, purity 99%) was purchased from Sigma-Aldrich, USA; 2,2-Bipydine (Bipy, AR) was obtained from Shanghai Runjie Reagent Company, China; NaN$_3$ (AR) was produced by Zhejiang Huilong Chemicals Factory, China; N,N-dimethyl formimide (DMF) ,Tetrahydrofuran (THF), 1,2-Dichlorobenzene (DCB), and methanol were all from Shanghai Reagent Company, Chinese Medicine, China.

Modification of carbon nanotube surface

Preparation of Pst-Br

CuBr and Bipy were added to a sealed reactor. The reactor was degassed and back-filled with N$_2$ three times, followed by adding styrene through syringe under N$_2$. The mixture was stirred for 1 h at room temperature. Then the reactor was heated to 110°C and EBP (CuBr : EBP : Bipy : St = 1 mol : 1 mol : 3 mol : 50 mol) was injected into the reactor under N$_2$. After certain time, the polymerization was stopped by opening the reactor to atmosphere. The mixture was diluted by THF and then precipitated into methanol to obtain PSt solid which was dissolved in THF and precipitated in methanol several times until white solid was obtain. The white solid PSt-Br was dried in vacuum.

Preparation of PSt-N$_3$

PSt-Br and NaN$_3$ were dissolved in DMF and stirred for 12 h at 25°C. The mixture was diluted by THF and

precipitated into methanol. The obtained white solid PSt-N$_3$ was washed with deionized water three times and finally dried under vacuum.

Modification of carbon nanotube surface with polystyrene (SWNT-g-PSt)

SWNT was mixed with PSt-N$_3$ in DCB solution. After stirring for 24 h at room temperature, the mixture was heated to 130°C and kept stirring under N$_2$ atmosphere for 60 h. Then the mixture was diluted with DCB and filtrated through 0.2 µm PVDF membrane. The black solid was sonicated for less than 2 min in DCB, filtrated and washed with DCB several times until no white floccules appeared when filtrate was dropped into methanol. The black solid SWNT-g-PSt was dried under vacuum.

Measurements and characterizations

GPC measurements were carried out at room temperature in THF using Waters 150 GPC meter at a flow rate of 1.0 mL/min. Detector was differential refractometer. The column set was calibrated with PSt standards. FTIR measurements were conducted at room temperature using EQUINOXSS FTIR Spectrometer. Thermal gravimeter analyses were performed using STA449 Thermal analysis instrument with a heating rate of 20°C/min in a nitrogen flow. Ultraviolet-visible (UV-vis) spectra were obtained from U-3310 Spectrometer with anhydrous ethanol as standard. Transmission electron microscope (TEM) was H-800 Electron Microscope at 200 kV. Raman spectra were obtained using LABRam-1B Spectrometer with a 4.3 mw diode laser source for 632.8 nm excitation. XPS was measured using PHI 5000C ESCA system with aluminum target, high voltage 14.0 kV, power 300 W. Binding energy correction was performed with C1s = 284.6 eV as reference.

RESULTS AND DISCUSSION

Preparation of Pst-Br by ATRP

Br terminated PSt was synthesized by ATRP with EBP/CuBr/Bipy as initiator system. The product was characterized by FTIR in Figure 1. 3030 cm^{-1} (corresponding to C—H stretching absorption in benzene ring), 2920 cm^{-1} (—CH$_2$ vis-symmetric stretching absorption), 2848 cm^{-1} (—CH$_2$ symmetric stretching absorption), 1729 cm^{-1} (C=O from initiator residue), 1601 cm^{-1} (C=C stretching absorption in benzene ring), 1497 and 1451 cm^{-1} (—CH$_2$ vis-symmetric distortion or benzene ring absorption), 763 cm^{-1} (bending vibrication five H atom on the benzene ring), and 703 cm^{-1} (bending vibracating of benzene ring)-were all observed. Peak at 538 cm^{-1} is from C—Br
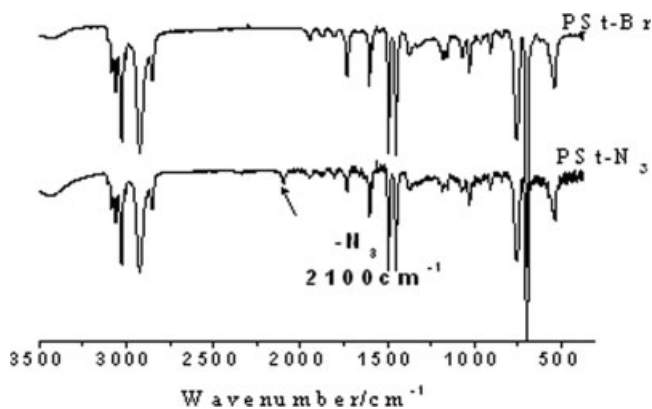
Figure 1 FTIR spectra of PSt before and after azidization.

stretching absorption. It could be concluded that PSt-Br is obtained by ATRP as expected.

### Preparation of PSt-N3 from PSt-Br

ATRP is often preferred for its efficiency to prepare polymer with special end group. ATRP was applied here to introduce one halogen atom at one end of PSt chain. After reacting with NaN_3, the halogen atom was substituted by $-N_3$ group. The formula is illustrated as follow.

$$Pst - Br + NaN_3 \longrightarrow Pst - N_3 + NaBr$$

By comparing FTIR spectra of PSt-N_3 with that of PSt-Br (Fig. 1), an obvious difference was displayed in former absorption at 2100 cm^{-1} appeared, which was attributed to -N_3 group. However, absorption at 538 cm^{-1} of C-Br was still present, although some smaller. This demonstrated that not all Br atoms had been converted to -N_3. It is difficult to find solvent to resolve both PSt-Br and NaN_3, so the conversion between halogen atom and -N_3 in a heterogeneous phase is incomplete unavoidably. Raising reaction temperature to promote conversion efficiency cannot be adopted considering it would promote the risk of crosslinking among -N_3 greatly.

Preparation of PSt functionalized SWNT

In the study of C_{60} chemistry, it is discussed that five membered ring is firstly formed by means of cycload-
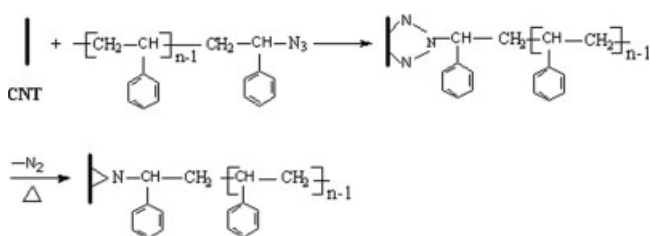
Scheme 1 Preparation process of modified CNT with PSt.

dition when -N_3 group reacts with C_{60}, and subsequently N_2 is released under high energy to constitute C—N—C ring.[19–21] Considering CNTs having similar C—C structure with C_{60}, it is supposed that the same principle can be applicable for SWNT (Scheme 1). A series of characterizations were performed to provide necessary evidence.

In the FTIR spectrum of SWNT (Fig. 2), extremely weak peaks at 3400, 1709, 1557, and 1193 cm^{-1} were displayed. The peaks at 3400, 1709, and 1193 cm^{-1} were attributed to —OH, C=O, and C—O group in carboxylic group respectively, which was introduced during purification of prepared SWNT. Peak at 1557 cm^{-1} corresponded to stretching vibration of C—C bond composing six-membered carbon ring at the surface.[24] After modification, new absorption peaks at 3024, 2914, 1554, 1490, 1451, 754, and 696 cm^{-1} emerged and these peaks were all characteristic peaks of PSt, which was consistent with the result reported elsewhere[24] but more complete. In the experiment, any free PSt that did not reacted with SWNT was removed through repeated washing in THF, which guaranteed that PSt in the sample was covalently grafted to SWNT surface.

Figure 3 is the TEM photographs of SWNT before and after modification with PSt. Because they were poorly dispersed in alcohol, SWNTs were observed intertwined together through TEM [Fig. 3(A)]. After modification with PSt, SWNT could be dispersed much better and a less quantity of SWNTs was included within the same scope [Fig. 3(B)]. Moreover the diameter of some modified SWNT grew greatly. Larger magnification enabled observing polymer layer covering the parts of SWNT where PSt was grafted to SWNT. The parts became rough and dark with tube hollow invisible [within rectangle frame in Fig. 3(C)], which is consistent with Qin's AFM result that the PSt clumps on the surface of the SWNT.[22]

UV absorptions of PSt took place at 201, 243, and 282 nm. UV absorption of SWNT reached its peak at 256 nm. But after modification with PSt, UV absorption of SWNT was divided into three peaks of 198, 230, and 260 nm (Fig. 4). Obviously, the break of UV
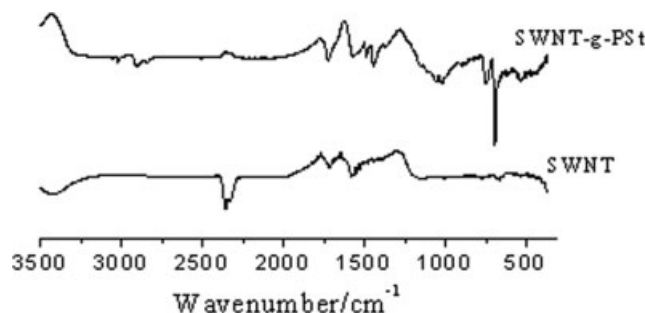

Figure 2 FTIR spectra of SWNT before and after modification with PSt.

(A)   (B)   (C)
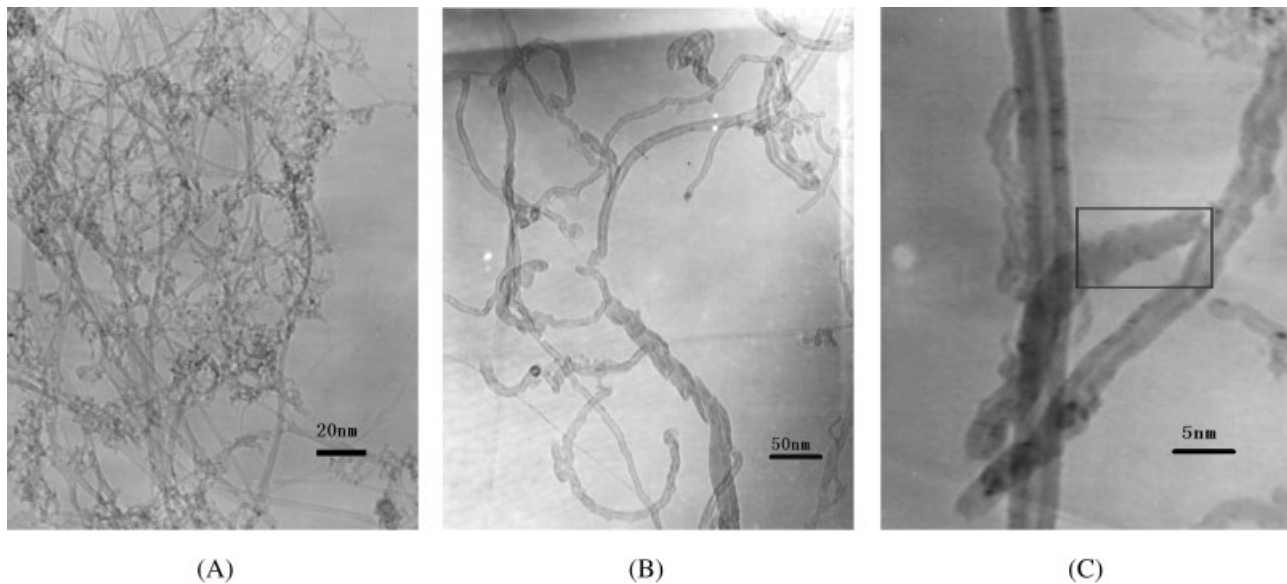
Figure 3 TEM image of CNTs before and after modification with PSt (A: SWNT, B and C: SWNT-PSt).

absorption was caused by conjugated structure of PSt grafted to SWNT. Moreover, it can be found that absorption peaks of PSt displayed certain blue shift for the influence from electron on SWNT surface.

Raman spectrum has been prevalently applied for characterization of carbon family including CNTs. Raman spectrum of SWNT displays two obvious peaks as shown in Figure 5. ω_t (1576 cm^{-1}) is generated by sp^2 C. ω_d (1320 cm^{-1}) exists because of vibration of sp^3 C or some disordered carbon structure. It can be concluded from theory that when polymer chain is grafted to surface of SWNT via covalent bond, original sp^2 C is transferred to sp^3 carbon, and therefore the percentage of sp^2 relatively decreases while sp^3 carbon increases in quantity, which would result in peak areas ratio between ω_d and ω_t ($I_{\omega d}/I_{\omega t}$) rise.[22] However, the result in this experiment was not consistent with theory analysis. On the contrary, $I_{\omega d}/I_{\omega t}$ declined a bit. The reason for the failure of

Raman evidence for introduction of covalent bond may be as followed: The ''pure'' SWNT is impure in actual, instead it is adhered to some amorphous carbon, which can be distinguished from TEM photograph [Fig. 3(A)]. The amorphous carbon constitutes one factor for high ω_d intensity. After certain percentage of amorphous carbon on the surface of SWNT was removed during modification process, correspondingly ω_d became less intense. The opposition of trends determined by the two factors for ω_d intensity led $I_{\omega d}/I_{\omega t}$ dependent on which factor stands priority. Meanwhile, ω_d and ω_t both increased to bigger Raman shift, which indicated sp^2 and sp^3 C altered however.

To evaluate the amount of polymer grafted to SWNT, thermal gravimeter analysis was used (Fig. 6). Under N$_2$ atmosphere, SWNT did not exhibit large weight loss until 700°C. The little loss was caused by decomposition and volatilization of impurity (amorphous carbon and catalyst). Comparatively, after it was grafted with polymer, evident weight loss ranged
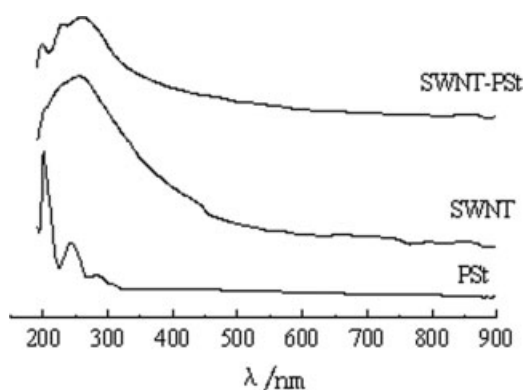

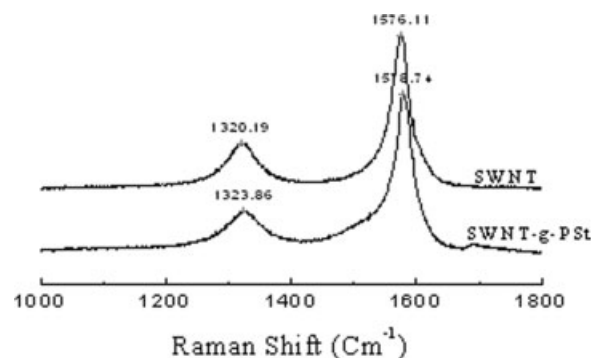**Figure 4** UV spectra of pure SWNT, pure PSt, and SWNT-PSt.

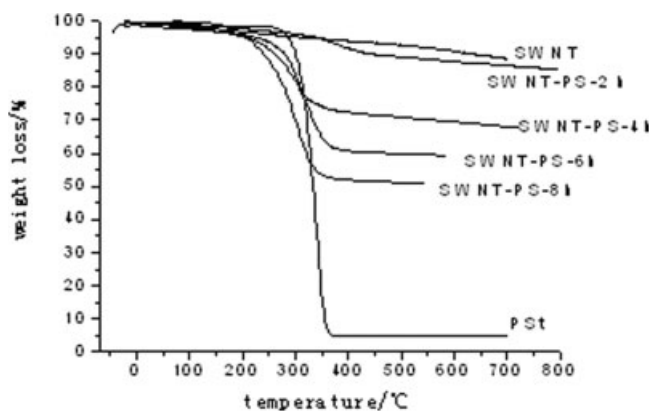**Figure 5** Raman spectra of SWNT before and after modification with PSt.

Figure 6 TGA of pure PSt and SWNT before and after modification with PSt.

Figure 7 Effect of PSt $\overline{M}_n$ on the modification of carbon nanotubes surface.

from 5.7 to 45.5% took place at around 337°C which was near the decompose temperature of PSt suggesting that the weight loss was resulted from decomposition of grafted PSt. Taking no consider of extremely small quantity of residues of PSt, content of PSt could be calculated. Moreover, the result was more credible than other approaches of modification of SWNT, since PSt obtained by ATRP was narrowly dispersed in molecular weight.

As a typical living/controllable polymerization, ATRP is easy to control the molecular weight of polymer. In this experiment, molecular weight of PSt was designed by altering reaction time. Products with 2, 4, 6, and 8 h reaction time were chosen to modify the surface of SWNT. The contents of PSt grafted to SWNT were determined by TGA. To justify the comparison, quantity ratio of CNTs to PSt remained constant. The TGA results are displayed in Table I.

From Table I and Figure 7 it can be seen, weight loss of modified SWNT increased with growing PSt molecular weight and modification density for $\overline{M}_n$ below 3400 changed on the same tendency, which suggested that the number of PSt chains grafted to individual SWNT increased firstly. This phenomenon can be explained as follows: during the process of azidation, halogen ends belonging to PSt of higher $\overline{M}_n$ were converted to -N$_3$ groups more exhaustively than PSt of lower $\overline{M}_n$, which was attributed to higher amount of -N$_3$ among the same quantity of PSt to

take cycloaddition reaction with the surface of SWNT. The amount of -N$_3$ was determined by two factors. The first is content of halogen end in PSt, which decreases with increasing molecular weight. The second is related with degree of crosslinking between -N$_3$ of PSt molecular chains. -N$_3$ group was highly reactive and tended to crosslink among each other, which was consistent with the fact that some white dissolvable solid existed after PSt reacted with NaN$_3$. When $\overline{M}_n$ was below a certain value, the second factor was dominate because with the lower halogen content in PSt of higher $\overline{M}_n$, the opportunity to crosslink decreased.

However, once $\overline{M}_n$ of PSt exceeded a certain value, the modification density began to go down with growing higher $\overline{M}_n$ (Fig. 7). This was caused by the first factor mainly and the amount of -N$_3$ group among the same quantity of PSt became so low that the opportunity to react decreased. This result indicates that it is possible to control the modification degree of polymer on SWNT to apply modified SWNT for special fields, considering that polymer on CNTs surface have influence on distinct properties of CNTs as well as dispersion ability in solvents.

TABLE I
Effect of $\overline{M}_n$ of PSt on the Modification of Carbon Nanotubes Surface

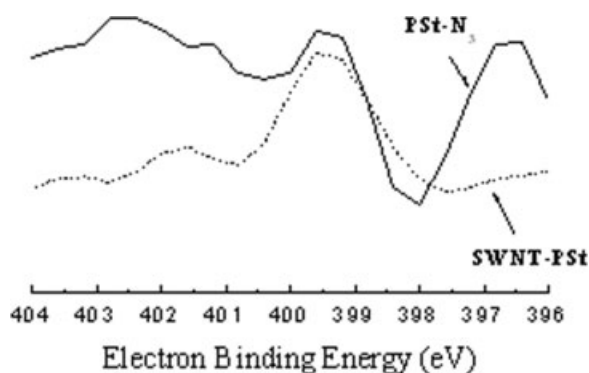| Code	$\overline{M}_n$	Weight loss/%	Modification density (PS/C)
SWNT-PS-2h	2000	5.7	1/2757
SWNT-PS-4h	2500	21.6	1/756
SWNT-PS-6h	3400	37.5	1/472
SWNT-PS-8h	7700	45.5	1/768

Figure 8 XPS Spectrum of N 1s of PSt-N3 and SWNT-PSt.

To verify the structure of C—N—C three membered ring grafting PSt to the surface of SWNT, XPS technology was applied on N1s electron whose binding energy was analyzed and shown in Figure 8. Peak at 396.8 eV for N1s electron belonging to -N_3 disappeared after reacting with SWNT. Peak between 404 and 401 eV was weakened while peak at 399.4 eV was broadened. Obviously, it was the change in surrounding microstructure of N1s electron exerted influence on its binding energy and the result was that quantivalence of N atom was simplified to single form in C—N—C from relatively complicated form in -N_3.

PSt of $\overline{M}_n = 3400$ modified SWNT was chosen to carry out elemental analysis, the content of N on modified SWNT was 0.28% (0.17%). Supposing that it was through one N atom in C—N—C that PSt and SWNT were linked, according to modification density of 1/472(PS/C) the N% should be 0.23%. The agreement of the two results also indicated that C—N—C three membered ring was formed during the modification with -N_3 derivative.

CONCLUSIONS

PSt modified SWNT were obtained through cycloaddition of -N_3 group. The reaction principle of forming C—N—C three membered ring was justified by XPS of N1s electron. The results from FTIR and UV could prove that PSt was grafted to SWNT through covalent bonds. TEM provided direct evidence that the aggregate of SWNT after modification was avoided. Raman Spectra failed to detect the structure of modified SWNT because of massive amorphous carbon on the surface of raw SWNT. The results from TGA demonstrated that the content of PSt on the surface of SWNT took tend of increase and then decrease with growing $\overline{M}_n$ of PSt.

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