A Novel Route for Well-Defined Polystyrene-Grafted Multiwalled Carbon Nanotubes Via the Radical Coupling Reaction

Kunyan Sui,[1,2] Chunjia Yang,[2] Song Gao,[2] Xin Shan,[2] Yanzhi Xia,[2] Qiang Zheng[1]

[1]*Department of Polymer Science, College of Materials Science and Chemical Engineering, Zhejiang University, Hangzhou 310027, China*
[2]*State Key Laboratory Cultivating Base for New Fiber Materials and Modern Textile, Qingdao University, Qingdao 266071, China*

Received 17 May 2008; accepted 4 February 2009
DOI 10.1002/app.30455

ABSTRACT: Multiwalled carbon nanotubes-*graft*-polystyrene (MWNTs-*g*-PS) was synthesized by atom transfer nitroxide radical coupling chemistry. MWNTs with 2,2,6,6-tetramethylpiperidine-1-oxy (MWNTs-TEMPO) groups was prepared first by esterification of 4-hydroxy (HO)-TEMPO and carboxylic acid group on the surface of MWNTs (MWNTs-COOH); PS with bromide end group (PS-Br) were then obtained by atom transfer radical polymerization using ethyl 2-bromoisobutyrate as initiator and CuBr/*N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine as catalyst. The MWNTs-TEMPO was mixed with PS-Br and heated to 90°C in the presence of CuBr/PMDETA to form MWNTs-*g*-PS. The product was characterized by FTIR, NMR, TGA, and TEM. TEM indicates that the MWNTs are enveloped by the polymer molecules. The content of grafted polymers is 46.7% by TGA measurements when the number-average molecular weight (M_n) of PS-Br is 10,200 g/mol. The as-prepared nanocomposites exhibit relatively good dispersibility in solvents such as CH_2Cl_2, THF, and toluene. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 1914–1920, 2009

Key words: MWNTs; polystyrene graft; ATRP; atom transfer nitroxide radical coupling

INTRODUCTION

Great interest has been shown in carbon nanotubes (CNTs) both in the theoretical understanding and in practical applications due to unique structural and superior properties of the materials,[1] such as remarkable strength and high thermal and electrical conductivities, since their discovery in 1991.[2] However, the extended π-conjugated framework that imparts these properties is also responsible for strong inter-nanotube van der Waals interactions, which aggregate nanotubes into large bundles that are completely insoluble in all organic and aqueous solvents. This lack of solubility poses a significant impediment to their exploitation in many potential commercial applications. Therefore, functionalization and modification of CNTs are essential prerequisites to improve the solubility and surface functionality. To date, two methodologies, namely noncovalent and covalent, have been developed to functionalize CNTs with a variety of organic, inorganic, biochemical, and polymeric structures.[3–8] Generally, the linkage of small or large molecules to the CNTs by covalent methods is more stable and effective.

Among the various covalent CNT functionalizations, binding polymers to the CNTs is a very attractive area because the individual properties of the two materials can be combined to give one hybrid material. This can be fulfilled by "graft onto" and "graft from" approaches. The former involves direct reaction of existing polymers with the carboxylic acid groups on the CNTs. This approach is easy to carry out, with many linear polymers having functional end groups.[9–19] The apparent limitation of the "graft onto" approach lies in the low grafting density due to the hindrance of the pregrafted polymer chains.[20] On the other hand, the "graft from" approach involves in situ polymerization of monomers from the preformed initiators on the CNTs surfaces, resulting in higher grafting density. Thus, atom transfer radical polymerization (ATRP),[21–24] radical polymerization,[25–27] anionic polymerization,[28–30] and ring-opening metathesis polymerization[31–35] techniques, reversible addition fragmentation chain transfer polymerization,[36–38] have been adopted to covalently grow polymers on the surface of CNTs. However, it is hard to

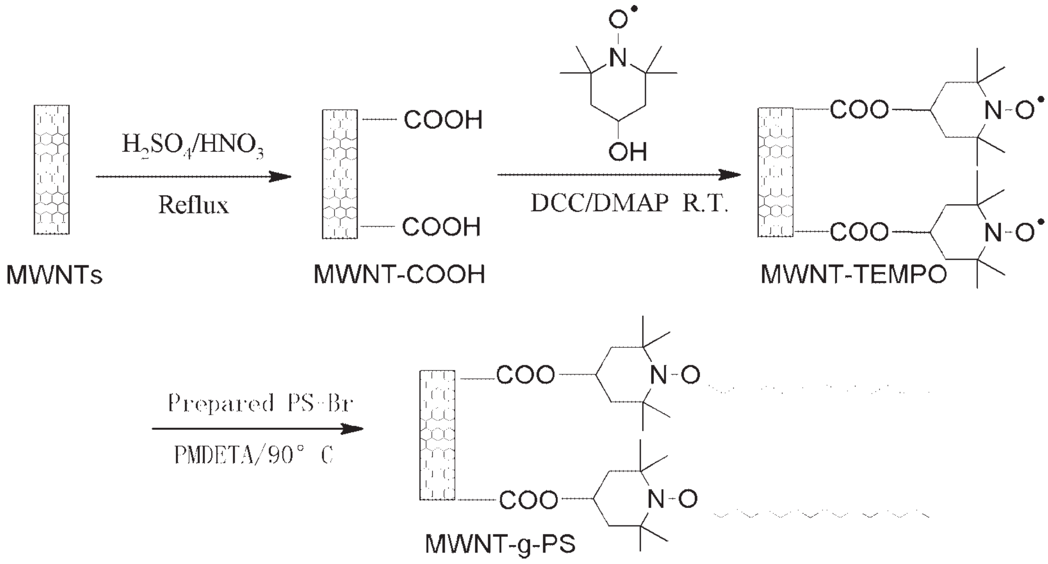
---

Correspondence to: K. Sui (kunyansui@163.com).

Contract grant sponsor: Civic Natural Science Foundation of Qingdao; contract grant number: 05-1-5C-90.

Contract grant sponsor: Natural Science Foundation of Shandong Province Education Department; contract grant number: J05E51.

Journal of Applied Polymer Science, Vol. 114, 1914–1920 (2009)



Scheme 1 Synthesis of PS-grafted MWNTs.

obtain well-defined polymer grafted onto the surface of CNTs through "graft from." Gao and coworkers[23] demonstrated that the polydispersity of the grafted polymer was considerably broad, ranging from 1.77 to 3.57 for the various polymer molecular weights. Obviously, there is a need to look for a strategy to obtain the well-defined polymer with high grafting density on the CNTs surfaces.

Huang[39] reported that when poly (4-glycidyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl-*co*-ethylen oxide) containing TEMPO group was mixed with another containing halide polystyrene (PS) in the presence of CuBr/PMDETA, the coupling reaction between TEMPOs and radicals could be realized in high efficiency. On the basis of this idea, we suggested that this strategy could be adapted to CNTs functionalization with well-defined polymer and high graft density.

Herein, we present an efficient "graft onto" approach via the radical coupling reaction to prepare the well-defined MWNTs-*g*-PS composites (Scheme 1). Two radical systems were pre-prepared: one was MWNTs functionalized with TEMPO nitroxide radical via the esterification of 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxy (HO-TEMPO) and carboxylic acid groups on the surface of MWNTs; the secondary radicals were the PS chains with mono-bromine atom end groups, which were obtained through ATRP polymerization. The two radical coupling reactions were readily accomplished, which resulted in grafting of PS chains onto MWNTs.

EXPERIMENTAL

Materials

The MWNTs (main range of external diameter, 10–15 nm) was purchased from Shen Zhen Bill Scientific and Technical Corporation (Shenzhen, China). Styrene (Shanghai Chemicals, Shanghai, China, CP) was washed with aqueous 15% NaOH solution and water successively, dried over anhydrous $MgSO_4$, further dried over CaH_2, and then distilled under reduced pressure twice before use. *N*,*N*,*N*′,*N*″,*N*″-Pentamethyldiethylenetriamine (PMDETA), 2,2′-bipyridy (bpy), and ethyl 2-bromoisobutyrate (EBiB) were purchased from Aldrich and used without further purification. CuBr (95%) was stirred overnight in acetic acid, filtered, washed with ethanol and diethyl ether successively, and dried in vacuo. HO-TEMPO was prepared by oxidation of 4-hydroxy-2,2,6,6-tetramethylpiperidine purchased from Beijing Tiangang Auxiliary Factory (Beijing, China). *N*,*N*-Dicyclohexyl carbodiimide (DCC), 4-*N*,*N*-dimethylaminopyridine (DMAP), 0.22-μm polyvinylidene fluoride (PVDF) membrane, tetrahydrofuran (THF; 99%), toluene (99%), dichloromethane, and other reagents were all purchased from Shanghai Reagents (Shanghai, China) and purified by standard methods before use.

Acid treatment of MWNTs

Into a 500-mL flask equipped with a condenser, crude MWNTs (3.0 g), HNO_3 (67%, 40 mL), and H_2SO_4 (98%, 120 mL) were added with vigorous stirring. The flask was then immersed in an ultrasonic bath for 15 min. The mixture was then stirred for 120 min under reflux (the oil bath temperature was increased gradually from 90 to 120°C). A dense brown gas evolved during this period, which was collected and treated with aqueous NaOH connected to the condenser by a plastic tube. After cooling to room temperature, MWNTs-COOH was separated from the reaction mixture via centrifugation. The solid was diluted with deionized water and then vacuum-filtered through a 0.22-μm PVDF membrane. A large amount of deionized water was used to wash the filter cake several times until the pH of the filtrate approached 7. The sample was dried under vacuum for 24 h at 50°C to give carboxylic acid–functionalized MWNTs.

Synthesis of MWNTs-TEMPO

The obtained MWNTs-COOH (0.9 g, ∼1.5 mmol COOH, based on the TGA data) was mixed with HO-TEMPO ($M = 172$; 0.432 g, 2.5 mmol), DCC (0.519 g, 2.5 mmol), DMAP (0.102 g, 0.98 mmol), and 20 mL of anhydrous dichloromethane, and the mixture was stirred for 24 h at room temperature. The solid was then diluted with dichloromethane and separated via centrifugation. This cycle was repeated several times to remove any adsorbed HO-TEMPO. The black solid (MWNTs-TEMPO) was collected and dried overnight at 50°C.

Synthesis of halogen-containing polystyrene (PS-Br) by ATRP

A 50-mL ampoule bottle with a magnetic stirrer, containing EBiB (0.2 mL, 1.34 mmol), CuBr (0.192 g, 1.34 mmol), bpy (0.209 g, 1.34 mmol), and styrene, was degassed by three freeze–pump–thaw cycles and then thermostated at 90°C under nitrogen atmosphere for 24 h. By the end of the reaction, the viscosity had increased dramatically. The mixture was subsequently diluted with dichloromethane and cleaned up by the column filled with neutral alumina to remove the copper complex before the polymer was precipitated in cold CH_3OH. The precipitate was collected and purified by dissolution/precipitation with THF/cold CH_3OH twice and then dried at 40°C in vacuo.

Coupling reaction between PS-Br and TEMPO groups on MWNTs

A 50-mL ampoule bottle with a magnetic stirrer, containing MWNTs-TEMPO (0.12 g, ∼0.090 mmol, based on TGA data), PS-Br (M_n: 10,226; 1.288 g, 0.126 mmol), PMDETA (0.053 mL, 0.252 mmol), and anhydrous toluene (5 mL), was degassed by three freeze–pump–thaw cycles. It was placed in an oil bath at 90°C for 24 h. By the end of the reaction, the mixture was subsequently diluted with dichloromethane and vacuum-filtered using a 0.22-μm PVDF membrane. Superfluous dichloromethane was used to wash the filter cake several times, which was then dried under vacuum.

Measurements

Fourier transfer infrared (FTIR) spectra of CNTs samples were measured with a Nicolet Magna-550 in a transmission mode using the KBr disk method at room temperature. Thermal gravimetric analyses (TGAs) of MWNTs powder samples were conducted on a NETZSCHTG-209 instrument at a heating rate of 20°C/min under nitrogen atmosphere. ^{1}H-NMR measurements were carried out on a Bruker (500 MHz) NMR instrument using $CDCl_3$ as the solvent and tetramethylsilane as the reference except for the MWNTs-TEMPO; the latter were determined in deuterated methanol in the presence of stoichiometric ammonium formate ($HCOONH_4$) and the catalyst palladium on carbon (Pd/C). Size exclusion chromatography (SEC) was performed on a Waters 5010 system equipped with a Waters 515 pump, three Styragel columns calibrated by narrow PS standards, and a Waters 410 RI detector. THF was used as the fluent at a flow rate of 1 mL/min at 40°C. Transmission electron microscopy (TEM) measurement was conducted on a JEOL JEL2010 electron microscope. Scanning electron microscopy (SEM) was carried out with JEOL JSM-6390LV.

RESULTS AND DISCUSSION

Characterization of MWNTs-COOH

To compare the effect of oxidative treatments on the physical and chemical structures of MWNTs, the

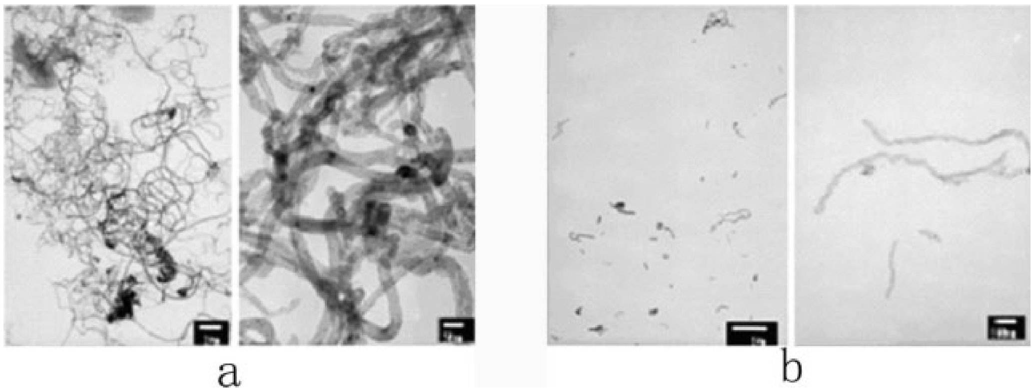


Figure 1 TEM micrographs of crude MWNTs (a) and acid-treated MWNTs (b).

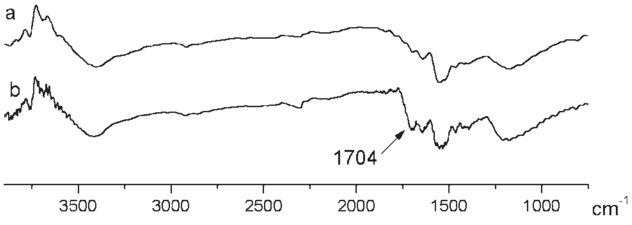


Figure 2 FTIR spectra of crude MWNTs (a) and MWNTs-COOH (b).

microstructures of crude, acids-treated MWNTs were examined by TEM. The TEM images of crude and modified MWNTs are shown in Figure 1. Under TEM magnification, we observed that all crude MWNTs were very long and entangled together due to allogation, and there were some amphorous graphite impurities [Fig. 1(a)]. After oxidizing by mixture acid for 2 h, MWNTs were cut off at different lengths and the individual tubes were separated from each other. The MWNTs wall was relatively smooth and clean [Fig. 1(b)].

After treatment with acid, MWNTs was functionalized with carboxylic groups at the open ends and at defects of the side walls. The FTIR spectrum (Fig. 2) clearly showed that the characteristic carboxyl group stretching vibrations appeared at 1704 cm^{-1} and that the crude MWNTs had no distinct absorption peaks close to 1700 cm^{-1}.

TGA measurements [Fig. 3(a)] showed that MWNTs were very stable. Even at 750°C, pure MWNTs had very little weight loss, which was mainly derived from the impurity remaining in the original MWNTs. After treatment with the acids, the weight loss increased to 6.5% below 350°C [Fig. 3(b)], which was ascribed to the COOH groups on the MWNTs surface. Nevertheless, a continuous weight loss was observed with further heating due to the defects resulting from the treatment with the strong acid. Based on the TGA data, it was estimated that there was one carboxyl group per 55 carbon atoms.

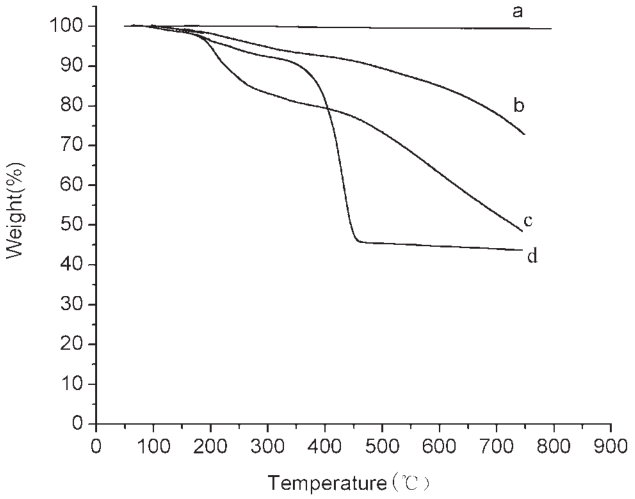


Figure 3 TGA thermograms of crude MWNTs (a), MWNTs-COOH (b), MWNTs-TEMPO (c), and MWNT-*g*-PS (d) under nitrogen.

TABLE I
Element Analysis of MWNTs by SEM

Sample	Element	Percent by Weight	Percent by Atom
MWNTs	O	0.13	0.10
	C	99.64	99.84
MWNTs-COOH	O	5.26	4.02
	C	94.23	95.89

Once more, according to the results of element analysis from SEM, we found the exact content of oxygen. The details are shown in Table I. It was clear that the content of oxygen was very small before treatment with acids. After oxidation, the content of oxygen was dramatically increased due to the carboxyl groups on the surface of the MWNTs. It was estimated that the density of the carboxyl group was one per 49 carbon atoms on the surface of MWNTs, which was consistent with the TGA results.

Characterization of MWNTs-TEMPO

TEMPO-functionalized MWNTs were prepared through esterification between HO-TEMPO and carboxyl groups on the MWNTs surface, as outlined in Scheme 1. Because of the paramagnetism of the TEMPO radicals, the ^{1}H-NMR was carried out in deuterated methanol in the presence of stoichiometric $HCOONH_4$ and catalytic Pd/C; the TEMPO radicals on the MWNTs were reduced to corresponding oximes, and ^{1}H-NMR spectra were then performed. The ^{1}H-NMR spectrum of MWNTs-TEMPO is shown in Figure 4, the inherent peaks of TEMPO at 1.21 ppm (—CH_3), 1.50 ppm, 1.84 ppm (—CH_2—), and 3.95 ppm (—CH—) confirmed the existence of TEMPO groups

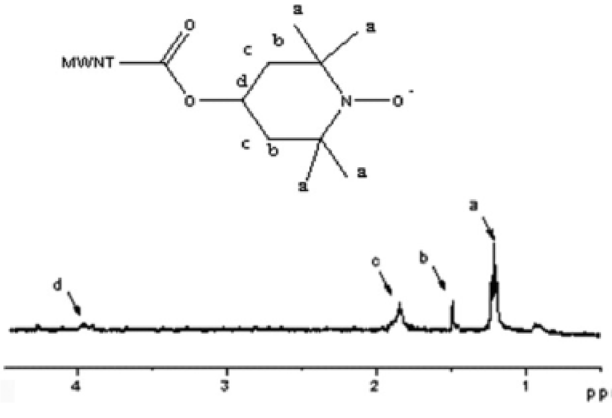


Figure 4 1H-NMR spectrum of MWNTs-TEMPO.

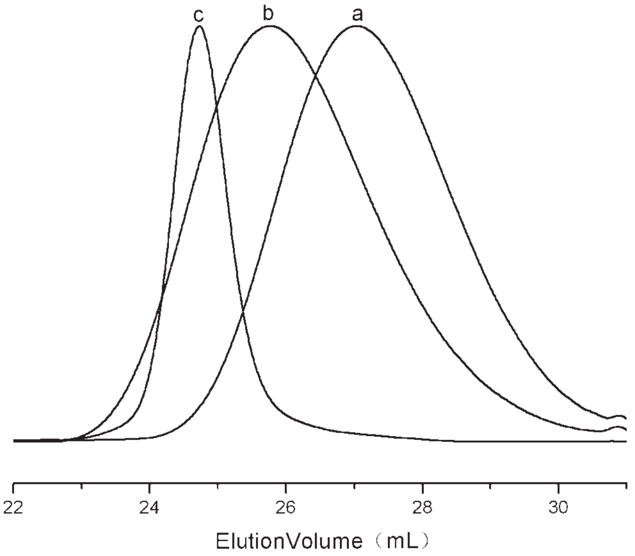


Figure 5 SEC traces of halogen-containing PS-Br (Table II).

on the surface of the MWNTs. Very weak signals can be found for MWNTs-TEMPO in the spectra, which may be attributed to the fact that the chain of small molecules attached on the MWNTs is short.

TGA measurements [Fig. 3(c)] showed that weight loss of MWNTs-TEMPO is about 16%, from 150 to 350°C, which is higher than that of MWNTs-COOH, which is ascribed to the weight gain (about 9.5%) from the introduced TEMPO groups on MWNTs surface. It could be estimated that the density of TEMPO was that there was one per 110 carbon atoms on the surface of MWNTs. Judging by a combination of TGA and ^{1}H-NMR results, we can say that the TEMPO groups were covalently anchored to the MWNTs.

Synthesis and characterization of PS-Br

ATRP is a versatile tool for the preparation of well-defined (co)polymers with predesigned molecular weight and narrow molecular weight distribution.[40–42] Herein, EBiB was used as initiator to synthesize PS with a bromine-ended group.

Three different polymerization conditions were conducted to prepare PS-Br chains. The SEC traces of these PS-Br are illustrated in Figure 5, in which all traces of PS-Br were accorded with a Gaussian distribution. All the details are listed in Table II. It was observed that the molecular weight distribution of sample c (1.06) prepared in the presence of PMDETA is much lower than those of sample a (1.44) and sample b (1.49), which were synthesized when bpy was used as the ligand. Moreover, with the same polymerization time, the molecular weight of sample c is about twice of that of sample b, which might be attributed to different catalysts used in polymerization. When bpy was used as the ligand, the transfer speed with the bromine atom at the end of PS was very fast, whereas with PMDETA as the ligand, the homologous transfer speed decreased and it was easy to get the polymer with a narrow molecule distribution. Based on these results, the PMDETA polymerization system was chosen to prepare PS-Br chains for the following radical coupling reaction.

TABLE II
Polymerization Condition and Characterization of PS-Br by ATRP

Sample	bpy (g)	PMDETA (mL)	St (mL)	Time (h)	M_n (g/mol)	M_w/M_n
a	0.209	–	12	2	2400	1.44
b	0.209	–	12	4	4300	1.49
c	–	0.28	7.6	4	10,200	1.06

Figure 6(a) shows the ^{1}H-NMR spectrum of PS-Br. There were two main regions. The resonances for the methylene and methane groups of PS occur at 1.25–2.25 ppm, and the resonances for the aromatic protons of PS occur in the region of 6.33–7.25 ppm. In addition, the methine resonance for the unique —C*H*(Ph)-Br functional group was observed at 4.41 ppm. The methyl and methylene resonances for the CH_3CH_2O—, —C(CH_3)2—), and CH_3CH_2O— groups from EBiB occur at 0.84, 0.95–1.10, and 3.45–3.65 ppm, respectively.

Coupling reaction between PS-Br and MWNTs-TEMPO

The whole coupling process using PS-Br as sample is described in Scheme 1. TEMPO is a radical scavenger in that it couples with carbon-centered radicals at diffusion-limited reaction rates. The reversibility of the reaction renders TEMPO an efficient mediator in

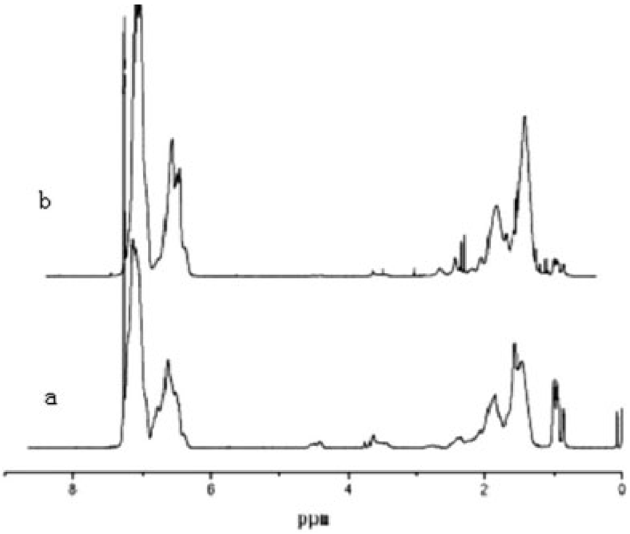


Figure 6 ^{1}H-NMR spectrum of PS-Br (a) and MWNT-g-PS (b) in $CDCl_3$.

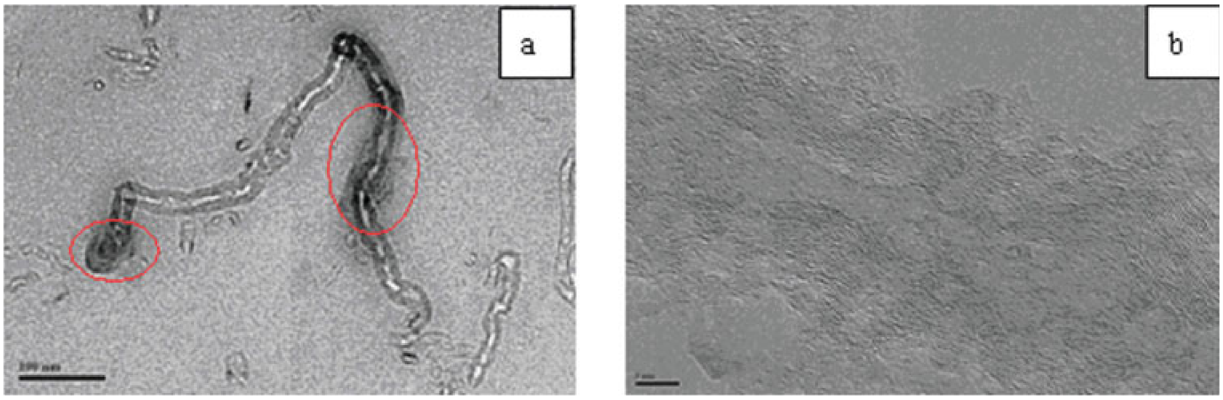


Figure 7 TEM images of MWNTs-*g*-PS (scale bar: a, 100 nm; b, 5 nm). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

controlled/"living" radical polymerization. Although the mobility of TEMPO would be reduced after attachment to MWNTs, it still is expected to have high capability to trap PS radicals to generate the final MWNTs-*g*-PS composite. When the mixture of PS-Br and MWNTs-TEMPO with TEMPO groups was heated to 90°C in the presence of CuBr/PMDETA, the bromine atoms at PS-Br chain ends serving as oxidant were reduced to bromine anions, and secondary carbon radicals of PS were then formed; CuBr was served as reductant, the Cu^{1+} was oxygenated to Cu^{2+}, and the $CuBr_2$ was formed. The macroradicals of PS were trapped by the nitroxide radicals of TEMPO groups on MWNTs to form the alkoxyamine shown in Scheme 1.[43,44]

Figure 6(b) presents the ^{1}H-NMR spectra of MWNTs-*g*-PS. Compared with Figure 6(a) of the PS-Br, the original resonance observed in the region 4.4–4.5 ppm for methine protons of -C*H*(Ph)-Br functional group disappeared. The resonances for aromatic ring of PS at 6.45–7.25 ppm and for methine or methylene groups of main chains at 3.48–3.64 ppm were observed. We concluded that the coupling reaction was successfully carried out.

The graft ratio, defined as the weight percent of the grafted polymer with respect to the nanotubes, was determined by TGA [Fig. 3(d)]. The onset of the decomposition temperature (T_d) of the PS moieties in MWNTs-*g*-PS approached 330–440°C. The quantity of the polymer shell calculated from the TGA data was about 46.7%. According to these TGA data, the graft density of PS is calculated to be one PS chain per 972 carbon atoms on the surface of MWNTs.

The grafted polymer content on the MWNTs in our system is much higher compared with Fan's work (30.7%)[25] and Lou's report (30%)[26] using nitroxide radical chemistry. Such a "grafting onto" approach through atom transfer nitroxide radical coupling reaction provides us a promising way to generate high-density, well-defined polymer-wrapped MWNTs.

Further measurements of TEM give the most direct evidence for functionalization of MWNTs with PS. The TEM images of the functionalized MWNTs are shown in Figure 7. The average internal and external diameters of the crude nanotubes are about 5 and 10–20 nm (Fig. 1), respectively. The average length of the MWNTs is approximately several micrometers. For the samples of MWNTs-*g*-PS, in the lower amplification image [Fig. 7(a)], it can be found that some parts of the tubes are covered with a polymer layer; individual tubes separated from each other are found. This indicates that the thickness of the polymer layer coated on the MWNTs and the coupling reaction between PS-Br and MWNTs-TEMPO occur not only at the end but also on the whole convex surfaces; the polymer chains also can disperse the tubes well. In the high-resolution images [Fig. 7(b)], the polymer shell is vividly impinged on the outer wall along the tube. Clearly,

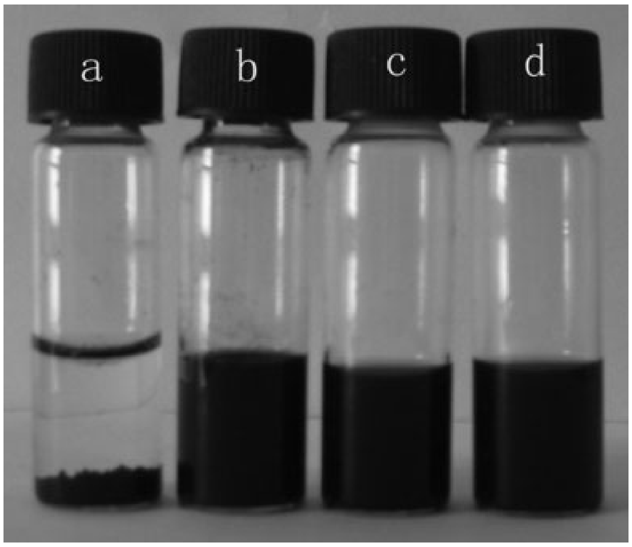


Figure 8 Photo of the crude MWNTs in CH2Cl2 (a) and MWNTs-g-PS in CH2Cl2 (b), THF (c), and toluene (d).

the TEM investigation provided more evidence for the successful synthesis of graft polymers by the coupling method.

Solubility of MWNTs-g-PS

The crude MWNTs could not be dissolved in regular solvents. However, after the PS chains were attached to the walls of the MWNTs, the MWNTs-*g*-PS showed a relatively good solubility in solvents that are good solvents for PS, including THF, CH_2Cl_2, and toluene. Figure 8 shows MWNTs-*g*-PS and crude MWNTs in some solvents, in which the homogeneous dispersion of MWNTs-*g*-PS is shown.

CONCLUSIONS

MWNTs-*g*-PS was successfully synthesized by means of a coupling reaction between bromine on the polymer chains and TEMPO groups attached on the MWNTs surface in the presence of CuBr. This approach was demonstrated to be efficient and facile and afforded another choice for preparation of polymers with different compositions and well-defined structures on MWNTs.

The authors thank Prof. Junlian Huang of the Key Laboratory of Molecular Engineering of Polymer of Fudan University for helpful discussions.

References

1. Wong, E. W.; Sheehan, P. E.; Lierber, C. M. Science 1997, 277, 1971.
2. Iijima, S. Nature 1991, 354, 56.
3. Kuo, C. S.; Tseng, Y. H.; Lin, H. Y.; et al. Nanotechnology 2007, 18, 465607.
4. Dyke, C. A.; Stewart, M. P.; Tour, J. M. J Am Chem Soc 2005, 127, 4497.
5. Moulton, S. E.; Minett, A. I.; Murphy, R.; Ryan, K. P.; McCarthy, D.; Coleman, J. N.; Blau, W. J.; Wallace, G. G. Carbon 2005, 43, 1879.
6. Carrillo, A.; Swartz, J. A.; Gamba, J. M.; Kane, R. S. Nano Lett 2003, 3, 1437.
7. Besteman, K.; Lee, J. O.; Wiertz, F. G. M.; Heering, H. A.; Dekker, C. Nano Lett 2003, 3, 727.
8. Rege, K.; Raravikar, N. R.; Kim, D. Y.; Schadler, L. S.; Ajayan, P. M.; Dordick, J. S. Nano Lett 2003, 3, 829.
9. Han, J. H.; Choi, J. H.; Oh, S. B.; Jang, J. H.; Han, J. H.; An, S. S. A.; Kim, H. K.; Kim, B. G.; Paik, H. J. Compos Interfaces 2006, 13, 321.
10. Li, S. Y.; Chen, H.; Bi, W. G.; Zhou, J. J.; Wang, Y. H.; Li, J. Z.; Cheng, W. X.; Li, M. Y.; Li, L.; Tang, T. J Polym Sci Part A: Polym Chem 2007, 45, 5459.
11. Yang, B. X.; Pramoda, K. P.; Xu, G. Q.; Goh, S. H. Adv Funct Mater 2007, 17, 2062.
12. Wang, S. R.; Liang, R.; Wang, B.; Zhang, C. Nanotechnology 2008, 19, 5710.
13. Tseng, C. H.; Wang, C. C.; Chen, C. Y. Chem Mater 2007, 19, 308.
14. Huang, W.; Taylor, S.; Fu, K.; Lin, Y.; Zhang, D.; Hanks, T. W.; Rao, A. M.; Sun, Y. P. Nano Lett 2002, 2, 311.
15. Rati, R. J.; Shanmugharaj, A. M.; Ryu, S. H. Macromol Chem Phys 2008, 209, 1137.
16. Qin, S.; Qin, D.; Ford, W. T.; Resasco, D. E.; Herrera, J. E. Macromolecules 2004, 37, 752.
17. Lin, Y.; Zhou, B.; Shiral Fernando, K. A.; Liu, P.; Allard, L. F.; Sun, Y. P. Macromolecules 2003, 36, 7199.
18. Hill, D. E.; Lin, Y.; Rao, A. M.; Allard, L. F.; Sun, Y. P. Macromolecules 2002, 35, 9466.
19. Fu, K.; Kitaygorodskiy, A.; Rao, A. M.; Sun, Y. P. Nano Lett 2002, 2, 1165.
20. Zhao, B.; Hu, H.; Haddon, R. C. Adv Funct Mater 2004, 14, 71.
21. Wu, H. X.; Tong, R.; Qiu, X. Q.; Yang, H. F.; Lin, Y. H.; Cai, R. F.; Qian, S. X. Carbon 2007, 45, 152.
22. Gao, C.; Muthukrishnan, S.; Li, W. W.; Yuan, J. Y.; Xu, Y. Y.; Muller, A. H. E. Macromolecules 2007, 40, 1803.
23. Kong, H.; Gao, C.; Yan, D. Y. Macromolecules 2004, 37, 4022.
24. Qin, S. H.; Qin, D. Q.; Ford, W. T.; Resasco, D. E.; Herrera, J. E. J Am Chem Soc 2004, 126, 170.
25. Fan, D. Q.; He, J. P.; Tang, W.; Xu, J. T.; Yang, Y. L. Eur Polym J 2007, 43, 26.
26. Lou, X. D.; Detrembleur, C.; Pagnoulle, C.; Jerome, R.; Bocharova, V.; Kiriy, A.; Stamm, M. Adv Mater 2004, 16, 2123.
27. Guo, G. Q.; Yang, D.; Wang, C. C.; Yang, S. Macromolecules 2006, 39, 9035.
28. Viswanathan, G.; Chakrapani, N.; Yang, H.; Wei, B.; Chung, H.; Cho, K.; Ryu, C. Y.; Ajayan, P. M. J Am Chem Soc 2003, 125, 9258.
29. Liu, I.; Huang, H.; Chang, C.; Tsai, H.; Hsu, C.; Tsiang, R. C. Macromolecules 2004, 37, 283.
30. Wu, W.; Zhang, S.; Li, Y.; Li, J.; Liu, L.; Qin, Y.; Guo, Z.-X.; Dai, L.; Ye, C.; Zhu, D. Macromolecules 2003, 36, 6286.
31. Liu, Y. Q.; Adronov, A. Macromolecules 2004, 37, 4755.
32. Feng, J. T.; Cai, W.; Sui, J. H.; Li, Z. G.; Wan, J. Q.; Chakoli, A. N. Polymer 2008, 49, 4989.
33. Buffa, F.; Hu, H.; Resasco, D. E. Macromolecules 2005, 38, 8258.
34. Yao, Y.; Li, W. W.; Wang, S. B.; Yan, D. Y.; Chen, X. S. Macromol Rapid Commun 2006, 27, 2019.
35. Zeng, H. L.; Gao, C.; Yan, D. Y. Adv Funct Mater 2006, 16, 812.
36. Hong, C. Y.; You, Y. Z.; Pan, C. Y. Chem Mater 2005, 17, 2247.
37. Wang, G. J.; Huang, S. Z.; Wang, Y.; Liu, L.; Qiu, J.; Li, Y. Polymer 2007, 48, 728.
38. Xu, G. Y.; Wu, W. T.; Wang, Y. S.; Pang, W. M.; Wang, P. H.; Zhu, Q. R.; Lu, F. Nanotechnology 2006, 17, 2458.
39. Fu, Q.; Lin, W. C.; Huang, J. L. Macromolecules 2008, 41, 2381.
40. Teodorescu, M.; Gaynor, S. G.; Matyjaszewski, K. Macromolecules 2000, 33, 2335.
41. Matyjaszewski, K.; Shipp, D. A.; Wang, J. L.; Grimaud, T.; Patten, T. E. Macromolecules 1998, 31, 6836.
42. Matyjaszewski, K.; Woodworth, B. E.; Zhang, X.; Gaynor, S. G.; Metzner, Z. Macromolecules 1998, 31, 5955.
43. Wang, J. S.; Matyjaszewski, K. Macromolecules 1995, 28, 7901.
44. Peleshanko, S.; Gunawidjaja, R.; Petrash, S.; Tsukruk, V. V. Macromolecules 2006, 39, 4756.