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Synthesis of water-soluble single-walled carbon nanotubes by RAFT polymerization

Guo-Jian Wang, Si-Zhe Huang*, Yao Wang, Lin Liu, Jun Qiu, Yan Li

School of Materials Science and Engineering, Tongji University, No. 1239, Siping Road, Shanghai 200092, PR China

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Abstract

Water-soluble single-walled carbon nanotubes (SWNTs) were synthesized by grafting poly(acrylamide) (PAM) from the surface of SWNT via reversible addition–fragmentation chain transfer (RAFT) polymerization. The RAFT agents were covalently attached to the SWNTs by functionalizing SWNTs with in situ generated diazonium compounds. The product was characterized by means of FT-IR, Raman, ^{1}H NMR, TGA and TEM. The results showed that PAM chains had successfully grafted from SWNT by RAFT polymerization. The amount of PAM grown from SWNT increased with the polymerization time. The acrylamide conversion increased linearly with the polymerization time, indicating the "living" characteristics of the RAFT polymerization. TEM was utilized to image PAM-*g*-SWNT, showing relatively uniform polymer coatings present on the surface of individual, debundled nanotubes.

Keywords: Single-walled carbon nanotubes; Water soluble; Reversible addition–fragmentation chain transfer (RAFT)

1. Introduction

Single-walled carbon nanotubes (SWNTs) have received special attention because of their possible technological applications in various fields of science, such as sensors [1], molecular electronics [2], field emission displays [3], and components of high-performance composites [4]. Recently, significant progress has been made in both their manipulation and chemical functionalization [5–9]. However, due to their inherent insolubility in aqueous solvents, the potential applications in biology and material science have not been fully exploited. Therefore, recent studies have demonstrated great interest in preparing water-soluble SWNTs [10–14]. It is reported that some polymers have been used to prepare water-soluble SWNTs in several ways [15,16]. However, the exploration in this field is not so satisfying, partially due to the difficulty in growing water-soluble, functional polymer chains from SWNTs.

Currently, covalent polymer–SWNT conjugates can be synthesized by either "grafting from" or "grafting to" techniques. "Grafting from" mechanism promises high graft densities, but attachment of initiator groups to SWNTs and control over polymer molecular weight and architecture can be difficult to achieve [17–19]. Conversely, the "grafting to" mechanism allows full control over polymer molecular weight and architecture, but it suffers from low theoretical polymer loadings due to steric repulsion between grafted and reacting polymer chains [20–23]. This problem was solved by controlled/living radical polymerization (CRP) [24]. These methods involve immobilizing radicals onto the surface of carbon nanotubes followed by CRP initiated by these radicals. Theoretically, these methods belong to "grafting from" technique, but their inherent character makes controlling over polymer molecular weight and architecture possible.

It has been reported that water-soluble multi-walled carbon nanotubes can be produced by RAFT (reversible addition–fragmentation chain transfer) polymerization [15], one of the most versatile methods of CRP [25–31]. However, to our knowledge, there is no general method reported to graft water-soluble

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* Corresponding author. Tel.: +86 21 65980593; fax: +86 21 65980009.
E-mail address: juehsz@hotmail.com (S.-Z. Huang).

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polymer chains from SWNTs by RAFT polymerization. We have explored a new process to graft water-soluble polymer chains from SWNTs by RAFT polymerization. It involves immobilizing RAFT agents on SWNTs with in situ generated diazonium compounds [32] and growing water-soluble polymer chains from these RAFT agents.

2. Experimental procedures

2.1. Materials

The SWNTs were provided by Chengdu Organic Chemicals Institute, Chinese Academy of Sciences; the purity is higher than 90%. 4-Bromoaniline and (1-bromoethyl)benzene were purchased from Aldrich and used as received. All other reagents and solvents were purchased from Shanghai Chemical Reagent Company and purified before use.

2.2. Synthesis of SWNT–PhBr

A typical experiment was given as follows: 50 mg of SWNTs was dispersed in 50 mL of oleum (20% free SO_3) with magnetic stirring (3 h). Sodium nitrite (1.16 g, 16.8 mmol) was added followed by 2.89 g of 4-bromoaniline (16.8 mmol) and 0.14 g of azobisisobutyronitrile (AIBN, 0.84 mmol). The mixture was magnetically stirred at 80 °C for 1 h and then carefully poured into distilled water, and the suspension was vacuum filtered through a 0.22-μm millipore polycarbonate membrane. The filter cake was washed with distilled water and acetone and then dried under vacuum at 40 °C for 24 h.

2.3. Synthesis of RAFT agent (SWNT–PhCS(S)C(C)Ph)

In a typical experiment, 50 mg of SWNT–PhBr and 0.4 g of magnesium turnings were added to 50 mL of dry tetrahydrofuran. The mixture was magnetically stirred at 40 °C in a nitrogen flow for 30 min, then carbon disulfide was added over 10 min and the reaction system was kept for 1 h. After that, 3.1 g of (1-bromoethyl)benzene was added to the resultant mixture and the reaction temperature was kept at 70 °C for 60 h. The product was vacuum filtered through a 0.2-μm poly(tetrafluoroethylene) (PTFE) membrane, and the filter cake was washed with distilled water for five times then washed with ether for five times. The obtained RAFT agent containing SWNT (SWNT–PhCS(S)C(C)Ph) was dried under vacuum at 25 °C for 48 h.

2.4. Water-soluble polymer growing from SWNT–PhCS(S)C(C)Ph

In this experiment, acrylamide (AM) was chosen to prepare polyacrylamide (PAM) as the water-soluble polymer. A typical experiment was as follows: SWNT–PhCS(S)C(C)Ph (50 mg), AM (1 g), and AIBN (12 mg) were added into a polymerization tube in the presence of benzene (5 mL). Then the tube was sealed under vacuum. The mixture was magnetically stirred at 60 °C for scheduled hours. The reaction mixture was dispersed in 400 mL of distilled water, and filtered through a 0.2-μm PTFE membrane. The resultant solid was washed with distilled water for five times and then dried under vacuum at 25 °C for 24 h.

2.5. Characterization

Fourier transform infrared (FT-IR) spectra were recorded using a Bruker EQUINOXSS spectrometer with a disc of KBr. Transmission electron microscopy (TEM) analyses were performed on a Hitachi H800 electron microscope at 200 kV. Raman spectra were recorded on a LabRam-1B Raman spectroscope excited at 632.8 nm. Thermal gravimetric analysis (TGA) was conducted on a STA449C thermal analysis instrument at a heating rate of 20 °C/min in a nitrogen flow. Light transmittances were analyzed on a 721 spectrometer. Elemental measurements were measured by VARIOEL elemental measurements instrument (Element Company, Germany). The content of Mg was measured by a Bruker SRS3400X X-ray fluorescence spectrometer. ^1H NMR spectra were analyzed on a Varian MERCURY-400 NMR spectrometer with D_2O as a solvent.

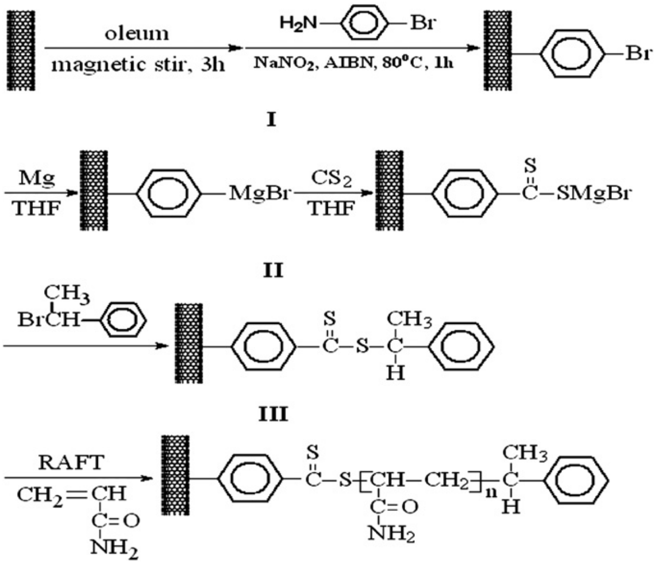
3. Results and discussion

3.1. Synthesis of RAFT agent containing SWNT

For the polymerization with RAFT agent (S=C(Z)S–R), it has been reported that the polydispersity and molecular weight obtained under a particular set of reaction conditions depend on the nature of the groups Z and R [33]. Z is a group that modifies the reactivity of the C=S bond and the derived adduct radical, whereas R is a leaving group. The radical $R^\bullet$ generated from group R must efficiently reinitiate polymerization to give chain transfer. In this experiment, (1-substituted ethyl)benzene was selected as a homolytic leaving group R, which makes the RAFT polymerization more active than using groups containing SWNT as the leaving group. For (meth)acrylate or styrene monomers, dithiobenzoate is an effective RAFT agent for controlled/living radical polymerization. Scheme 1 shows the process of RAFT agent immobilizing to SWNT and PAM chain growing from SWNT via RAFT polymerization.

Because the yield of reactions was not 100% and the resulting product was a mixture. Thus, the yield of reactions can be obtained by elemental measurements. Table 1 shows the results of elemental measurements. From those results, it can be concluded that the yield of reactions from SWNT–PhBr to SWNT–PhCS(S)MgBr was 74.6%, and the yield of reaction process III was 83.0%.

Fig. 1 shows the Raman spectrum of the pristine SWNTs and SWNT–PhCS(S)C(C)Ph, and characteristic absorptions at ca. 190–260 and 1550–1590 cm^{-1} are corresponding to the radial breathing modes and the tangential G mode of the SWNTs, respectively. The overall intensity of the scattered light of the SWNT–PhCS(S)C(C)Ph is lower than that of SWNTs. However, the intensity of the disorder mode (1320 cm^{-1}) of the SWNT–PhCS(S)C(C)Ph increased significantly. It indicates the increase of sp^3-hybridized carbons in the SWNTs'



Scheme 1. Process of RAFT agent immobilizing to SWNT and PAM chain growing from SWNT via RAFT polymerization.

framework, which shows that the structure of SWNTs has been changed and covalent attachment to the SWNTs has been generated. The increased intensity of the disorder mode also can be taken as a crude measure of the degree of functionalization. The FT-IR spectrum of SWNT–PhCS(S)C(C)Ph (Fig. 2) shows the characteristic absorptions of group –PhCS(S)C(C)Ph, such as C–H at 2925 and 2847 cm^{-1}, C=S at 1637 cm^{-1}, C–S at 1127 cm^{-1}, and C–H on the benzene ring at 562 cm^{-1}. Together with the results from Raman spectrum, these results indicate that the RAFT agents are covalently attached to the SWNT.

Elemental measurements and TGA were utilized to indicate the amount of functional group –PhCS(S)C(C)Ph immobilized on the surface of SWNTs. As shown in Table 2, the elemental measurements result shows that the weight content of element sulfur in SWNT–PhCS(S)C(C)Ph is 5.6%, which can be concluded that there are about 2 sulfur atoms per 72 carbon atoms in SWNT–PhCS(S)C(C)Ph. The TGA shows that the weight content of the RAFT agent on the SWNT is 23.1%, which can be concluded that there are about 2 sulfur atoms per 70 carbon atoms in SWNT–PhCS(S)C(C)Ph. These two results are very similar.

3.2. Growth of PAM from SWNT by RAFT polymerization

Previous studies showed that RAFT polymerization could be employed to graft polymer chains from the solid surface and microsphere surface with a controlled behavior [34,35]. In this experiment, polyacrylamide chains were grafted from SWNT via the RAFT polymerization in the presence of

Table 1
Relative weight content of atoms in the products

	Relative weight content (%)		
	Br	Mg	S
Products from process I	12.1	–	–
Products from process II	10.8	3.0	6.4
Products from process III	4.1	0.5	5.6

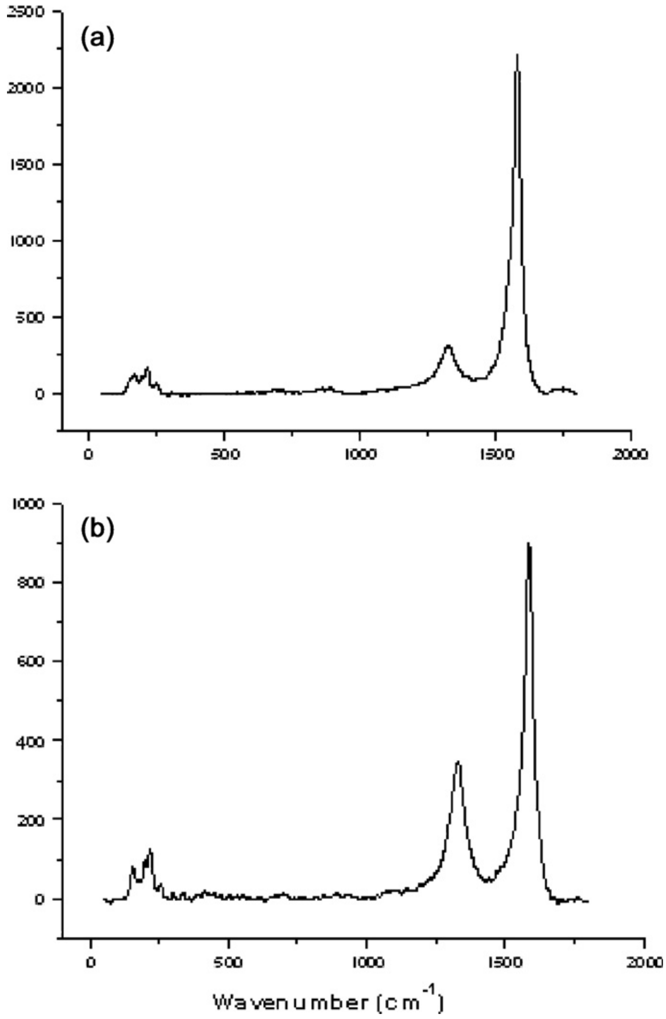


Fig. 1. Raman spectrum of (a) pristine SWNTs and (b) SWNT–PhCS(S)C(C)Ph.

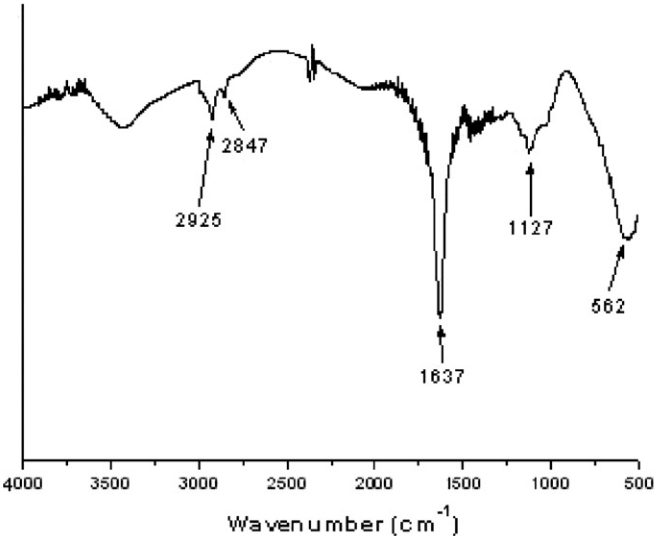


Fig. 2. FT-IR spectrum of SWNT–PhCS(S)C(C)Ph.

Table 2
TGA and elemental measurement results of SWNT–PhCS(S)C(C)Ph

Weight loss (TGA)	Weight content of element sulfur
23.1%	5.6%

RAFT agents containing SWNT. As a kind of CRP, in a typical RAFT polymerization, the monomer conversion increases linearly with the polymerization time. Thus, a series of reaction time was investigated in order to obtain PAM-*g*-SWNT with different acrylamide conversion.

The structure of the PAM-*g*-SWNT was analyzed by FT-IR and the results are shown in Fig. 3. The characteristic absorption peaks of PAM, such as N–H at 3433 cm^{-1}, C=O at 1641 cm^{-1}, –CH–CO– at 1450 cm^{-1}, and C–H at 1101 cm^{-1} can be found in Fig. 3. Meanwhile, the characteristic absorptions of SWNT–PhCS(S)C(C)Ph, such as C–H at 2925 and 2847 cm^{-1}, C=S at 1641 cm^{-1} can also be found. This indicates that PAM chains have been successfully grafted from SWNT via RAFT polymerization. The chemical structure of PAM-*g*-SWNT was also determined by ^{1}H NMR (Fig. 4). In the ^{1}H NMR spectrum, the characteristic peaks of PAM, such as the peak at $\delta = 1.5-2.1$ ppm ascribed to methine and methylene protons in the main chain of PAM. Moreover, some small peaks originating from RAFT agent functions on SWNT, such as peaks at $\delta = 7.2-8.0$ ppm ascribed to benzene ring protons, can also be found in this ^{1}H NMR spectrum, indicating that the RAFT agents on SWNT participated in the polymerization of PAM. For comparison, the ^{1}H NMR of PAM was also recorded (Fig. 5). Different from the ^{1}H NMR spectrum of PAM-*g*-SWNT, there was no peak originating from RAFT agent functions on SWNT except the characteristic peaks of PAM.

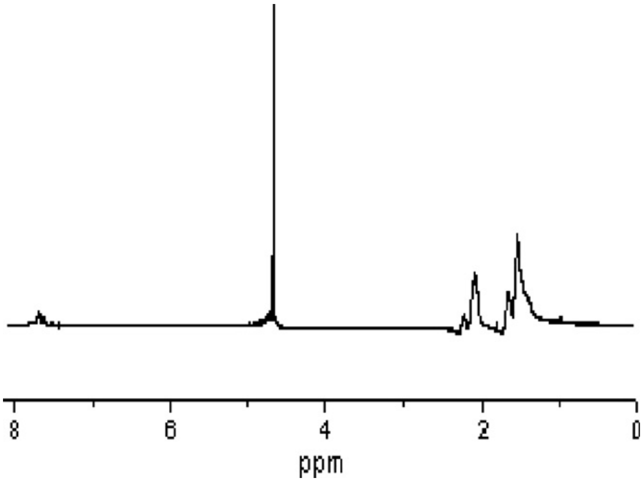


Fig. 4. ^{1}H NMR spectrum of PAM-*g*-SWNT.

TGA analysis was employed to determine the relative amounts of PAM and RAFT agent functions on SWNT compared with that of SWNT. It can also determine the acrylamide conversion. As polymerization time increases from 12 to 50 h, the amount of PAM attached to SWNT determined by TGA varies from 46.3% to 77.9% (as shown in Fig. 6).The amount

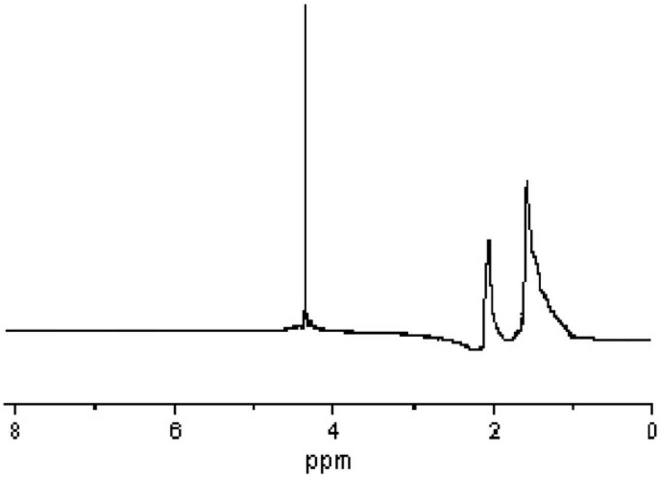


Fig. 5. ^{1}H NMR spectrum of PAM.

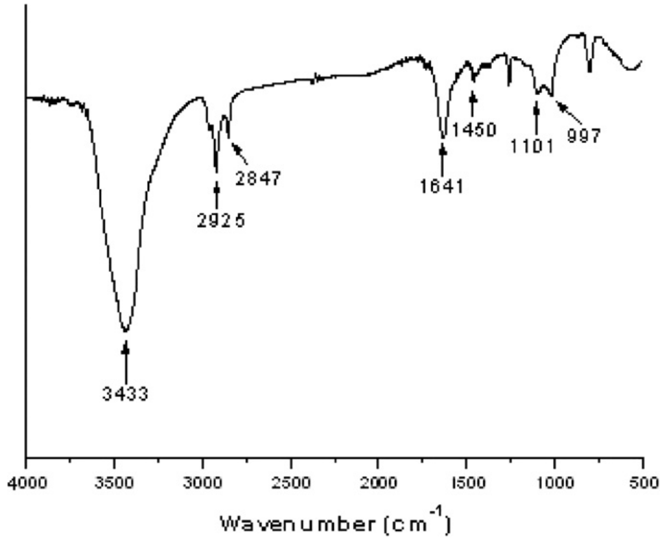


Fig. 3. FT-IR spectrum of PAM-*g*-SWNT.

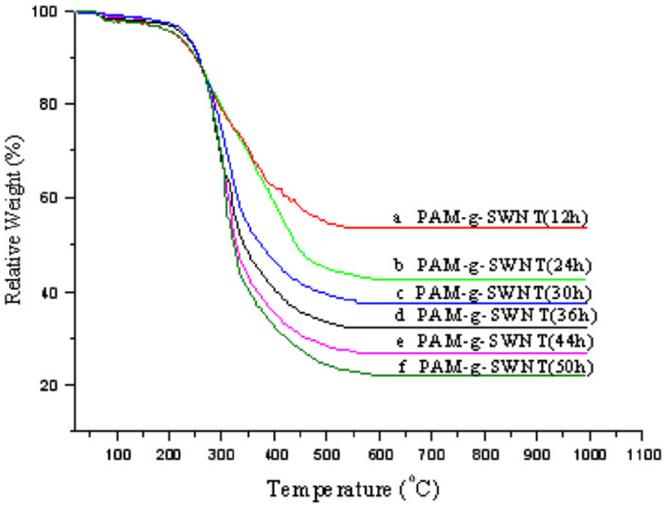


Fig. 6. TGA curves of PAM-*g*-SWNT at different polymerization time.

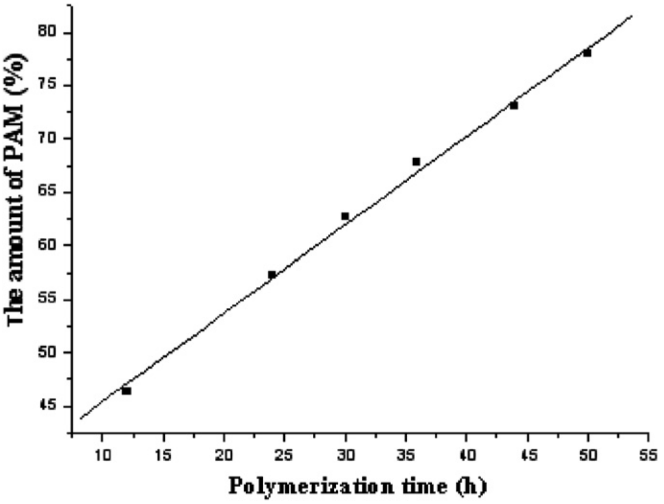


Fig. 7. Relationship between the amount of PAM and polymerization time.

of PAM versus polymerization time curve was plotted (as shown in Fig. 7). The amount of PAM exhibited a linear increase with increasing polymerization time, indicating that the acrylamide conversion increased linearly with the polymerization time.

TEM was utilized to image the pristine SWNTs and PAM-*g*-SWNT and the results are shown in Fig. 8. It is clear that PAM-*g*-SWNT is dispersed individually while the pristine SWNTs are piled up. A high quantity of the grafted polymer exists on the surface of the SWNTs (Fig. 8b). The results show that PAM can be grafted from SWNT and SWNTs can be separated into individual tubes by RAFT polymerization.

The solubility of PAM-*g*-SWNT in aqueous solution was also tested. Dispersion of SWNTs in water is very difficult. Ten milligrams of SWNTs in 4 mL of distilled water was sonicated, but sedimentation appeared after a few minutes (as shown in Fig. 9A). However, PAM-*g*-SWNT was soluble in water. PAM-*g*-SWNT (20 mg) dispersed in 4 mL of distilled water was prepared by sonication for 5 min, and no tube precipitation was observed from this solution even after two weeks. All of the results proved that PAM-*g*-SWNT synthesized by RAFT polymerization enhanced the solubility of SWNTs in water. Light transmittance analysis was also employed to test the solubility of SWNTs and PAM-*g*-SWNT in water. One milligram of each sample was added into a tube with 20 mL of distilled water and was sonicated for 10 min, and then the tubes were held still for 48 h. After that, light transmittances of the solutions from the top of the tubes were tested, and the results are shown in Table 3. The results show that the solubility of PAM-*g*-SWNT is much better than SWNTs, and the solubility of PAM-*g*-SWNT is increased with polymerization time at the beginning and then kept the same.

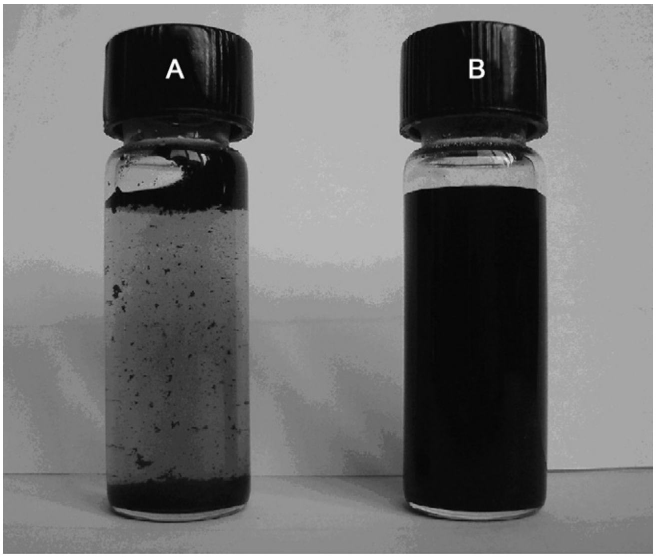


Fig. 9. SWNTs (A) and PAM-*g*-SWNT (B) in water.

Table 3
Transmittance of water with dispersed SWNT

Sample	Transmittance (%)
SWNTs	100
PAM-*g*-SWNT (12 h)	12
PAM-*g*-SWNT (24 h)	9
PAM-*g*-SWNT (30 h)	8
PAM-*g*-SWNT (36 h)	8
PAM-*g*-SWNT (44 h)	8
PAM-*g*-SWNT (50 h)	8

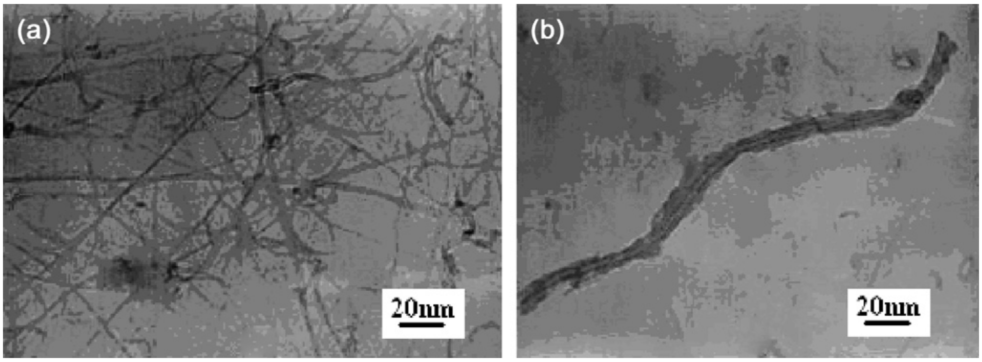


Fig. 8. TEM images of pristine SWNTs (a) and PAM-*g*-SWNT (b).

4. Conclusions

SWNTs have been successfully grafted with PAM via RAFT polymerization. RAFT agents were fixed on SWNTs with in situ generated diazonium compounds, and then the PAM chains grew from these RAFT agents. The polymer chains were covalently attached to the SWNTs. The grafted polymer content can be controlled by adjusting the polymerization time, because the polymer content has linear relationship with the polymerization time. SWNTs grafted with PAM have good solubility in water. This new approach to prepare water-soluble SWNTs represents a significant advance compared to traditional approaches. Further more, this approach can be extended to other polymers to obtain functionalized SWNTs. Currently, we are extending this approach to accomplish water-soluble SWNTs with other polymers.

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