"Fishing" Polymer Brushes on Single-Walled Carbon Nanotubes by in-Situ Free Radical Polymerization in a Poor Solvent

Guiquan Guo,[†] Dong Yang,[†] Changchun Wang,*,[†] and Shu Yang[‡]

Key Laboratory of Molecular Engineering of Polymers and Department of Macromolecular Science, Fudan University, Shanghai 200433, China, and Department of Materials Science and Engineering, University of Pennsylvania, 3231 Walnut Street, Philadelphia, Pennsylvania 19104

ABSTRACT: Single-walled carbon nanotubes (SWNTs) exhibit unique thermal and electrical conductivity and high mechanical strength. The ability to effectively functionalize the SWNT surface and control their dispersion in a polymer matrix will be crucial to exploit their physical properties in nanocomposites. Here we report the first example of grafting polymers onto SWNTs in a poor solvent through a "fishing" process. The SWNTs act as "fishhooks", and the "living" polymer radicals are "fish", which are enthalpically favored to absorb onto the surface of SWNTs and continue to propagate until all the active sites are consumed. We demonstrate to graft 1 g of SWNTs with ~20 wt % poly(methyl methacrylate) in 100 mL of methanol/water (1/4 by volume) with monomer concentration as low as 5 mg/mL and monomer/SWNTs ratio of 0.5:1 by weight. The structure of functionalized SWNTs was characterized by Raman spectroscopy, UV−vis spectroscopy, HRTEM, and AFM. The polymer grafting method we described is fundamentally different from the reported approaches, where the polymerization takes place either solvent-free or in a good solvent but requires much higher monomer concentrations and monomer/SWNTs ratios. The promise of synthesizing gram-scale functionalized SWNTs from a wide range of polymers in a small volume of solvent may greatly improve our ability to engineer novel SWNT composites.

Introduction

Isolated single-walled carbon nanotubes (SWNTs) exhibit unique thermal, mechanical, and electrical properties and are of great interest in exploitation of their physical properties in nanocomposites for applications, including molecular electronics, sensors, field emission displays, and ultrahigh-strength materials.[1−3] However, the intertube attraction due to van der Waals interaction is very strong, ~40 $k_B T$/nm,[4,5] resulting in poor dispersion of SWNT in common organic solvents and polymeric matrices, which significantly hinders the high loadings of SWNTs in composites. To improve the dispersal of SWNTs in solvents or polymers with a sufficiently high concentration, various surface functionalization methods have been investigated, including physical bonding (e.g., coating SWNTs with surfactants) and chemical bonding. Although the physical bonding is simple and straightforward and has the advantage of maintaining the nanotube structure and its electronic properties, the choices of surfactants and polymers are rather limited. By covalent bonding, a wide range of chemical functionalities, including long alkyl chains, aromatic groups, hydrophilic and hydrophobic polymers, and biomolecules, can be readily attached to SWNTs either by direct radical reaction with SWNTs or via carboxylic groups,[6−11] which can be further functionalized through esterification or amidation to graft hydroxyl-terminated oligomers and polymers,[12−16] respectively.

Since high grafting density is necessary for high solubility of SWNTs, grafting high-molecular-weight polymer chains onto the surface of the SWNTs holds promise to improve the interfacial adhesion and the load transfer efficiency. This can be achieved through either "graft to" or "graft from" approach.[17] The "graft to" method involves chemical bonding of preformed,

[†] Fudan University.
[‡] University of Pennsylvania.
* Corresponding author: Fax 86-21-65640291, Tel 86-21-65642385, e-mail ccwang@fudan.edu.cn.

Table 1. Grafting Efficiency of PMMA on SWNTs Dependence on Reaction Time[a]

sample code	reaction time (h)	solubility in ethyl acetate (mg/mL)	grafting amount of PMMA,[b] wt %
PMMA-*g*-SWNTs-1	0.5	0.01	2.5
PMMA-*g*-SWNTs-2	1	0.15	19
PMMA-*g*-SWNTs-3	2	0.26	25
PMMA-*g*-SWNTs-4	3	0.28	23
PMMA-*g*-SWNTs-5	10	0.27	27

[a] Polymerization recipe: 5 g of MMA, 0.1 g of SWNTs, and 0.05 g of AIBN in 100 mL of methanol. Reaction temperature, $T = 60$ °C. [b] This result was according to TGA measurement. All samples were heated from 50 to 800 °C at a heating rate of 10 °C/min under nitrogen flow (20 mL/min).

end-functionalized polymers to a reactive surface. The "graft from" method involves immobilization of initiators on the substrate, followed by in-situ surface-initiated polymerization to generate tethered polymer chains. It has been demonstrated to grow polymers up to 70 wt % from carbon nanotubes using a "graft from" strategy.[18−20] This is in sharp contrast to the considerably lower level (<15 wt %) of polymers grafted on nanotubes using the "graft to" approach, especially in the case of a high-molecular-weight, end-functionalized polymers.[21] This is because the diffusion of long polymer chains to the available reactive sites could be sheltered by the existing brushes and the reaction is rather heterogeneous in the "graft to" approach.

Alternatively, a relatively high degree of functionalization, 20−30 wt % of organic molecules, has been achieved in a solvent-free system,[22] although partial deroping of the bundles is necessary before the reaction, for example by mechanical stirring. Qin et al.[23,24] have reported an effective method that grafts ~40 wt % of polymers on *as-prepared* SWNTs by in-situ radical polymerization in a good solvent of the polymers. It was proposed that propagating polymer radicals were covalently bound to SWNT bundles and the continued attachment of polymer chains deroped the pristine SWNTs to single tubes

Scheme 1. Illustration of a "Fishing" Process to Graft Polymer Radicals on SWNTs
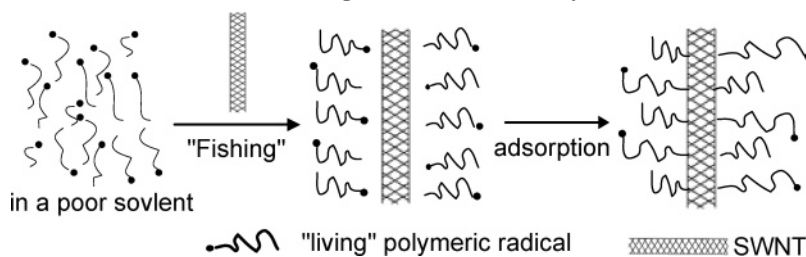
and smaller bundles to give a stable solution. Chen et al.[25] have recently reported irradiation-induced graft polymerization to functionalize multiwalled carbon nanotubes (MWNTs) in a good solvent. A small amount of Cu^{2+} was necessary to suppress the homopolymerization of poly(acrylic acid) in the solution, which in turn increased the grafting amount of PAA to ~20 wt %. Nevertheless, high monomer concentration (e.g., 67[23] and 142 mg/mL[24]), high monomer/CNTs ratios (typically 100:1[23]–200:1[24] g/g), and large volumes of solvent (~2 L/g) are necessary to produce a composite in milligram scale with appreciable amount of polymers.[6] It will be highly desirable to improve the load transfer of polymer radicals to the surface of nanotubes for a large-scale functionalization.

Here we report a completely new synthetic strategy that efficiently graft poly(methyl methacrylate) (PMMA) on SWNTs by in-situ free radical polymerization in a *poor* solvent of PMMA. This process is analogous to a "fishing" process; that is, during polymerization the "living" polymeric radicals ("fish") are expelled from the poor solvent and enthalpically favored to absorb to the surface of SWNTs ("fishhook"), which could further propagate to grow thicker films (see Scheme 1). We show that 1 g of SWNTs is effectively functionalized with ~20 wt % PMMA in 100 mL of methanol/water (1/4 by volume) with monomer concentration as low as 5 mg/mL and monomer/ SWNTs ratio of 0.5:1 by weight. The new approach is fundamentally different from the past grafting methods and applicable to a wide range of polymers. It appears particularly promising for mass production of SWNT–polymer nanocomposites for various applications.

Experimental Section

Materials. The SWNTs were purchased from Shenzhen Nanotech Port Co. Ltd., synthesized by the chemical vapor deposition method (purity ~80%, diameter <2 nm). Methyl methacrylate (purity ≥98%, MMA) was purchased from Shanghai Chemical Reagent Corp. and was distilled under vacuum. 2,2′-Azobis-(isobutyronitrile) (purity ≥98%, AIBN) was purchased from Shanghai Chemical Reagent Corp. and was recrystallized from ethanol. Methanol, ethyl acetate, toluene, acetone, and dimethyl-formamide (DMF) were purchased from Shanghai Chemical Reagent Corp.; all the above reagents (purity >99.5%) were used as received.

Functionalization of SWNTs. In a typical experiment, 2.0 g of methyl methacrylate (MMA) was added to a three-neck round-bottom reaction flask, which was charged with 100 mL of methanol and 0.1 g of SWNTs. After 10 min sonication, the solution was purged under dry nitrogen for 30 min to remove oxygen from the reaction flask, followed by addition of 0.05 g of free radical initiator, AIBN. The reaction was kept at 60 °C for 0.5–10 h to vary the graft amount of PMMA on SWNTs. The polymer-functionalized SWNTs, PMMA-*g*-SWNTs, were carefully washed by ethyl acetate in an ultrasonication bath (59 kHz) for five times to remove physically absorbed PMMA from SWNTs. The composite was dried in a vacuum oven at 40 °C for 16 h, and black powders were recovered for further characterization. The grafting amounts of

PMMA on SWNTs are from 2.5 to 27 wt % (see Table 1) according to TGA measurements.

Characterization. Raman spectra were taken on a Jobin Yon micro-Raman system (Lab Ram-1B, Instruments Dilorcom, France) using a He–Ne laser (Spectra-Physics) at excitation wavelength of 632.8 nm. UV–vis spectra of the dimethylformamide (DMF) solutions of the pristine SWNTs and the functionalized SWNTs were recorded on a Lambda 35 spectrophotometer using a quartz cuvette with 1 cm optical path length. DMF was used as reference. Weight loss of PMMA-*g*-SWNTs was measured by Pyris 1 TGA (Perkin-Elmer Instruments) using platinum pans to determine the grafting amount of polymers on SWNTs. The samples were heated from 50 to 800 °C at a heating rate of 10 °C/min under nitrogen flow (20 mL/min). The morphology of polymer grafted SWNTs was studied by scanning electron microscopy (SEM) on a Philips XL30 FEG and atomic force microscopy (AFM) on a Nanoscope IV (Digital Instruments/Veco Metrology Group). AFM images were obtained by contact mode with standard silicon nitride tips. High-resolution transmission electron microscopy (HR-TEM) images were recorded on a JEOL JEM2011 electron microscope operating at 200 kV. The samples were prepared by dispersing the PMMA-*g*-SWNTs in ethyl acetate and casting the solution onto a Cu grid, followed by solvent evaporation in air at room temperature.

Results and Discussion

Grafting SWNTs with Radical Polymerization of PMMA in Different Solvent Systems. Most reported grafting reactions in solution were carried out in a good solvent of the monomers/ polymers. Chen et al. have noticed the importance of suppression of the homopolymerization in solution to increase the grafting efficiency of polymer radicals onto the surface of MWNTs.[25] Since the adsorption of polymer radicals to the surface of nanotubes is diffusion-controlled and limited by entropy loss, we suspect that in a poor solvent the polymer radicals might have a prolonged lifetime to reach the active sites on SWNTs, and the polymer–nanotube interaction might be enthalpically favored when the entropy loss due to adsorption could be somehow reduced. Therefore, an increased grafting efficiency could be expected in poor solvent.

To test the hypothesis, we first performed the in-situ radical polymerization of MMA on as-prepared SWNTs in methanol, a poor solvent of PMMA, at variable reaction time. The reaction product was carefully washed by ethyl acetate five times until no detectable free polymer chains in solution. Since the absolute solubility of functionalized SWNTs in the solution can be influenced by the initial concentration of functionalized SWNTs and the undisturbed time,[26] we fixed the initial concentration of PMMA-*g*-SWNTs in ethyl acetate at 0.5 mg/mL. The solubility of functionalized SWNTs was measured after the solution sat still for 1 month at room temperature. The results are summarized in Table 1. The weight loss of PMMA-*g*-SWNTs measured by TGA and the solubility in ethyl acetate suggests that an appreciable amount of PMMA (up to 27 wt %) was successfully grafted on SWNTs, and the reaction approached completion after 3 h.

Table 2. Influence of Solvent Quality and Concentration of MMA on the Functionalization of SWNTs[a]

solvent	MMA/SWMTs (g/g)	solubility in ethyl acetate (mg/mL)	grafting amount of PMMA[b] (wt %)	solubility parameter, δ (cal/cm^3)$^{1/2}$
methanol	20:1	0.23	22	
	10:1	0.02	1.3	14.5
	5:1	0.03	1.8	
	2.5:1	≈0	0.5	
methanol/water (v/v = 1/4)	20:1	0.21	21	
	10:1	0.20	22	21.5
	5:1	0.17	20	
	2.5:1	≈0	1.5	
toluene	20:1	0.023	2.6	
	10:1	0.032	2.4	8.9
	5:1	≈0	≈3	
	2.5:1	≈0	1	

[a] Polymerization recipe: 0.1 g of SWNTs and 0.05 g of AIBN in 100 mL of solvent. The reaction condition is 60 °C for 8 h. [b] According to TGA measurement. All samples were heated from 50 to 800 °C at a heating rate of 10 °C/min under nitrogen flow (20 mL/min). Note: δ of PMMA is 9.5.

To the best of our knowledge, this is the first example of effectively grafting polymers on SWNTs in a poor solvent. To systematically study the influence of solvent quality on grafting efficiency, we conducted a series of experiments in three different solvents. The reaction time was kept for 8 h to ensure the completion of grafting. As seen from Table 2, more PMMA were grafted on SWNTs in its poor solvent than that in its good solvent. For example, when MMA concentration is 20 mg/mL (i.e., MMA/SWMTs = 20:1 g/g), the grafting amount of PMMA on SWNTs is ~22 wt % in methanol and ~21 wt % in the methanol/water mixture (v/v = 1/4), in contrast to 2.6 wt % in toluene. It seems clear that poor solvent promotes the adsorption of PMMA on SWNTs. Another interesting result is that when MMA concentration in methanol was lowered to 10 mg/mL (MMA/SWMTs = 10:1 g/g), the grafting amount of PMMA was substantially decreased to 1.3 wt %; however, the grafting amount of PMMA in methanol/water mixture remained high, ~20 wt %, even at a lower MMA/SWMTs ratio, 5:1 g/g. The large difference in grafting efficiency might again be attributed to the solvent quality. The excess free energy of mixing $\Delta G^E \propto (\delta_{solvent} - \delta_{polymer})^2$, where $\delta_{solvent}$ and $\delta_{polymer}$ are the solubility parameters of solvent and polymer, respectively. At low monomer concentration, the difference of solubility parameters between methanol (14.5) and PMMA (9.5) (see Table 2) is not large enough that methanol becomes a good solvent of short PMMA chains, thus dramatically decreasing the grafting efficiency. In contrast, the difference of solubility parameters between methanol/water (21.5) and PMMA (9.5) is large; thus, the methanol/water mixture remains to be a poor solvent of PMMA. When MMA concentration is lowered to <2.5 mg/mL, the grafting amount decreases <2 wt % for all solvent systems.

Characterization of PMMA Grafted SWMTs by Raman, UV−Vis, HRTEM, and AFM. For deeper insights into the morphology and grafting nature of the prepared PMMA-*g*-SWNTs, we focus on characterization of samples prepared in methanol (MMA/SWMTs = 20:1). The Raman spectrum of the functionalized SWNT in Figure 1A shows a large increase of a disordered (D) band at 1315 cm^{-1} and broadening of a tangential (G) band at 1590 cm^{-1}, which can be attributed to the covalent interaction between polymer radicals and nanotube walls.[11] The intensity is indicative of the degree of covalent functionalization of the nanotube framework. The UV−vis spectrum of PMMA-*g*-SWNTs in DMF displays a loss of features compared to that of pristine SWNTs (Figure 1B), indicating some disruption of the electronic structure of SWNTs. Both the Raman and UV−vis spectra suggest that PMMA is covalently attached to the sidewalls of SWNT, not physically wrapped around the SWNTs.
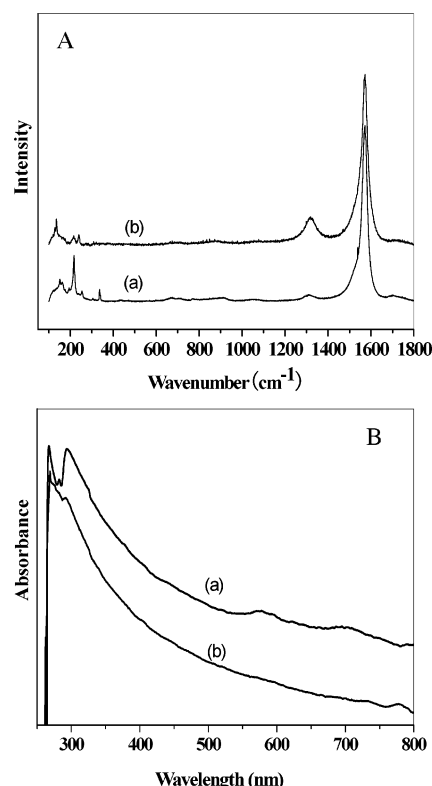

Figure 1. (A) Raman spectra of (a) pristine SWNTs and (b) PMMA grafted SWNTs (PMMA-*g*-SWNTs), which were taken on a Jobin Yon micro-Raman system using a He−Ne laser (Spectra-Physics) at excitation wavelength of 632.8 nm. (B) UV−vis spectra of (a) pristine SWNTs and (b) PMMA-*g*-SWNTs in dimethylformamide (DMF) at the same concentration (0.001 mg/mL), which were recorded on a Lambda 35 spectrophotometer using a quartz cuvette with 1 cm optical path length. The PMMA-*g*-SWNTs were prepared in 100 mL of methanol containing 2.0 g of MMA, 0.1 g of SWNTs, and 0.05 g of AIBN at 60 °C for 8 h.

High-resolution transmission electron microscopy (HRTEM) and atomic force microscopy (AFM) are effective tools to explore the contour length of functionalized CNTs.[27] In the carefully washed PMMA-*g*-SWNTs, a PMMA shell can be clearly identified from both HRTEM (Figure 3A) and AFM images (Figure 3B), further confirming the covalent nature of grafting.

The chemically functionalized SWNTs show very different dispersibility in ethyl acetate from physically wrapped ones. In a control experiment, pristine SWNTs were dispersed in PMMA/ethyl acetate solution under sonication. The mixture was extracted, dried, and redispersed in ethyl acetate. Within 30 min, the physically wrapped SWNTS precipitated completely out of
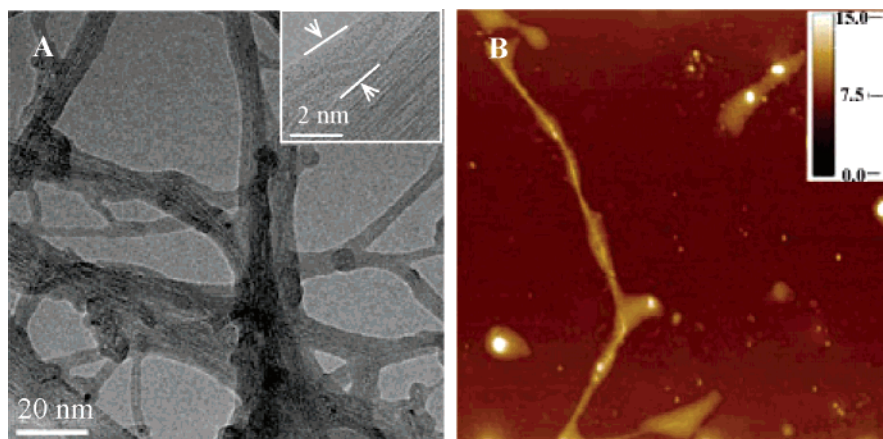
Figure 2. (A) High-resolution transmission electron microscopy (HRTEM) images of PMMA-*g*-SWNTs (the arrows in inset indicate the thickness of grafted PMMA shell), which were recorded on a JEOL JEM2011 electron microscope operating at 200 kV. (B) Atomic force microscopy (AFM) images (5 *μ*m × 5 *μ*m) of PMMA-*g*-SWNTs, which was recorded on a Nanoscope IV (Digital Instruments/Veco Metrology Group) using contact mode with standard Si/N tips. The PMMA-*g*-SWNTs were prepared in 100 mL of methanol containing 2.0 g of MMA, 0.1 g of SWNTs, and 0.05 g of AIBN at 60 °C for 8 h.
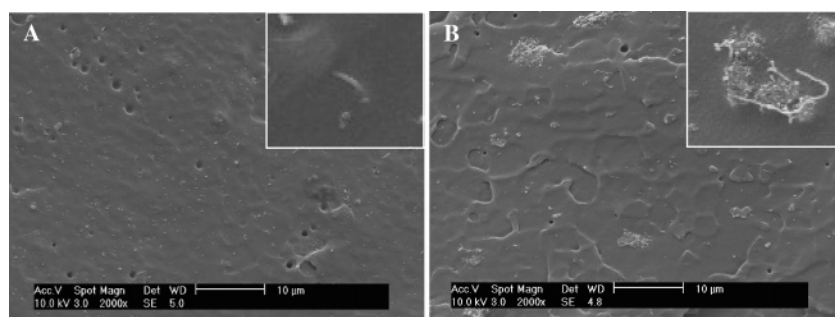

Figure 3. Cross-sectional scanning electron microscopy (SEM) images of nanocomposites of 1 wt % of SWNTs dispersed in PMMA matrix, which were recorded on a Philips XL30 FEG scanning electron microscopy from (A) functionalized SWNTs and (B) pristine SWNTs, respectively. Insets: magnified images. The nanocomposites were prepared by mixing 0.01 g of SWNTs with 1.0 g of MMA and sonicated for 10 min before addition of 0.02 g of AIBN to initiate bulk polymerization at 60 °C for 3 h.

the solution, while the chemically grafted SWNT remained stable in solution for at least 1 month. Control of the dispersion of SWNTs in a polymer matrix plays a critical role in utilization of their extraordinary physical properties in nanocomposites for various applications. We expect the functionalized SWNTs show much improved dispersion in PMMA matrix than pristine SWNTs. 0.01 g of SWNTs was mixed with 1 g of MMA and sonicated for 10 min before addition of 0.02 g of AIBN to initiate bulk polymerization at 60 °C for 3 h. From cross-sectional SEM images (Figure 3), it is clear that functionalized SWNTs are well-dispersed in PMMA matrix (Figure 3A), while 1 wt % of pristine SWNTs show random aggregates in PMMA (Figure 3B).

Mechanistic Study of the Functionalization of SWNTs in a Poor Solvent. The unusually high grafting polymers on SWNTs in a poor solvent, especially at low monomer concentration, suggests that there might be a completely different grafting mechanism in a poor solvent from the previously reported radical polymerization in a good solvent.[23,24] For the latter, SWNTs are effectively functionalized at relatively high monomer concentration and high monomer/SWNT ratios but not at low monomer concentration, which could significantly limit the large-scale synthesis of the functionalized SWNTs. Grafting efficiency is dependent on the competition between the polymer radicals whether to remain in the bulk solution or to adsorb onto the surface of SWNTs. In other words, it is dependent on the balance between enthalpic gain due to polymer−surface interaction and the entropy loss upon adsorption of polymers at solid surface. In the case of absorption of

linear polymers in a good solvent, a favorable polymer segment−segment interaction between different chains near the surface can be established at relatively high monomer concentration, whereas the polymer radical−radical coupling is favored in solution at low monomer concentration,[28] resulting in low grafting on the surface of SWNTs at low monomer concentration.

In the case of grafting in a poor solvent, short-chain polymer radicals are likely formed first in solution (Scheme 2, (1)). Because of the unfavorable interaction between the growing polymer chains and the solvent, further propagation of the radical chains for longer chain length in solution is prohibited, whereas enthalpically favorable polymer−surface contacts can be established, thereby promoting adsorption of short-chain polymer radicals to surface even at low monomer concentration.[28]

When the growth of polymer radicals reaches a critical chain length, there are two possible paths of grafting polymer chains to SWNTs. One is through self-assembly nucleation process. In the poor solvent, since polymer−polymer interaction is favored over polymer−solvent interaction, polymer globules could form (Scheme 2, (2)). Some of them will absorb onto SWNTs, while the larger ones may precipitate out of the solution (Scheme 2, (3)). For those absorbed on the SWNTs surface, physical wrapping the nanotubes is likely more dominant because the mobility of radical chain ends within the globules is highly restricted, thus, limiting the chain ends to find the active sites of the SWNTs. In this process, a large amount of polymer globules should be observed as the polymerization
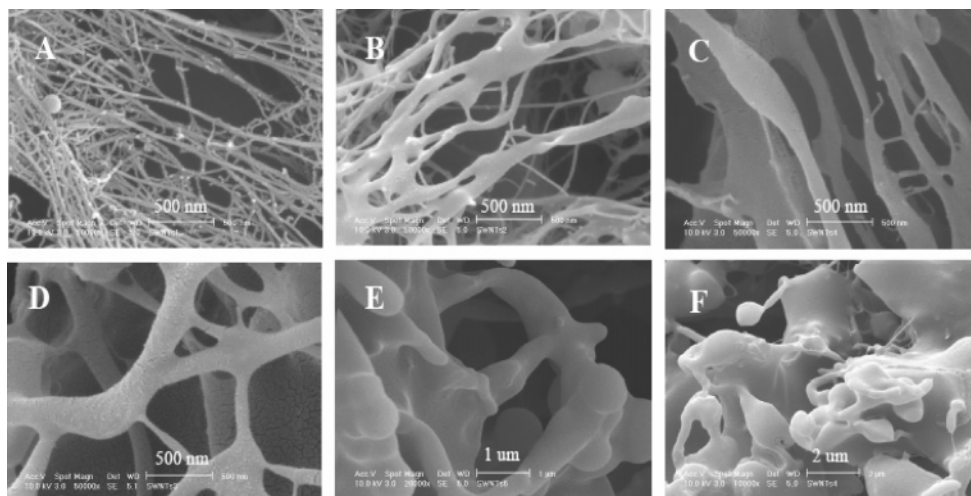
Figure 4. Scanning electron microscopy (SEM) images of real-time products sampled directly from the methanol solution during the polymerization of MMA on SWNTs at different intervals: (A) 0, (B) 1, (C) 1.5, (D) 2, (E) 3, and (F) 5 h. All images were recorded on a Philips XL30 FEG scanning electron microscope. Polymerization recipe: 0.1 g of SWNTs, 3 g of MMA, and 0.05 g of AIBN in 100 mL of methanol; the reaction temperature is 60 °C.

Scheme 2. Proposed Mechanism of Grafting Polymers on SWNTs in a Poor Solvent through a "Fishing" Process (B) vs Self-Assembly Nuleation Process (A)[a]
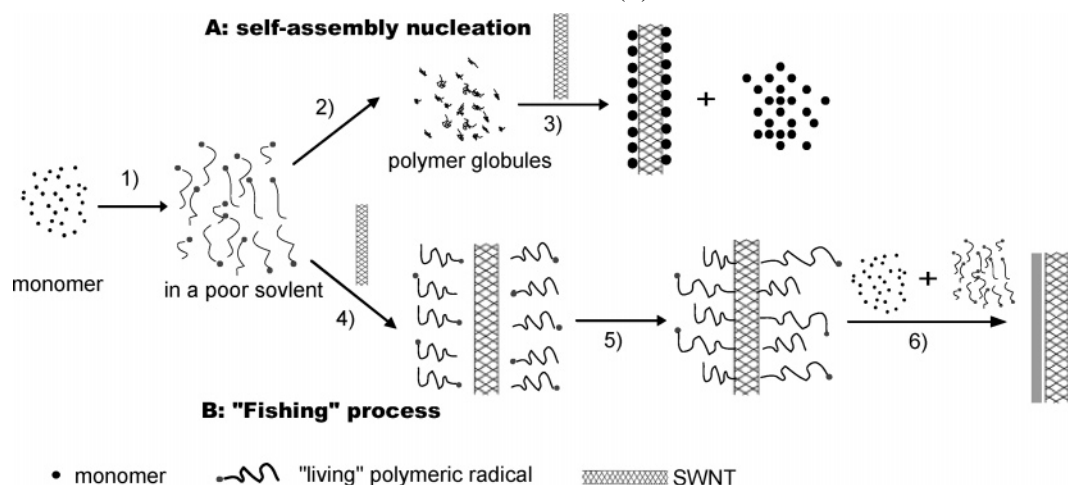
[a] (1) Radical polymerization, (2) globulation, (3) adsorption and precipitation of polymer globules, (4) "Fishing" polymer radical chains with critical chain lengths onto SWNTs, (5) grafting reaction, and (6) chain propagation.

Table 3. Scaling-Up Experiments of Functionalized SWNTs in Different Solvents[a]

solvent	MMA/SWMTs (g/g)	grafting amount of PMMA,[b] wt %	grafting yield (grafted PMMA/feed MMA), wt %	solubility in ethyl acetate, mg/mL
toluene	2:1	3.1	1.6	0.02
	1:1	1.5	1.5	0.03
methanol	2:1	25	12.5	0.21
	1:1	3.1	3.1	0.05
methanol/water (v/v = 1/4)	1:1	22.5	22.5	0.19
	0.5:1	20	40	0.20

[a] Polymerization recipe: 1 g of SWNTs, 0.05 g of AIBN in 100 mL of solvent. The reaction condition: 60 °C for 8 h. [b] This result was according to TGA measurement. All samples were heated from 50 to 800 °C at a heating rate of 10 °C/min under nitrogen flow (20 mL/min).

proceeds, and the grafting amount would be limited by the entropy loss of adsorption. In the second path, the "living" polymeric radicals with critical chain length are absorbed onto the SWNTs in analogous to a "fishing" process (Scheme 2, (4)). Polymer radicals, "fish", are covalently bound to the active sites of SWNTs, "fishhooks" (Scheme 2, (5)), and polymer–polymer interaction near the SWNT surface through entanglement and interpenetration could stabilize the absorption of radical chains.[28] Some polymer chains are terminated on the surface of SWNTs, while the others continue to propagate (Scheme 2, (6)) until SWNTs are completely covered and monomers

are consumed. However, globulation of polymer chains in solution and physical wrapping on SWNTS are possible. The grafting data from carefully washed PMMA-*g*-SWNT shown in Table 1 seem to support the proposed "fishing" process: the grafting amount increases quickly within 1 h and levels off after 3 h.

To better understand the reaction mechanism and reveal the true nature of the grafting process, we sampled the reaction products directly from solution without washing at regular intervals. The samples were directly observed under SEM after methanol was evaporated. SEM images showed that the grafted

polymer thickness increased with the reaction time until after 3 h, and polymer globules were rarely discerned on SWNTs in the whole process (Figure 4). This again supports the proposed "fishing" process over the self-assembly nucleation.

Scaling-Up of the Functionalized SWNTs through the "Fishing" Process. In comparison to existing approaches to functionalize SWNTs, our method holds significant advantages of preparing a large quantity (gram scale) of functionalized SWNTs in one-pot reaction. To prove the principle of concept, we scaled-up the reaction and functionalized 1 g of as-prepared SWNTs in 100 mL of solvents of different solvent qualities, including toluene, methanol, and methanol/water mixture (1/4 v/v) (Table 3). For the highest MMA/SWNTs ratio, 2:1, the grafting yield of MMA (grafted PMMA/feed MMA) is about 1.6% in toluene (grafting amount of 3.1 wt %) in comparison to ~12.5% in methanol (grafting amount of 25 wt %). Similar to the earlier study of grafting 0.1 g of SWNTs in 100 mL of solvent (data shown in Table 2), when the MMA/SWNTs ratio was decreased to 1:1, the grafting amount and grafting yield decreased dramatically in both toluene and methanol but remained high in the methanol/water mixture, ~22.5 wt %. Even MMA/SWNTs was as low as 0.5:1, ~40 wt % of feed MMA was found grafted onto SWNTs with a grafting amount of 20 wt %. It was previously reported that at least 2 L of solvent was necessary to prepare 1 g of highly functionalized SWNTs in a good solvent,[6,22] and the monomer/SWNTs ratio was considerably higher (100:1[23]−200:1 g/g[24]). In this prospect, functionalization of SWNTs in a poor solvent appears a promising green and cost-effective process.

Conclusions

Polymer-functionalized SWNTs are prepared through in-situ radical polymerization in a poor solvent of polymer chains. The "living" polymer radicals are enthalpically favored to absorb onto the surface of SWNTs and propagate continuously until all the active sites are consumed. The reaction can be carried out at low monomer concentration (as low as 5 mg/mL of MMA) and low monomer/SWNT (0.5:1 by weight) in methanol/water mixture (1/4 by volume) with nearly 40% of feed monomer covalently grafted onto SWNTs. The structure of functionalized SWNTs was characterized by Raman spectroscopy, UV−vis spectroscopy, HRTEM, and AFM. A "fishing" mechanism was proposed and verified. The demonstrated polymer grafting method is fundamentally different from the prior reported solvent-free system or polymerization in a good solvent. This method can be conveniently applied to mass-produce functionalized SWNTs in gram scale in a small volume of solvent (~100 mL). Besides PMMA, water-soluble polymers from poly(acrylic acid) (PAA) and polyacryamide (PAM) were also successfully grafted to the surface of SWNTs in acetone (poor solvent of PAA and PAM), respectively. The reported new grafting approach may offer important insights to improve our ability of engineering novel SWNT composites.

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