Efficient Grafting of Hyperbranched Polyglycerol from Hydroxyl-Functionalized Multiwalled Carbon Nanotubes by Surface-Initiated Anionic Ring-Opening Polymerization

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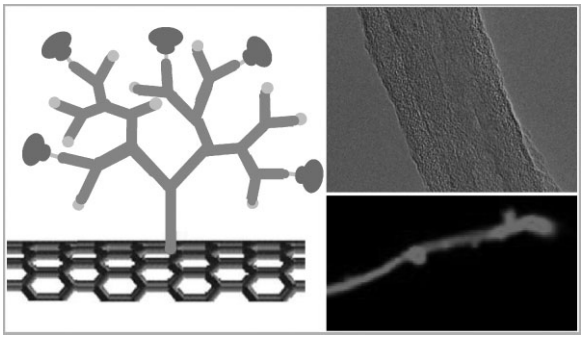
Biocompatible hyperbranched polyglycerol (HPG) has been covalently grafted from the surfaces of multiwalled carbon nanotubes (MWNTs) by the "grafting from" method based on in situ anionic ring-opening polymerization. The macroinitiator of hydroxyl-functionalized MWNTs (MWNT-OH) with hydroxyl density of 1.39 mmol per gram of nanotubes was prepared by one-pot nitrene chemistry in *N*-methyl-2-pyrrolidone (NMP) at 160 °C for 12 h. The amount of HPG grafted from MWNTs can be readily adjusted in a wide range up to 90.8wt.-% by tuning the feed ratio of glycidol to MWNT-OH. The resulting HPG-grafted MWNTs (MWNT-*g*-HPG) nanohybrids were characterized by TGA, FT-IR, and NMR spectroscopy, HRTEM, and SEM. The as-prepared nanohybrids show good dispersibility in polar solvents such as water, DMF, DMSO, and methanol. On the basis of numerous functional hydroxyl groups of the HPG grown on MWNTs, fluorescent molecules of rhodamine 6B were conjugated to the surface of MWNT-*g*-HPG by *N*, *N*′-dicyclohexylcarbodiimide (DCC) coupling, affording fluorescent MWNTs. The multifunctional MWNT-*g*-HPG nanohybrids promise potential applications in drug delivery, cell imaging and bioprobing.



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Introduction

During the past decade, polymer-functionalized carbon nanotubes (CNTs) have attracted intense attention because the individual properties of the two materials can be combined to give one novel hybrid nanomaterial with strong mechanical strength, good solubility, high thermal conductivity, and excellent processing ability.[1] Until now, "noncovalent" and "covalent" methods have been utilized to functionalize CNTs with polymers, and the "covalent"

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method admits much more stable linkage.[2] Three techniques so called "grafting to", "grafting from", and "Gemini-grafting" have been developed to covalently bind polymer chains on surfaces of CNTs. The "grafting to" approach allows to grafting a polymer with functional end/side groups (e.g., $-OH$, $-NH_2$, $-COOH$ and $-COCl$) onto CNTs. So this technique is easy to carry out with various topologic polymers including linear[3] as well as dendritic ones,[4] whereas the grafting efficiency is always low owing to the steric hindrance of the pre-grafted macromolecular chains.[5] On the contrary, the "grafting from" approach grants in situ polymerization of monomers initiated from the initiating groups immobilized on CNTs. Consequently, high and even grafting effect associated with possibly controlled structures and tailor-made properties can be achieved. For example, free radical polymerization,[6] reversible addition fragmentation chain-transfer (RAFT) polymerization,[7] anionic polymerization,[8] cationic polymerization,[9] ring-opening polymerization (ROP),[10] and atom transfer radical polymerization (ATRP)[11] have been employed to covalently grow polymers from the surfaces of CNTs. The recently presented "Gemini-grafting" approach promises to construct amphiphilic/Janus polymer brushes on a solid substance by a combination of both "grafting to" and "grafting from" techniques.[12]

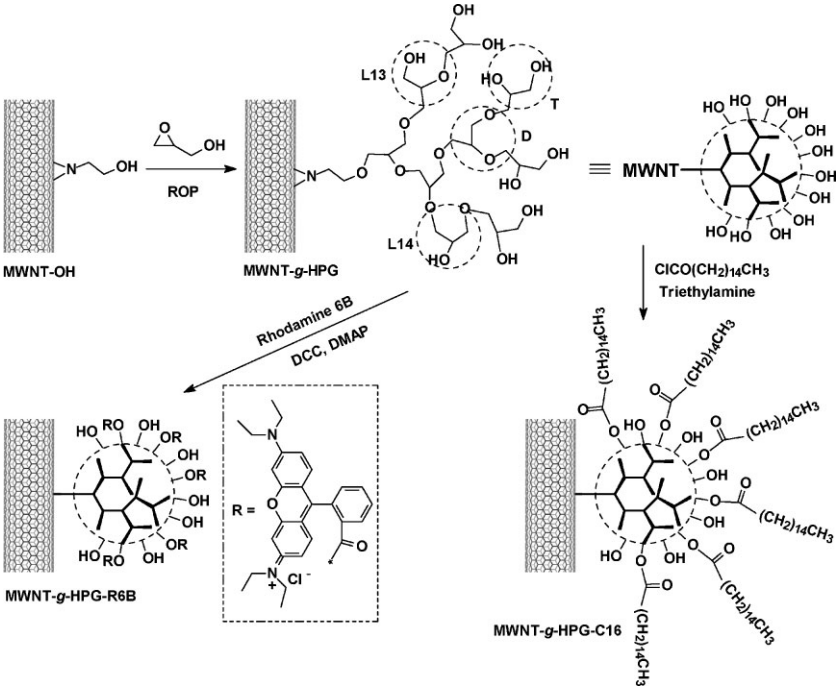
To access the multifunctional nanoobjects of CNTs and other nanomaterials, hyperbranched polymers (HPs) have received increasing attraction as building blocks to functionalize nanomaterials due to their unique properties and features such as high solubility, abundance of functional groups, and facile availability as compared to dendrimers.[13] We have previously reported the growth of multihydroxyl hyperbranched polymers by in situ cationic ring-opening polymerization[14] and hyperbranched glycopolymers by self-condensing vinyl copolymerization (SCVCP) via ATRP[15] from the surfaces of multiwalled carbon-nanotubes (MWNTs). Hong et al. synthesized HP-grafted MWNTs by self-condensing ATRP.[16] Baek et al. reported acid-terminated hyperbranched poly(ether-ketone) grafted MWNTs by direct Friedel-Crafts acylation.[17] Hyperbranched poly(urea-urethane) and poly(amido amine) can also be grafted onto MWNTs by a one-pot polycondensation.[18] Despite the aforementioned great efforts, however, highly efficient and adjustive functionalization of CNTs with HPs, is still a challenge, mainly due to the fact that the growth of HPs generally tends to obey the rules of polycondensation (e.g., SCVP, SCVCP, and self-condensing ROP) rather than those of living polymerization.

Herein we present a novel technique of anionic ROP to functionalize CNTs with hyperbranched polyglycerol (HPG), as illustrated in Scheme 1. HPG is selected favoringly because it is a readily available, water-soluble and biocompatible polymer with multihydroxyl groups, and can be controllably prepared by the anionic ROP technique.[19] The difficulty to graft HPG from CNT surfaces lies in the introduction of suitable initiating groups because the previous macroinitiator of hydroxyl-functionalized CNTs made by esterification is not in favour of anionic polymerization due to the existence of self-biting side-reaction between anions and ester bonds. Therefore, we used an alternative strategy to obtain the macroinitiator that is stable under the presence of anions by one-step [2 + 1] cycloaddition of nitrenes to the pristine MWNTs.[20] Moreover, palmitoyl chloride and rhodamine 6B are used as model molecules to demonstrate the high reactivity of the multihydroxyl groups of resulting HPG-grafted MWNTs (MWNT-*g*-HPG). There is no doubt that the MWNT-*g*-HPG hybrids offer a versatile toolbox or reactive nanoplatform for bionanotechnology.

Experimental Part

Materials

The multiwalled carbon nanotubes (MWNTs) were purchased from the Tsinghua-Nafine Nano-Powder Commercialization Engineer-



Scheme 1. Functionalization of multiwalled carbon nanotubes (MWNTs) with hyperbranched polyglycerol (HPG) by anionic ring-opening polymerization (ROP) and modification of the grafted HPG.

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Table 1. Reaction conditions and selected results for grafting HPG from MWNT surface.

Sample	R_{wt} [a)]	R_{mole} [b)]	f_{wt}% [c)]	$\overline{M}_{n,GPC}$ [d)]	PDI [d)]	$\overline{M}_{n,TGA}$ [e)]	m_{nongra}/m_{gra} [f)]
				$g \cdot mol^{-1}$		$g \cdot mol^{-1}$	
MWNT-*g*-HPG1	5.75/1	56/1	22.8	1 300	1.37	1 230	11.6
MWNT-*g*-HPG2	13.8/1	134/1	39.2	8 300	1.79	4 640	7.2
MWNT-*g*-HPG3	34.5/1	335/1	49.6	21 100	1.74	7 080	4.8
MWNT-*g*-HPG4	63.25/1	614/1	66.1	57 600	1.54	14 200	5.1
MWNT-*g*-HPG5	74.75/1	726/1	74.5	81 300	1.69	21 020	4.5
MWNT-*g*-HPG6	103.5/1	1 005/1	90.8	100 600	1.58	71 000	4.2

[a)]Weight feed ratio of glycidol to MWNT-OH; [b)]Mole feed ratio of glycidol to hydroxyl groups of the MWNT-OH; [c)]Weight fraction of grafted polymer in the product of MWNT-*g*-HPG calculated from corresponding TGA data between 200–500 °C; [d)]Number-average molecular weight ($\overline{M}_n$) and polydispersity index (PDI) of the free polymer collected from the centrifugated solution, measured by GPC with DMF as the eluent and PS as the calibration; [e)]Average molecular weight of the grafted HPG calculated from TGA data: $\overline{M}_{n,TGA} = m_{gra}/n_{gra} = f_{wt}/[(1 - f_{wt}) \cdot 1.39 \cdot 10^{-3}]$; herein, 1.39 represents the concentration of initiating sites per gram of MWNTs (mmol $\cdot g^{-1}$), m_{gra} and n_{gra} represent the mass and molar amount of the grafted HPG, respectively. $\overline{M}_{n,TGA}$ for MWNT-*g*-HPG1 is the molar mass of neat HPG units excluding the weight fraction of organic moieties attached onto MWNT-OH, because of the great influence of such weight fraction on the calculation for such a low R_{mole}; [f)]Mass ratio of non-grafted polyglycerol to grafted amount.

ing Centre (purity >95%, 10−30 nm in diameter). Glycidol (Aldrich, 96%) was purified by vacuum distillation and stored over 4Å molecular sieves in a refrigerator (2–4 °C) before use. 2-Azidoethanol was prepared in our lab.[21] Dioxane and methanol was distilled before use. Potassium methylate solution in methanol (25%, Aldrich) was used as received. All other chemicals were analytical grade and used as received without further purification.

Preparation of MWNT-OH from MWNTs

Typically, 498.8 mg of pristine MWNTs, 15 mL of *N*-methyl-2-pyrrolidone (NMP) and 9.5 mL of 2-azidoethanol were placed in a dry flask. The mixture was treated with an ultrasonic bath (40 kHz) for 30 min, and then stirred at 160 °C for 12 h. The solution was precipitated with ether. The obtained viscous solid was then dispersed in acetone and separated by centrifugation and washed with acetone. After repeated washing and centrifuging steps, the resulting solid was dried overnight in a vacuum oven at 60 °C, obtaining 527.3 mg of MWNT-OH.

Growing Hyperbranched Polyglycerol from MWNT-OH by Emulsion Polymerization

Typically, to a dry flask, 100 mg of as-prepared MWNT-OH, 20 μL of potassium methylate solution (25 wt.-%) and 4.5 mL of anhydrous tetrahydrofuran (THF) were added. The mixture was stirred for 30 min at 50 °C, before which methanol was removed by vacuum. Then 15 mL of dioxane was added and the flask was kept in an oil bath at 95 °C. Glycidol (5.5 mL, 85.4 mmol) was added dropwise over a period of 2 h. After completion of monomer addition the mixture was stirred for an additional 2 h. After cooling to room temperature, the mixture was quenched by methanol and dispersed in additional methanol (8.0 mL), and subsequently centrifuged and washed several times with methanol. After repeated washing and centrifuging steps, the resulting solid product was dried overnight to give hyperbranched polyglycerol-grafted MWNTs (MWNT-*g*-HPG4 in Table 1, 284.6 mg). The free HPG collected from the clear centrifugated liquid was obtained by precipitation with acetone.

For comparison, bulk polymerization (no dioxane was used) and solution polymerization (DMF as solvent instead of dioxane) were carried out in the same condition of the above emulsion polymerization to investigate the grafting efficiency comparatively.

Modification of MWNT-*g*-HPG with Hydrophobic Tails

Typically, 25 mg of MWNT-*g*-HPG4 dispersed in 5 mL of *N*,*N*-dimethylformamide (DMF) was placed in a 25 mL flask, and the mixture was sonicated in a bath (40 KHz) for 3 min. Then triethylamine (150 mg, 1.49 mmol) and palmitoyl chloride (50 mg, 0.18 mmol) were added to the flask. The mixture was stirred at 45 °C for 24 h in a nitrogen atmosphere. The resulting sample was separated by centrifugation and washed thoroughly with ether and water. After dried in a vacuum for 24 h, 38.6 mg of the product (designated as MWNT-*g*-HPG4-C16) was obtained.

Functionalization of MWNT-*g*-HPG with Rhodamine 6B

In a typical procedure, 50 mg of MWNT-*g*-HPG4, 10 mg of rhodamine 6B (0.02 mmol) and 5 mL of DMF were placed in a dry flask, and treated in an ultrasonic bath for 3 min. Then, 50 mg of *N*,*N*′-dicyclohexylcarbodiimide (DCC) and 15 mg of 4-dimethylaminopyridine (DMAP) were added to the flask, and the mixture was stirred at 80 °C for 24 h. The product was separated by

centrifugation and washed with ethanol repeatedly until the washed ethanol became colorless. After dried overnight under vacuum, 53.2 mg of final product (designated as MWNT-*g*-HPG4-R6B) was obtained.

Characterization

Thermo gravimetric analysis (TGA) was carried on a Perkin-Elmer (PE) TGA-7 instrument with a heating rate of 20 °C min^{-1} in a nitrogen flow (20 $mL \cdot min^{-1}$). Nuclear magnetic resonance (^1H NMR and ^{13}C NMR) measurements were conducted using a Varian Mercury Plus 400 MHz spectrometer. The molecular weight was measured by PE Series 200 gel permeation chromatography (GPC), with polystyrene as the standard and using LiBr/DMF (0.01 $mol \cdot L^{-1}$) as the eluent at a flow rate of 1 $mL \cdot min^{-1}$. Fourier transform infrared (FT-IR) spectra were recorded using a PE Paragon 1000 spectrometer (KBr disk). Transmission electron microscopy (TEM) studies were performed on a JEOL JEL2010 electron microscope at 200 kV. Scanning electron microscopy (SEM) images were recorded using FEI SIRION 200 field-emission microscope. Fluorescence images were obtained with Zeiss LSM-510 confocal laser-scanning microscope using a 1 mW He-Ne laser at 543 nm.

Results and Discussion

In order to graft HPG from MWNTs by in situ anionic ROP controllably and efficiently, the MWNT-supported macroinitiator with high density of hydroxyl groups (MWNT-OH) should be pre-synthesized. Previously, hydroxyl groups were introduced to MWNTs through three steps of acid-oxidation, conversion of carboxyl into acyl chloride and reaction with glycol. The density of hydroxyl groups can approach as high as 1.06 mmol per gram of functional nanotubes. However, the ester bonds are not stable under attack of strong anions. So this kind of linkage is unfavorable for anionic polymerization. Recently, we developed a novel one-step strategy to prepare multifunctional CNTs and carbon nanoonions (CNOs) via nitrene chemistry, which opens a facile approach to macroinitiator without linkage of ester bonds.[22] As shown in Scheme 1, one-step [2 + 1] cycloaddition of nitrenes decomposed from 2-azidoethanol to the pristine MWNTs affords MWNT-OH. Subsequent in situ anionic ROP of glycidol results in HPG-grafted MWNTs and free HPG. After complete removal of the free HPG by repeated centrifugation and washing with methanol, pure MWNT-*g*-HPG can be obtained.

The content of the organic moiety linked on MWNTs was determined by thermo gravimetric analysis (TGA) (see Figure 1). The pristine MWNTs show good thermal stability and almost no weight loss below 600 °C. In contrast, the MWNT-OH shows a weight-loss of 8.2% between 200–500 °C, indicating that the hydroxyl groups have been covalently linked to the MWNT surfaces and the group density is ca. 1.39 mmol per gram. This concentration is higher than that obtained from the classic acid-oxidation

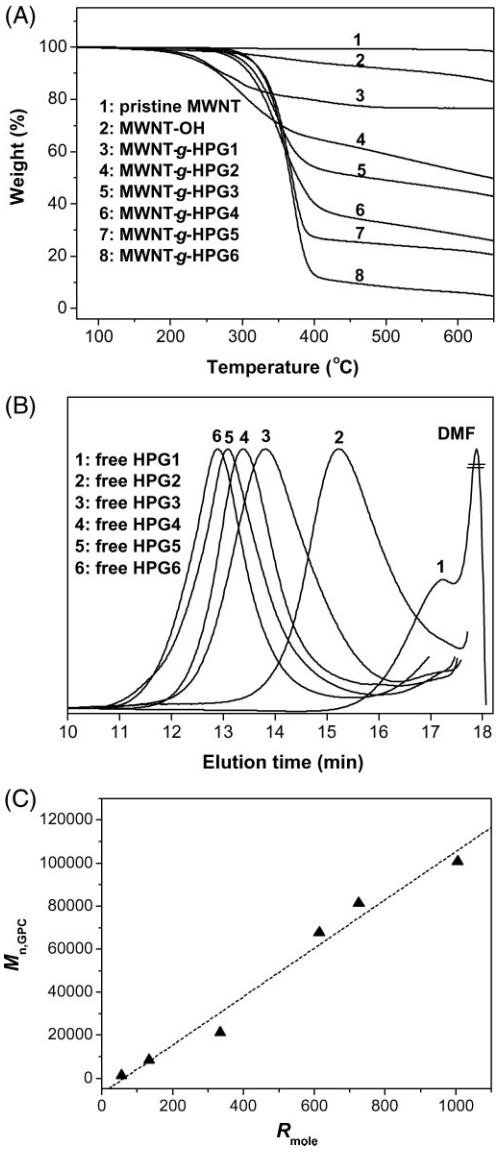

Figure 1. A) TGA thermograms of pristine MWNTs (1), MWNT-OH (2), MWNT-*g*-HPG1 (3), MWNT-*g*-HPG2 (4), MWNT-*g*-HPG3 (4), MWNT-*g*-HPG4 (5), MWNT-*g*-HPG5 (6), and MWNT-*g*-HPG6 (7). B) GPC curves showing the evolution of molecular weight with the elution time for the free HPGs. C) Average molecular weight of the free HPG obtained from GPC as a function of molar feed ratio (R_{mole}).

method likely due to the one-step reaction.[10] Such a high concentration of initiating sites on the surfaces of MWNTs provides a good platform for the successful surface-initiated anionic ROP.

Considering the fact that glycidol can also self-polymerize to form free HPGs during the experiments, we collected both products of MWNT-*g*-HPG and free HPG. Two means are generally employed to understand the information of grafted polymer: cleavage of the polymer chains from the surface to measure its molecular parameters directly,[14,23] and investigation of free polymer to speculate the

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information of grafted polymer indirectly.[15] Since the linkage between nanotube and HPG is a stable C–N bond rather than a degradable ester bond (–COO–), we tried the indirect mean to probe the information of grafted HPG. We conducted six experiments under the same conditions except the feed ratio of glycidol monomer to MWNT-OH macroinitiators in order to check the controllability of anionic ROP. The results are shown in Figure 1 and Table 1. The grafted polymer content calculated from the TGA weight loss curves increases from ca. 22.8 to 90.8 wt.-% as the weight feed ratio (R_{wt}) rises from ca. 5.75:1 to 103.5:1, indicating that the weight fraction of grafted HPG (f_{wt}) can be well adjusted in a wide range by R_{wt} and the grafting efficiency is quite high up to 90.8wt.-%. Such a good grafting effect in both adjustability and efficiency was rarly observed in the previous cases of dendritic polymer-grafted CNTs even though cases of linear polymer-functionalized CNTs have been reported on the basis of controlled/living polymerizations.[7–11] The onset temperature of decomposition for the functionalized nanotubes with low f_{wt} (e.g., ca. 200 °C for MWNT-*g*-HPG1) is obviously lower than that of nanotubes with higher f_{wt} (e.g., 285 °C for MWNT-*g*-HPG6), implying that the higher grafting effect resulted mainly from greater molecular weight instead of more initiating efficiency. This was confirmed by the increase of the average molecular weights of the grafted HPGs calculated from the corresponding TGA weight loss ($\overline{M}_{n,TGA}$)[15] (e.g., 1 230 g · mol^{-1} for MWNT-*g*-HPG1 and 71 000 g · mol^{-1} for MWNT-*g*-HPG6). At the same time, we found that the mass ratio of non-grafted polyglycerol to the grafted amount decreases from ca. 11.6 to 4.2 as the R_{wt} rises from ca. 5.75:1 to 103.5:1. This again demonstrated that the grafting efficiency can be adjusted by tuning the R_{wt}. Furthermore, we measured the molecular weight and polydispersity index (PDI) of the free HPGs by GPC. It is found that the number-average molecule weight ($\overline{M}_n$) of the corresponding free HPG increases from 1 300 to 100 600 g · mol^{-1} linearly with the increase of the mole feed ratio of monomer to initiating sites (R_{mol}) (see Figure 1B). This linear correlation suggests that the anionic ROP preserves the similar character of a living polymerization indeed in the presence of CNTs, which in turn uncovers the mechanism for the controlled grafting effect of surface-initiated polymerization. In addition, all of the PDIs of the free HPGs are relatively narrow (<1.8) despite the formation of hyperbranched macromolecules, which is in accordance with the typical characteristic of a controlled/living polymerization.[24] It should be noted that if no dioxane was used in the polymerization (or DMF was used as solvent in the polymerization), the grafted polymer contents were never more than 45 wt.-% in the bulk polymerizations even for the R_{wt} as high as 120/1. This phenomenon is similar to the results reported by Brooks[25] on synthesis of high molecular weight of neat HPGs and ourselves on other nanosurface-initiated anionic ROP (data not shown). They ascribe this phenomenon to the high viscosity of the reaction mixture in bulk polymerization and the dioxane can be used as an emulsifying agent.[25] So the low grafting content in the cases of bulk polymerization can be attributed to the low molecular weight of the grafted polymer. All these data suggest that our anionic ROP-based "grafting from" technology in dioxane is facile and highly efficient.

As compared to the pristine MWNTs, the functionalized MWNTs exhibited much better dispersibility/solubility in polar solvents such as water, methanol, DMF, and dimethylsulfoxide (DMSO) because of the grafted polar HPG. The molecular structures of the resulting products and free HPGs were analyzed by FT-IR and NMR spectroscopy. As shown in Figure 2A, the two weak peaks at 2 872 and 2 930 cm^{-1}, associated with sp^3 C–H stretching, can be observed in the FT-IR spectrum of MWNT-OH. In contrast, the peaks of sp^3 C–H stretching for the pristine MWNTs are hardly observed in the FT-IR spectrum. After polymerization, the absorption intensity of the sp^3 C–H stretching is

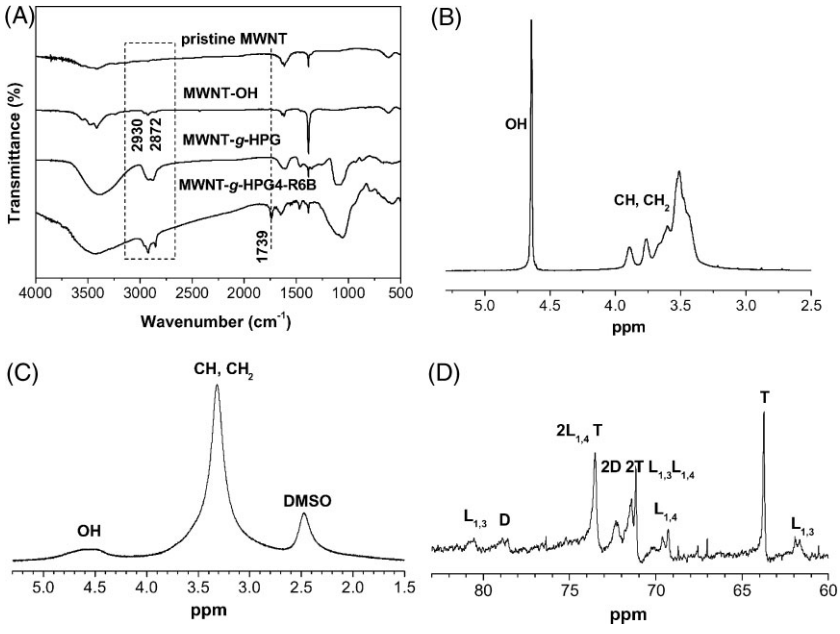

Figure 2. A) FT-IR spectra of pristine MWNTs, MWNT-OH, MWNT-*g*-HPG4, and MWNT-*g*-HPG4-R6B. B) ^{1}H NMR spectrum of free HPG. C) ^{1}H NMR spectrum of MWNT-*g*-HPG3. D) ^{13}C inverse-gated NMR spectrum of MWNT-*g*-HPG3. The NMR spectra were obtained in DMSO-d_6.

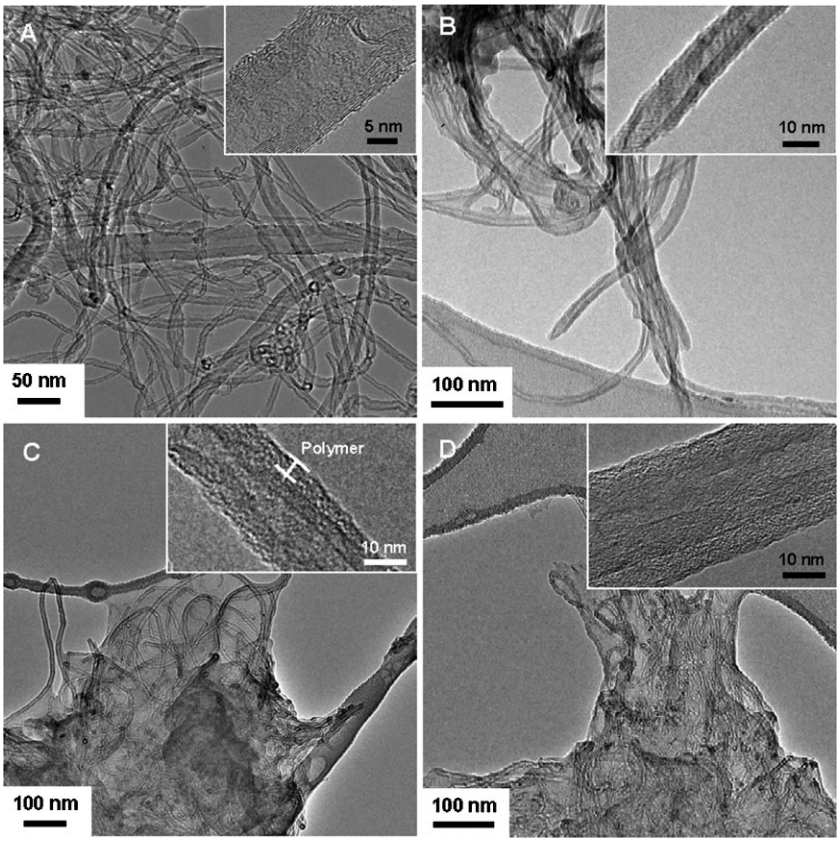

Figure 3. TEM images of MWNT-OH (A), MWNT-*g*-HPG1 (B), MWNT-*g*-HPG2 (C), and MWNT-*g*-HPG3 (D) at low magnification and high magnification (inset).

obviously increased, revealing that much more organic components have been coated on the surfaces of the MWNTs. Figure 2B and 2C show the ^{1}H NMR spectra of the free HPGs and MWNT-*g*-HPGs, respectively. For both samples, the active-hydrogen peak of −OH can be found distinctly and separately at ca. 4.65 or 4.55 ppm. The protons of $-CH_2-$ and −CH- units of the free HPG are observed at 3.2–3.8 ppm with four-divided peaks, whereas the corresponding protons of MWNT-*g*-HPG are only observed as one overlapped peak during 2.8–3.8 ppm. Besides, the hydrogen peaks of MWNT-*g*-HPG are broadened as compared with those of free HPG. This broadening phenomenon is attributed to the covalent linkage of polymer and CNT surface, which was also widely found in the previous reports on linear polymer-grafted CNTs.[26] To our delight, the ^{13}C NMR spectrum of the MWNT-*g*-HPGs can be clearly obtained due to their high solubility, as shown in Figure 2D. The degree of branching (DB) can be calculated on the basis of the intensity of NMR signals from the fraction of structural units using the following equation:[27]

$$DB = 2D/(2D + \mathrm{L13} + \mathrm{L14}) \quad (1)$$

Herein, *D* designates the number of dendritic units, L13 and L14 the numbers of linear units (see Scheme 1). The *DB* value for the MWNT-*g*-HPGs (ca. 0.61) is close to the reported values for neat HPGs (from ca. 0.53 to 0.59) prepared by anionic ROP without CNTs.[25,27] Therefore, hyperbranched HPG with high DB can be grown successfully from the nanotube surfaces by the anionic ROP technique.

The nanoscale structures and surface morphology of the MWNT-*g*-HPGs were observed by high-resolution transmission electron microscopy (HRTEM) (see Figure 3). For MWNT-OH, almost all of the tubes are individually distributed and their surface looks smooth and clear without any extra phase adhering to them (Figure 3A). In the high magnification image, the multiwalled graphite nanostructures can be clearly observed. For the MWNT-*g*-HPGs, however, as shown in Figure 3B to D, there is an obvious polymer layer which envelopes the MWNT. The core-shell structure of the nanohybrids is clearly observed under a high magnification. It is found that the higher the grafted polymer amount, the thicker the coated polymer layer (e.g., the thickness of the polymer shell is ca. 2–3 and 5–8 nm for MWNT-*g*-HPG1 and MWNT-*g*-HPG3, respectively). The morphology of MWNT-*g*-HPG was also evaluated by scanning electron microscopy (SEM) measurements (see Figure 4). For the MWNT-OH, the individual tubes can be clearly seen (Figure 3E). After the growth of HPG from the tubes surface, the resulting solid became a composite in which the tubes are individually enveloped in the continuous phase of HPGs (Figure 3F to H). This is in accordance with the TEM observations. With the increase of the grafted-polymer content, the polymer phase becomes more continuous, and the nanowire-like morphology of MWNTs gets more indistinct.

The hydroxyl groups associated with MWNT-*g*-HPGs are expected to have the ability to undergo a multitude of postfunctionaliztion reactions, giving rise to multifunctional nanohybrids. To obtain amphiphilic hyperbranched polymer-grafted MWNTs, palmitoyl chloride was used as the hydrophobic tails to react with MWNT-*g*-HPGs in the presence of triethylamine. The resulting product showed good solubility in weakly polar or non-polar solvents such as THF, chloroform and dichloromethane instead of polar solvents such as water and methanol (see Figure 5A). Since HPG is attractive for its biocompatibility and potential

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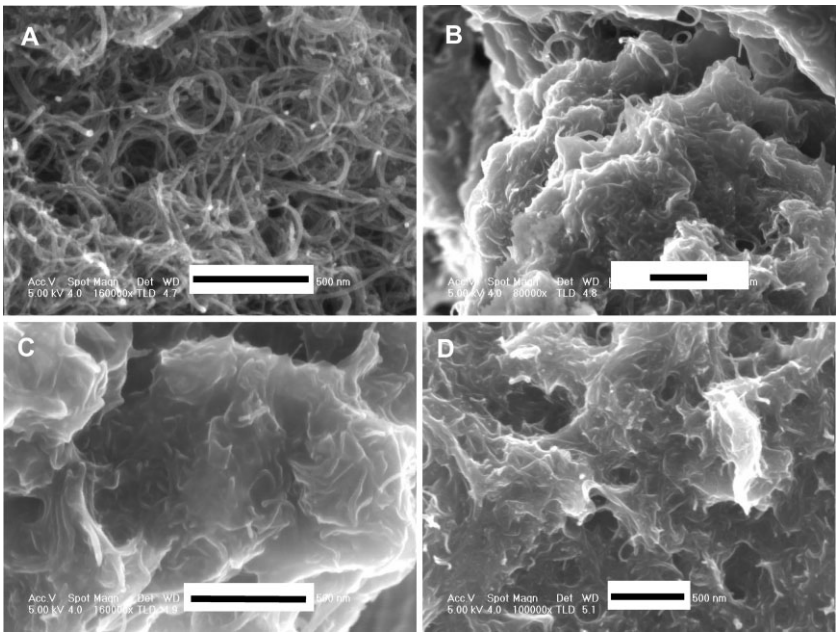

Figure 4. SEM images of MWNT-OH (A), MWNT-*g*-HPG1 (B), MWNT-*g*-HPG3 (C), and MWNT-*g*-HPG5 (D). All of the scale bars are 500 nm.

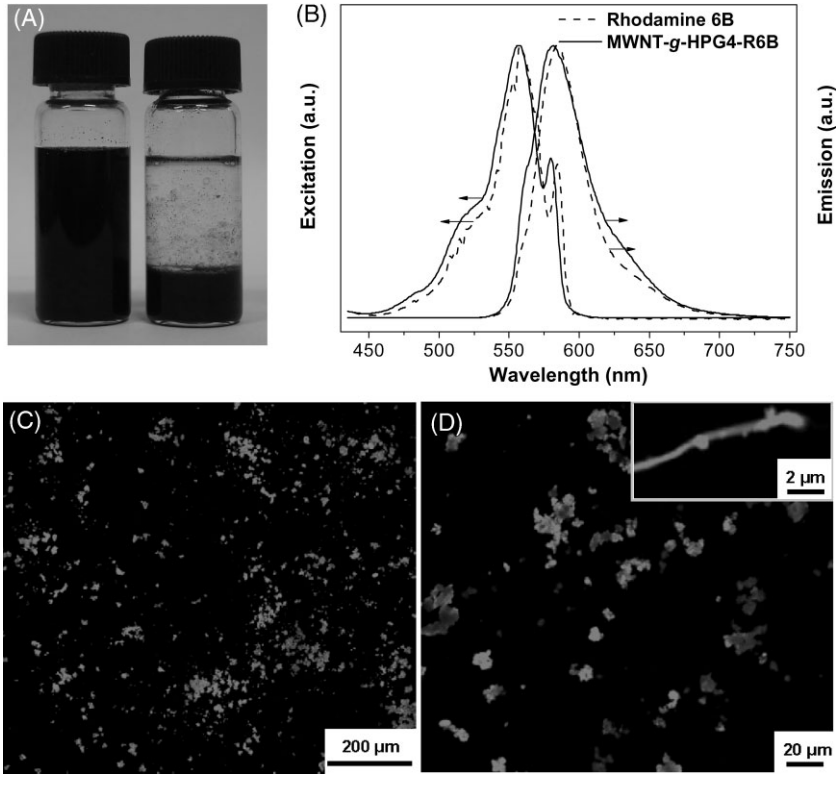

Figure 5. A) Photographs of MWNT-*g*-HPG4 in water (left) and MWNT-*g*-HPG4-C16 in water/chloroform mixture (right). B) Emission and excitation spectra of rhodamine 6B and MWNT-*g*-HPG-R6B. Confocal fluorescence images of MWNT-*g*-HPG-R6B at low magnification (C) and high magnification (D). The inset of D shows an individual fluorescent MWNT, demonstrating the uniform dispersion and strong fluorescence of MWNT-*g*-HPG-R6B.

application in drug delivery, rhodamine 6B is utilized as a model molecule of fluorescence probe to functionalize the MWNT-*g*-HPG (named MWNT-*g*-HPG-Rh6B) by DCC coupling chemistry. After reaction, a strong peak at 1739 cm^{-1} corresponding to the carbonyl groups appeared in the corresponding FT-IR spectrum (see Figure 2A), which is in accordance with the chemical structure of MWNT-*g*-HPG-Rh6B. The emission and excitation spectra of the MWNT-*g*-HPG-Rh6B in methanol, depicted in Figure 5B, are comparable to the spectra of neat rhodamine 6B in methanol. Confocal fluorescence imaging confirmed the strong fluorescence and also demonstrated their relatively uniform dispersion (Figure 5C and D). The inset of Figure 5D clearly presents an individual fluorescent nanotube. Except the fluorescent molecule of rhodamine 6B, other functional molecules can also be conjugated to the MWNT-*g*-HPG nanohybrids for bio-nanoapplications. All these results show that the grafted hyperbranched polymer not only improves the solubility of MWNTs significantly, but also serves as a versatile platform for further chemical modification and bioconjugation of the MWNTs because biomolecules can be covalently linked to the periphery of HPG likewise.

Conclusion

A powerful "grafting from" approach based on surface-initiated anionic ring-opening polymerization has been developed to covalently graft hyperbranched polyglycerol from MWNT surfaces. The MWNT-OH macroinitiators can be facilely obtained by one-step nitrene chemistry. Through tuning the feed ratio of glycidol monomer to MWNT-OH macroinitiator, the grafted HPG content or molecular weight can be easily adjusted. The chemical structure of the MWNT-*g*-HPG was confirmed by FT-IR, ^{1}H NMR and ^{13}C NMR spectra. The dispersibility of the HPG-grafted MWNTs have been significantly improved compared with the pristine MWNTs. TEM and

SEM studies show that MWNTs can be enveloped in the continues polymer phase to form uniform nanocomposites. Because of the numerous functional hydroxyl groups associated with the HPG, conjugation of functional molecules such as rhodamine 6B fluorescent molecules to the MWNTs surface can be easily achieved. We consider that the simplicity of this "grafting from" approach and the versatility of the hybrid materials will open up new opportunities for applying MWNT-*g*-HPG in bionano-fields such as drug delivery and bio-imaging. These works are in progress and will be reported elsewhere.

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