2606 *Macromolecules* **2005,** *38,* 2606−2611

Multiwalled Carbon Nanotubes Grafted with Hyperbranched Polymer Shell via SCVP

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Received November 3, 2004; Revised Manuscript Received January 17, 2005

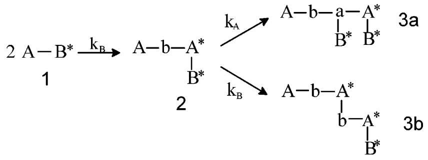
ABSTRACT: A self-condensing vinyl polymerization (SCVP) strategy via atom transfer radical polymerization (ATRP) was employed to grow hyperbranched macromolecules on the surfaces of multiwalled carbon nanotubes (MWNTs). The MWNT surface fixed with ATRP initiators [MWNT-$COOCH_2CH_2OCOC(CH_3)_2Br$, MWNT-Br] was prepared by reaction of MWNT-COCl with excess of 2-hydroxyethyl 2′-bromoisobutyrate. Then, using the MWNT-Br as polyfunctional initiator (B^*_f), hyperbranched macromolecules were covalently grafted on MWNTs by self-condensing vinyl polymerization of 2-((bromobutyryl)oxy)ethyl acrylate (BBEA, AB* inimer) via the ATRP process. The resultant products were characterized by FT-IR, NMR, and TEM. TGA measurements showed that the weight ratio of the as-grown hyperbranched polymers on the MWNT surfaces reached 80%. The as-prepared MWNTs grafted with hyperbranched polymers exhibit relatively good dispersibility in organic solvents such as THF and chloroform.

Introduction

The potential utility of carbon nanotubes in a variety of technologically important applications, such as molecular wires and electronics, sensors, and probes, high-strength fibers, field emission, and hydrogen storage, is now well established.[1,2] However, despite significant research progress,[3] successful applications of such composite systems require well-dispersed nanotubes having good adhesion with the host matrix and good solubility in organic solvents, which, unfortunately, is not easily realized. Processing is very difficult due to the poor solubility of single-walled carbon nanotubes (SWNTs) or multiwalled carbon nanotubes (MWNTs). Exfoliation of nanotube bundles is a major challenge in fabricating molecular electronics and producing homogeneously dispersed conducting layers within electroluminescent devices. Thus, many research groups have focused on functionalizing carbon nanotubes with various organic and organometallic structures and linear polymers to increase their solubility.[4]

Hyperbranched polymers and dendrimers have distinctive, special chemical and physical properties, and they have played a vital role in interface and surface sciences, which can be used advantageously as functional surfaces and interfacial materials.[5] In addition, dendrimers and hyperbranched polymers have good solubility, lower melt viscosity, and extremely high density of functional groups at the surface compared with the linear analogues. Dendrimers and hyperbranched polymers should therefore increase the solubility of MWNTs and enable further functionalization of MWNTs. Most molecular wires have poor solubility and processing ability; however, when these insoluble molecular wires are wrapped with highly branched polymers, the branched polymers not only protect and stabilize the central conjugated backbone of molecular wires by preventing intermolecular actions but also improve the solubility and processability without altering their electronic characteristics.[6] Moreover, some research groups reported that dendrimers or hyperbranched polymers have been successfully immobilized onto the surface of Au and silicon wafer;[7] the hyperbranched polymers can be covalently modified with a broad range of functional groups, such as fluorophores, electroactive groups, perfluorinated moieties, dyes, and other linear polymers;[7a] and also the surface-confined hyperbranched polymers are suitable for a number of technical applications, including corrosion inhibition, chemical sensing, cellular engineering, and micrometer-scale patterning.[4] Therefore, hyperbranched polymers and dendrimers may be ideal materials to coat and functionalize carbon nanotubes.

Scheme 1



The recent discovery of SCVP made it easy to use vinyl monomers for the one-step synthesis of hyperbranched structures.[6] This reaction is based on an initiator-monomer (“inimer”) of the general structure AB*, where the double bond is designated A and B* is a functional group which can be transformed to an active center (such as a cationic, radical, or anionic active center) and initiates the polymerization of the double bonds. The activated B* adds across the double bond A to form the dimer. Scheme 1 shows the idealized case of one addition of monomer followed by deactivation to form the new group A*. The dimer, **2**, can now be reactivated at either B* or A*. Addition of monomer at A* results in **3a**, while addition at B* yields **3b**. Further

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10.1021/ma047736r CCC: $30.25

addition of monomer, or *n*-mer, to either **3a** or **3b**, can result in a polymer that is highly branched. Matyjaszewski first reported that atom transfer radical polymerization (ATRP) can be applied to the syntheses of hyperbranched polymers by SCVP. In the SCVP system via ATRP, AB* should contain a double bond and a halogen atom.[8]

Although many research groups have used linear polymer chains to modify the surface of carbon nanotubes by ATRP, anionic, cationic, and ring-opening polymerizations[5] and Yan reported a SCVP via ring-opening polymerization method to graft hyperbranched polymer on MWNTs,[9] there are still few reports on highly branched polymers functionalizing the surface of carbon nanotubes. Here, we report an easy method to coat the surface of MWNT with a hyperbranched polymer shell by self-condensing vinyl polymerization (SCVP) via atom transfer radical polymerization (ATRP).

Experimental Section

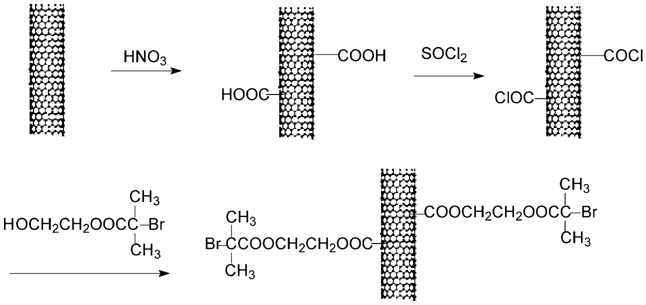
Materials. MWNT was provided by the Tsinghua-Nafine Nano-Powder Commercialization Engineering Centre. Bromoisobutyric acid (98%), glycol (99%), bromobutyric acid (99%), and CuBr (98%) were purchased from Aldrich. 1,1,4,7,7-Pentamethyldiethylenetriamine (PMDETA, 99%) was purchased from Acros. All chemical reagents were used directly without further purification.

Synthesis of 2-Hydroxylethyl 2′-Bromoisobutyrate (HEBrIB). HEBrIB was prepared as follows: Ethylene glycol (42.0 g, 0.67 mol), 2-bromoisobutyric acid (11.2 g, 0.067 mol), *p*-toluenesulfonic acid (0.2 g, 9.0×10^{-4} mol), and 50 mL of benzene were heated at 96 °C while stirring for 36 h, and the water generated by esterification reaction was removed by an oil−water separator. Then the reaction mixture was poured into 500 mL of distilled water, and the lower, light-yellow organic phase was separated. The organic portion was dissolved in methylene chloride and dried over anhydrous magnesium sulfate overnight. After filtration from the magnesium salt, removal of solvent, the 2-hydroxylethyl 2′-bromoisobutyrate, was obtained as a colorless liquid (10 g, yield 70%). ^{1}H NMR of $HOCH_2CH_2OCOC(CH_3)_2Br$ (δ, ppm): 1.0 (s, 6H, 2-$C\boldsymbol{H}_3$), 3.7 (t, 2H, $OCH_2C\boldsymbol{H}_2OH$), 4.30 (t, 2H, $-COOC\boldsymbol{H}_2CH_2-$). The synthesis of 2-hydroxylethyl 2′-bromobutyrate (HEBrB) was similar to that of HEBrIB. ^{1}H NMR of $HOCH_2CH_2OCOCH(C_2H_5)Br$ (δ, ppm): 1.05 (t, 3H, $-CH_2C\boldsymbol{H}_3$), 2.0 (m, 2H, $-C\boldsymbol{H}_2CH_3$), 3.7 (t, 2H, $OCH_2C\boldsymbol{H}_2OH$), 4.12 (t,1H, $C\boldsymbol{H}(Br)CH_2CH_3$), 4.30 (t, 2H, $-COOC\boldsymbol{H}_2CH_2-$).

Synthesis of 2-((Bromobutyryl)oxy)ethyl Acrylate (BBEA) (AB* Inimer). A solution of acrylyl chloride (5.0 g, 0.055 mol) in 10 mL of dichloromethane was added dropwise to an ice-cooled solution of HEBrB (10.6 g, 0.05 mol) and triethylamine (5.6 g, 0.55 mol) in dichloromethane (80 mL) over 1 h under nitrogen. The reaction continued for 24 h under room temperature. After removing the precipitate produced during evaporation of dichloromethane by filtration, a yellow oil was obtained, which was washed with distilled water three times and dried over anhydrous magnesium sulfate for 24 h. The solvents were evaporated under reduced pressure to obtain a crude product. Pure BBEA (9.0 g, yield 66.7%) was obtained by passing a solution of BBEA in dichloromethane through silica gel column. ^{1}H NMR (δ, ppm): 1.05 (t, 3H, $-CH_2-C\boldsymbol{H}_3$), 2.0 (m, 2H, $-C\boldsymbol{H}_2-CH_3$), 4.11 (t, 1H, $-C\boldsymbol{H}(Br)-$), 4.30 (s, 4H, $-OC\boldsymbol{H}_2C\boldsymbol{H}_2O-$), 5.88 (d, 1H, $C\boldsymbol{H}_2{=}CH-$), 6.18 (dd, 1H, $CH_2{=}C\boldsymbol{H}$), 6.48 (d, 1H, $C\boldsymbol{H}_2{=}CH-$).

Attachment of Initiators to the Surface of MWNTs. In a typical experiment, crude MWNTs (2.0 g) were added to 60% HNO_3 aqueous solution (30.0 mL). The mixture was treated with ultrasonic bath (40 kHz) for 10 min and stirred for 18 h at reflux. Then, the mixture was vacuum-filtered through 0.22 μm Millipore polycarbonate membrane and washed with distilled water until the pH of the filtrate was 7. The filtered solid was dried under vacuum for 24 h at 50 °C, obtaining MWNT-COOH (1.50 g).

Scheme 2. Synthetic Route of MWNT-*g*-$COOCH_2CH_2OCOC(CH_3)_2Br$ (MWNT-Br)



MWNT-COOH (1.4 g) was suspended in $SOCl_2$ (30 mL). This suspension was stirred at 70 °C for 16 h. The solid was then separated by filtration and washed with anhydrous CH_2Cl_2. Subsequently, it was dried under vacuum at 40 °C for 1 h, obtaining MWNT-COCl (1.18 g, yield 77%). 2-Hydroxyethyl 2′-bromoisobutyrate (9.6 g) in toluene (15 mL) was added to the one-neck flask that contained MWNT-COCl (1.0 g), and the reaction was stirred at 100 °C for about 24 h under a pure N_2 atmosphere. After the reaction was finished, the solvent was completely removed under vacuum, and the products were washed several times with ethanol (500 mL) and filtered. The

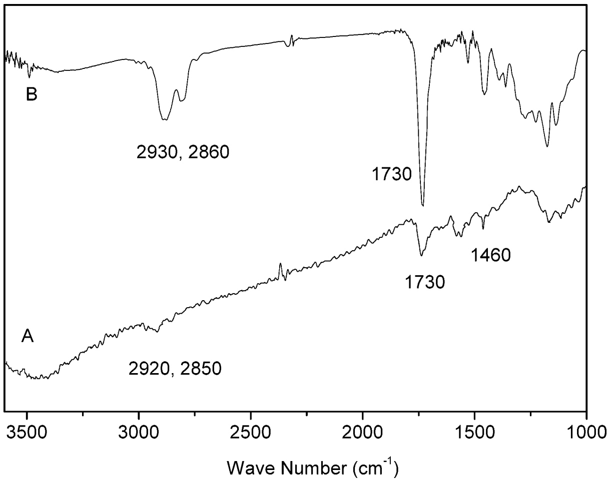


Figure 1. FT-IR spectra of multiwalled carbon nanotube (MWNT) surface grafted with $COOCH_2CH_2OCOC(CH_3)_2Br$ group (MWNT-Br, A) and multiwalled carbon nanotube grafted with hyperbranched polymers 1 (HP-MWNT, B).

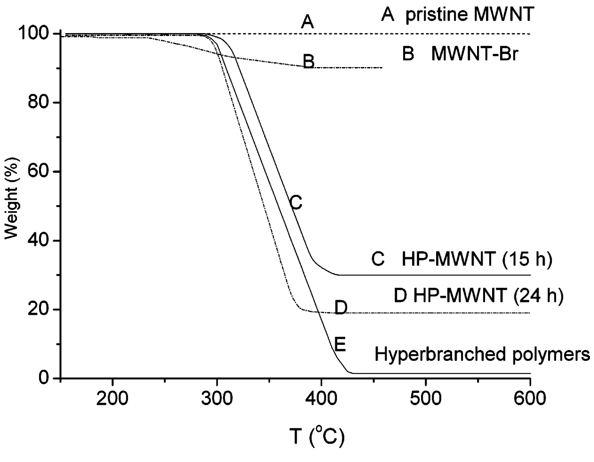
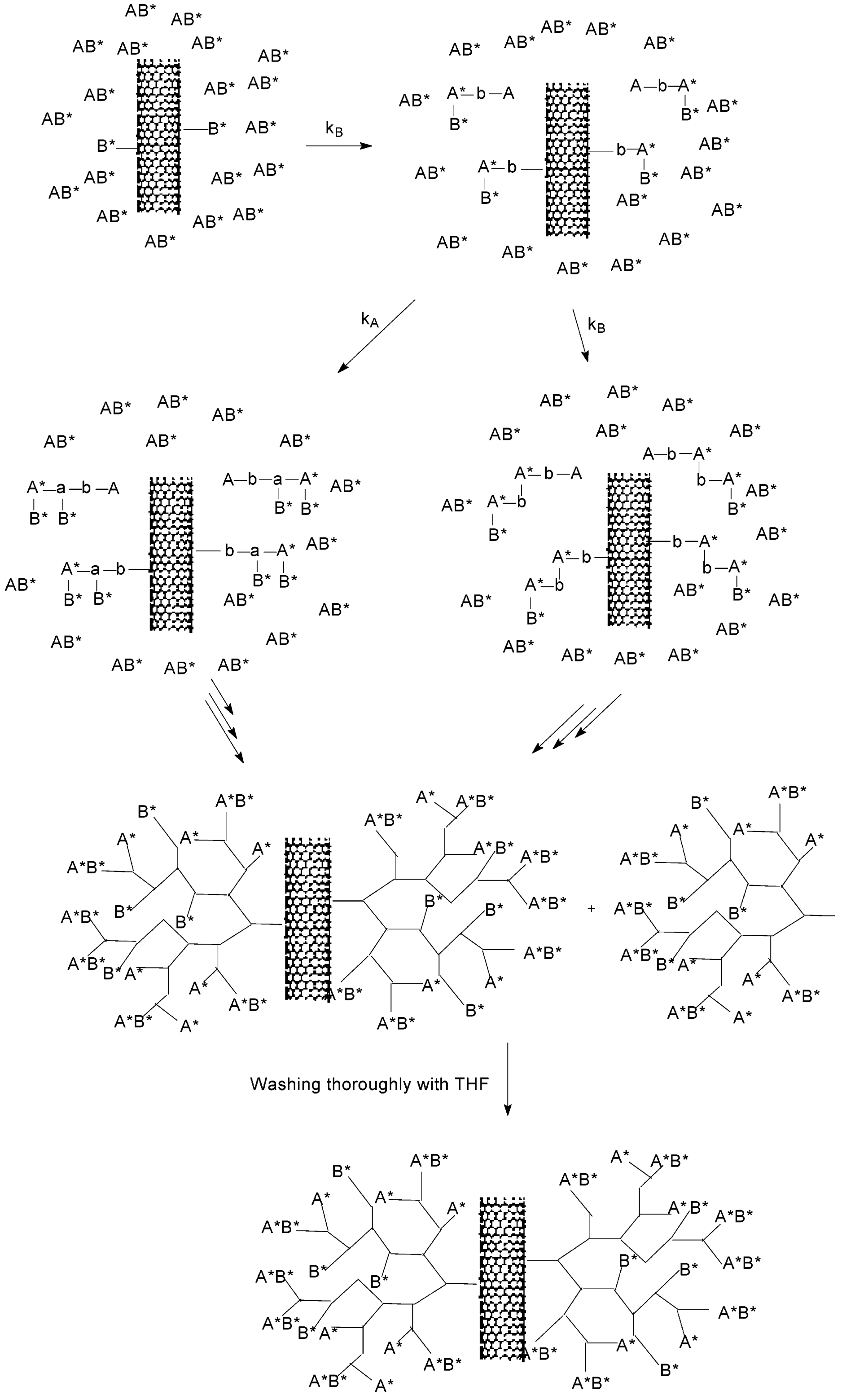


Figure 2. TGA curves of pristine multiwalled carbon nanotubes (MWNTs, A), MWNT-$COOCH_2CH_2OCOC(CH_3)_2Br$ (MWNT-Br, B), MWNT grafted with hyperbranched polymers 1 (C, polymerization time was 15 h), MWNT grafted with hyperbranched polymers 2 (D polymerization time was 24 h), and hyperbranched polymer (E) under N_2.

Scheme 3. Detailed Procedure of Hyperbranched Polymers Growing from the Surface of MWNT



initiator-attached MWNTs were dried at 50 °C for 10 h under vacuum. FT-IR (KBr): 2920 (C−H stretching), 1730 (C=O stretching), 1460 (C−H bending). TGA: 10% total weight loss at 250−420 °C. Anal. Found: C, 92.9; H, 0.47; Br, 3.8, which corresponds to about 0.63 initiator groups per 100 carbons.

SCVP of AB* Using MWNT-Br as Polyfunctional Initiator. In a typical polymerization, MWNT-Br (100.0 mg, 0.042 mmol initiators) was placed in a clean two-neck flask, and a solution of CuBr (7.2 mg, 5.0×10^{-5} mol) and ligand (1,1,4,7,7-pentamethyldiethylenetriamine, 17.5 mg, 1.0×10^{-4} mol) ([CuBr]:[L] = 1:2) in toluene was added into the flask with a syringe under N_2. The flask was placed in an oil bath maintained at 100 °C, then BBEA (1.0 mL, 3.7 mmol) was added into the flask slowly over 3 h, and the reaction was stirred for another 24 h. After 24 h, the heterogeneous polymerization solution was diluted with THF (50 mL) and kept stirring in a round-bottom flask for 1 h to dissolve the soluble polymer. The resultant products in THF were filtered by using 0.22 μm Millipore polycarbonate membrane and washed thoroughly with THF; this washing was repeated until the filtrate contained no polymer. The polymer-grafted MWNTs were dried at 40 °C for 24 h under vacuum.

SCVP of AB* in the Presence of Pristine MWNT. For comparison, SCVP of BBEA (1.0 mL, 3.7 mmol) catalyzed by CuBr (7.2 mg, 5.0×10^{-5} mol) and 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA, 17.5 mg, 1.0×10^{-4} mol) was carried out at 100 °C for 36 h in the presence of pristine MWNTs (80 mg). After finishing the polymerization, the product was washed with THF thoroughly. The resultant product was dried in an oven at 40 °C for 24 h under vacuum.

SCVP of AB* and *tert*-Butyl Acrylate Using MWNT-Br as Polyfunctional Initiator. MWNT-Br (100.0 mg, 0.042 mmol initiators) was placed in a clean two-neck flask, and a solution of CuBr (7.2 mg, 5.0×10^{-5} mol) and ligand (1,1,4,7,7-pentamethyldiethylenetriamine, 17.5 mg, 1.0×10^{-4} mol) ([CuBr]:[L] = 1:2) in toluene was added into the two-neck flask with a syringe under N_2. The flask was placed in an oil bath maintained at 100 °C, then a mixture of BBEA (1.0 g, 3.7 mmol) and *tert*-butyl acrylate (1.0 g, 7.8 mmol) was added into the flask slowly over 3 h, and the reaction was stirred for another 24 h. After 24 h, the heterogeneous polymerization solution was diluted with THF (100 mL) and kept stirring in a round-bottom flask for 1 h to dissolve the soluble polymer. The resultant products were filtered by using 0.22 μm Millipore polycarbonate membrane and washed thoroughly with THF; this washing was repeated until the filtrate contained no polymer. The polymer-grafted MWNTs were dried at 40 °C for 24 h under vacuum.

Results and Discussion

In SCVP via ATRP, when polyfunctional initiator (B^*_f) was added in the SCVP system, B^*_f can participate in the initiating polymerization of AB* to form B_f-containing hyperbranched polymers.[7] To attach a hyperbranched polymer shell to a multiwalled carbon nanotube (MWNT), ATRP surface initiator, a bromoisobutyryl fragment immobilized on MWNT was prepared as shown in Scheme 2. First, the carboxyl MWNT (MWNT-COOH) was prepared by oxidation of the crude MWNT with 60% HNO_3. Then MWNT-COCl, obtained from treating the MWNT-COOH with thionyl chloride, was reacted with excess 2-hydroxyethyl 2′-bromoisobutyrate in the presence of triethylamine to produce bromoisobutyrate functionalized MWNT (MWNT-Br). MWNT-Br was washed thoroughly with ethanol until the filtrate showed no 2-hydroxyethyl 2′-bromoisobutyrate. MWNT-Br was confirmed from the characteristic C−H and carbonyl stretching vibrations centered at 2920 and 1730 cm^{-1}, respectively, in the FT-IR spectrum (Figure 1). The quantity of the bromoester attached to the surface of MWNT was determined from its thermogravimetric analysis (TGA), which showed that the product was stable to 250 °C, upon which the product degraded, but it becomes stable above 420 °C, and the total weight loss was about 10%, corresponding to the decomposition of the bromoester on the surface of MWNT-Br (Figure 2B). The molar percent of the bromoester (B*) is about 0.6% with respect to carbon, which is consistent with the result obtained from elemental analysis.

MWNT-Br was used as a polyfunctional initiator (B^*_f) in the SCVP via ATRP to produce hyperbranched macromolecule functionalized MWNTs, as illustrated in Scheme 3.[6,10] During the SCVP of BBEA (AB*) via the ATRP process, because both the AB* inimer and the MWNT-Br have initiating groups capable of initiating the polymerization of vinyl groups, the chain growth can be started from both B* in the MWNT-Br and B* group in the inimer. Both the activated B* can add to the double bond, A, to form the ungrafted or grafted dimer with a new propagating center, A*. Further addition of AB* inimer or dimer to A* and B* centers results in hyperbranched macromolecules.[6] From the structures of B* of MWNT-Br and B* in AB* inimer, it is clear that B* of MWNT-Br has a higher activity of adding to the double bond than that of AB*;[7,11] thus, most of the B* immobilized on the surface of multiwalled carbon nanotubes has participated in initiating self-condensing vinyl polymerization via slow addition of AB* inimer. Of course, some ungrafted hyperbranched polymers were still produced during the polymerization. After the polymerization, the reaction mixture was diluted with THF, and the nanotubes were washed thoroughly with THF and then filtered to remove soluble ungrafted hyperbranched polymers. Washing was done until no polymer was found in the filtrate. The weight of the gray or black MWNT grafted with hyperbranched polymers (HP-MWNT) was much greater than MWNT-Br initiator added, indicating the presence of surface-grown hyperbranched macromolecules.

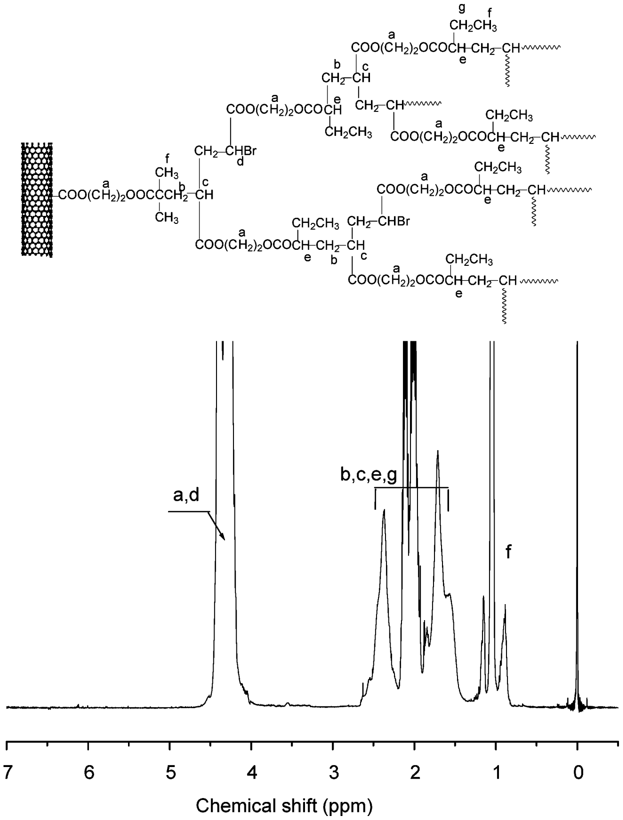


Figure 3. ^{1}H NMR spectrum of multiwalled carbon nanotubes (MWNTs) grafted with hyperbranched polymers 1 (polymerization time was 15 h).

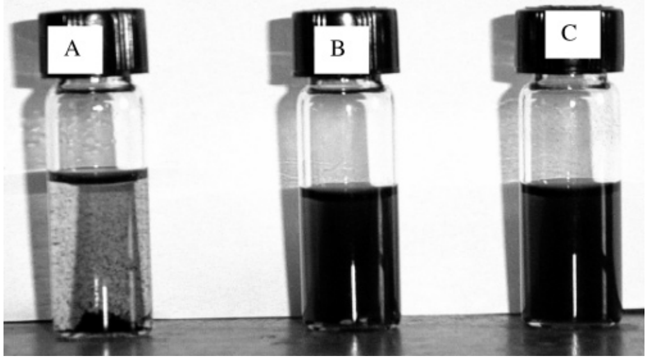


Figure 4. Solubility in organic solvent: MWNT-*g*-$COOCH_2CH_2OCOC(CH_3)_2Br$ in THF (A), MWNT grafted with hyperbranched polymers 1 in THF (B) and $CHCl_3$ (C).

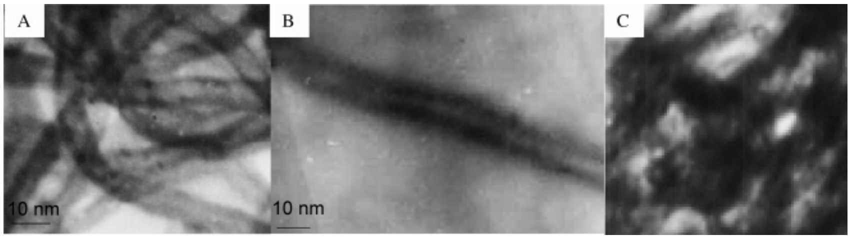


Figure 5. TEM images of MWNT-*g*-$COOCH_2CH_2OCOC(CH_3)_2Br$ (A), MWNT grafted with hyperbranched polymers (B), and dispersion of MWNT-*g*-$COOCH_2CH_2OCOC(CH_3)_2Br$ in hyperbarnched polymer solution in THF (C).

For comparison, SCVP of AB* was carried out in the presence of pristine MWNT. After the products was washed with THF thoroughly, it was found that there was no increased weight of MWNT and almost no hyperbranched macromolecules absorbed on MWNT from FT-IR result, which indicates that the ungrafted hyperbranched polymers can be removed from MWNT by washing with THF.

MWNT will decompose around 500 °C in the presence of air and around 800 °C under nitrogen.[5] The weight of hyperbranched polymers grafted on MWNT can be obtained from the TGA method. The TGA analysis of HP-MWNT in the presence of nitrogen showed a major decomposition in the temperature range at 280−420 °C, corresponding to surface grown hyperbranched polymers (Figure 2). Hyperbranched polymer was grown from the surface of MWNTs. To further confirm that the surface of MWNTs was grafted with the hyperbranched polymer, the sample was characterized by FT-IR and ^{1}H NMR. Comparison of the FT-IR spectra of HP-MWNT and MWNT-Br shows that the characteristic C−H and carbonyl stretching vibrations centered at 2920 and 1730 cm^{-1} were strengthened very much (Figure 1B), which indicates that the hyperbranched polymers were successfully grafted from the surface of MWNTs. Hyperbranched polymers grown from the surface of MWNT are clearly seen in the ^{1}H NMR spectrum (Figure 3). The observed proton signals are entirely due to hyperbranched polymers grown from MWNT.

Dispersion of MWNT-Br into THF was very difficult even after the carbon nanotubes were sonicated; sedimentation of MWNT-Br from THF appeared a few minutes after sonication. However, dispersion of HP-MWNT in THF and chloroform was very easy. Figure 4 shows the solubility of MWNT-Br in THF and HP-MWNT in THF and chloroform. It is clear that MWNT-Br is insoluble in THF, and there was much sedimentation of MWNT-Br at the bottom of the vial. However, the HP-MWNT is soluble in THF and chloroform, forming a homogeneous solution; there was no sedimentation observed even after 10 days.

For comparison, we attempted to disperse the mixture MWNT-Br (20%) and hyperbranched polymers (80%) into THF. This hyperbranched polymer is a poor dispersant for multiwalled carbon nanotubes in THF; some MWNT-Br precipitated from solvent in 1 day. All of the evidence supports solubilization of the MWNT by covalently bounded hyperbranched polymers and not adsorbed hyperbranched polymers. The images of the resultant MWNT obtained after 15 h polymerization and MWNT-Br were detected with transmission electron microscopy (TEM), as shown in Figure 5. In comparison with its precursor, we can find from TEM images that the HP-MWNT had a thin hyperbranched polymer layer (2−4 nm), and HP-MWNT was separated individually; however, it is clear that (MWNT-Br)s are bounded together. The TEM images of dispersion of MWNT-Br in hyperbranched polymers solution in THF were obtained and shown in Figure 5C; the images are similar to those of MWNT-Br, and carbon naotubes are also entangled together.

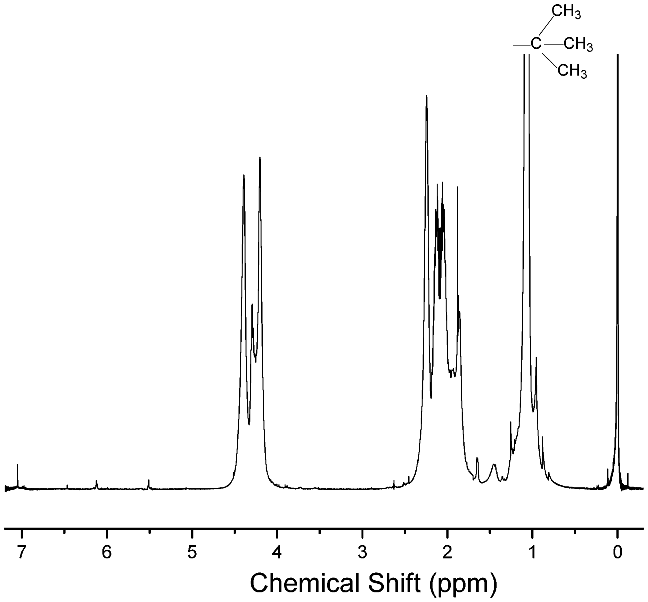


Figure 6. ^{1}H NMR spectrum of multiwalled carbon nanotube grafted with hyperbranched polymers containing *tert*-butyl acrylate units.

These MWNTs coated with hyperbranched shell have many terminal bromo-functional groups; these bromo-functional groups can be used as active sites for further functionalizing. In addition, this SCVP method can be extended to self-condensing atom transfer radical copolymerization to create MWNTs coated with a different functional shell. This self-condensing atom transfer radical copolymerization of the inimer (BBEA, AB*) and *tert*-butyl acrylate can produce multiwalled carbon nanotubes coated with hyperbranched polymer shell containing *tert*-butyl acrylate units. Its ^{1}H NMR spectrum is shown in Figure 6; it is clear that the characteristic peaks for poly(*tert*-butyl acrylate) can be observed besides the characteristic peaks for hyperbranched polymers. The hydrolysis of the ester functionality of branched poly(*tert*-butyl acrylate) creating acid-containing hyperbranched polymer shell coating MWNTs and the corresponding properties are in progress.

Conclusion

The self-condensing atom transfer radical polymerization method is successfully applied to functionalize MWNT, resulting in MWNT with a hyperbranched polymer shell. MWNT with a hyperbranched polymer shell has good solubility and is easy to disperse individually. This approach also provides an easy way to functionalize MWNTs further due to the hyperbranched polymers having a large number of functional groups and provides a method to homogeneously disperse MWNT conducting layers within electroluminescent devices.

Acknowledgment. The authors thank the support from the National Natural Science Foundation of China (50403015 and 20404003).

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MA047736R