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Polymers Grafted to Single-walled Carbon Nanotubes by Radical Polymerization

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Summary: Polymers have been grafted from single-walled carbon nanotubes (SWCNT) by ATRP and grafted to SWCNT by use of ATRP and azide end groups and by in situ polymerization. The SWCNT/polymer products are soluble indefinitely in good solvents for the polymers. AFM images indicate that the SWCNT are present as individual or bundles of only a few nanotubes.

Keywords: ATRP; composites; grafted polymers; polymer brushes; radical polymerization; single-walled carbon nanotubes

Introduction

Since single-walled carbon nanotubes (SWCNT) became commonly available, hundreds of papers and patents have reported modification of the nanotubes with polymers and dispersion of the nanotubes into polymer composites. The objectives generally are to enhance properties of the polymers by taking advantage of the high mechanical strength and the high electrical and thermal conductivity of the SWCNT.[1–7] Processing of the nanotubes, however, is difficult because the SWCNT exist as large bundles. Strong van der Waals attractions usually prevent attaining any large amounts of individual tubes, which would enable the maximum improvements in properties of composites. Consequently two research strategies have been pursued. (1) When the properties of individual SWCNT are essential, a very small amount of individual nanotubes is separated from a large amount of bundles of nanotubes. (2) When individual SWCNT are not essential, researchers work with the bundles. Multiwalled carbon nanotubes (MWCNT) are available in larger quantities and at lower cost than SWCNT. MWCNT do not have as high mechanical strength and electrical conductivity per unit mass as individual SWCNT. Because research in our laboratory emphasizes fundamental properties of materials more than applications, we have investigated only SWCNT. We have both materials objectives and processing objectives. The materials objectives are to make SWCNT polymer composites with improved electrical conductivity and mechanical strength at as low loading of nanotubes as possible, to prepare strong layer-by-layer thin films from polyelectrolyte grafted SWCNT, and to create electron acceptor components of photovoltaic materials. The process objectives are to devise simple procedures for preparation of these materials, to make efficient use of commercially-available nanotubes without extensive purification, and to disperse SWCNT efficiently into a variety of polymer composites. This short paper reviews progress toward meeting these objectives.

Methods for Polymer Binding to SWCNT

Polymers have been used to disperse SWCNT into composite materials by three general methods: noncovalent adsorption, *grafting from*, and *grafting to*.[1,5,8] Surfactants or polymers containing functional groups that adsorb to the sidewalls of SWCNT assist their dispersion into water or organic solvent with sonication or

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vigorous mechanical agitation. Many of the reported aqueous dispersions of individual SWCNT employ large excesses of anionic surfactants such as sodium dodecyl sulfate or sodium cholate or polyelectrolytes such as poly(sodium 4-styrenesulfonate). Among the most efficient dispersants in organic solvents are surfactants containing pyrene units and conjugated polymers such as poly(*m*-phenylene vinylene). The advantages of noncovalent dispersants are that they (1) require only mixing with the SWCNT in solvent and (2) have little effect on the electronic properties of the nanotubes. The disadvantage of noncovalent dispersants is that because they must be used in excess, the dispersions contain large amounts of unbound surfactant or polymer.

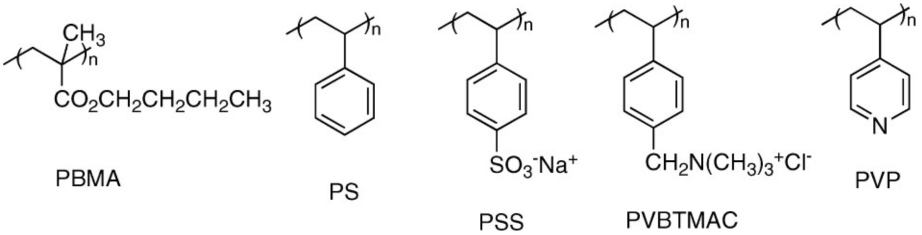
Grafting polymers from SWCNT offers advantages of control of the degree of functionalization of the nanotubes with grafted chains and control of the molecular weight distribution of grafted chains by living polymerization methods. The disadvantages are that initial functionalization of the nanotubes and subsequent chemical reactions of the functional nanotubes are necessary to create the nanotube-bound initiator sites. Functionalization converts sp^2 hybridized carbon atoms to sp^3, thereby altering the electronic properties. The electronic structures of SWCNT are most often observed by resonance Raman spectra and visible-NIR absorption and emission spectra. *Grafting from* procedures usually produce some unbound polymer as well as grafted polymer, so that removal of unwanted unbound polymer may be necessary.

Grafting polymers to SWCNT is experimentally simpler than grafting from because chemical functionalization of the nanotubes is not needed. Carbon-carbon double bonds on the sidewalls and end caps (if any) of SWCNT are strained and react by addition of radicals. C_{60} reacts with polymer radicals at rate constants only one or two powers of ten slower than diffusion controlled.[9] Rate constants for addition of polymer radicals to SWCNT must be slower than to C_{60} because SWCNT are less strained than C_{60}, but still much faster than propagation of polymer radicals with carbon-carbon double bonds of monomers. It is well known from other polymer grafting investigations that the number of chains that can be *grafted to* a surface is smaller than the number of chains that can be *grafted from* the surface. During a *grafting to* process a grafted chain occupies a large hydrodynamic volume near the surface that prevents additional polymer chains from entering that volume in space and forming new polymer-to-nanotube bonds. The much smaller degree of functionalization of *grafted to* SWCNT means that the electronic structures of the *grafted to* materials are much more like those of the parent SWCNT than are the electronic structures of *grafted from* SWCNT materials. The disadvantage of *grafting to* is that a large excess of unbound polymer is formed at the same time, which may not be a problem if the intended application is dispersion into a matrix of that same polymer, but requires extensive separation of nanotube-bound polymer from unbound polymer for an application such as photovoltaic thin films.

The structures of the polymers grafted to and from SWCNT that are described in this paper are in Scheme 1, and the specific samples that are described are listed in Table 1.

Grafting From

Adronov[10] and we[11] published the first *grafting from* experiments to produce polymer brushes from SWCNT, and Gao[12] published grafting polymer from MWCNT, without prior knowledge of each other's research. Our example was poly(butyl methacrylate) (PBMA) following the procedure in Scheme 2. HiPco SWCNT were oxidized in refluxing 2.6 M nitric acid for 18 hours to purify the nanotubes and to create carboxylic acid groups on the surface. (Such long nitric acid treatment destroys a large fraction of the nanotubes and cuts the tubes into short pieces. Milder



Scheme 1.
Polymers grafted to SWCNT by free radical methods.

nitric acid treatments retain all of the nanotube material, shorten the tubes much less, and still incorporate carboxylic acid groups that assist in dispersion of the nanotubes into polar solvents such as water and DMF.)[13] The carboxylic acid groups were converted to acid chloride groups and esterified with a pre-formed initiator of atom transfer radical polymerization (ATRP) to produce SWCNT with 4.1-4.3 initiator groups per 1000 SWCNT carbon atoms according to elemental and thermal gravimetric analyses. ATRP of BMA initiated by the functional nanotubes in 1,2-dichlorobenzene (DCB) produced both nanotube-grafted and ungrafted PBMA. The SWCNT/PBMA was separated by filtration through a PTFE membrane and washed thoroughly to remove soluble PBMA. The recovered gray solid contained 31% of SWCNT and 69% PBMA according to TGA analysis. The PBMA recovered from the filtrate and the PBMA recovered after cleavage from the nanotubes had the same molecular weight. AFM images of the PBMA-grafted nanotubes had an average height of the backbone of 2-3 nm, vs. 0.8-1.4 nm for the starting SWCNT. The AFM heights are consistent with bundles of original SWCNT breaking apart into individual tubes by functionalization and polymerization. NIR and Raman spectra of the PBMA-grafted SWCNT showed little change from those of the starting nanotubes, indicating that the polymer had little effect on the electronic structure. Polystyrene (PS) also was grafted from the same SWCNT by ATRP with similar results.[14]

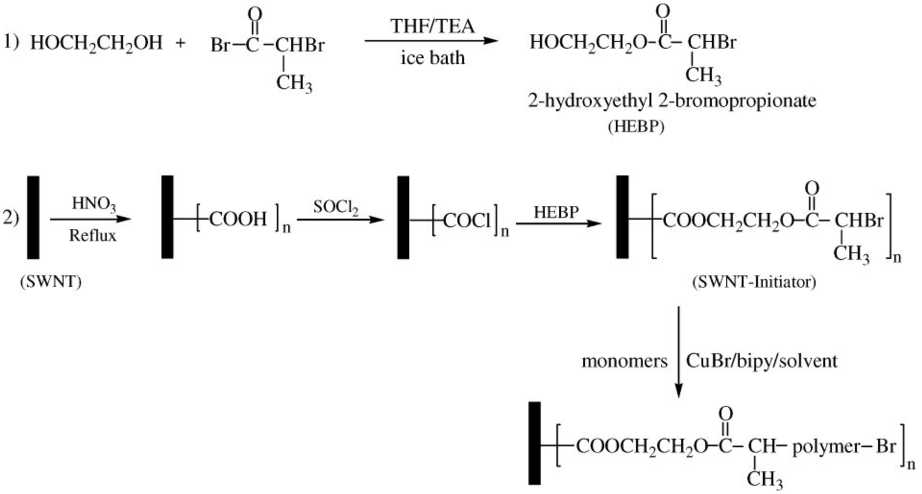
Grafting To

A variety of polymers have been *grafted to* SWCNT via reactions such as amidation and esterification of polymer amine and alcohol groups to nanotube carboxylic acid groups, cycloaddition of polymer azide end groups to nanotube alkyne groups, and in our laboratory by cycloaddition of nitrenes generated by thermolysis of azide end groups on polystyrene to sidewall double bonds of SWCNT.[14] Addition of PS-azide of $M_n = 3300$, which was synthesized by

Table 1.
Radical polymer-grafted SWCNT

Polymer	SWCNT	Method	Solvent	% SWCNT [a]	Tube diameter, nm [b]
PBMA	HiPco [c]	ATRP from	DCB	31	2-3
PS	HiPco	ATRP from	DCB	25	1.8
PS	HiPco	ATRP-PS-N_3 to	DCB	15	2.5
PS	HiPco	PS-TEMPO to	NMP	70-75	not measured
PSS	HiPco	in situ radical to	H_2O	55	1.2
PVBTMAC	CoMoCat [d]	in situ radical to	H_2O	62	0.4-2
PVP	HiPco	in situ radical to	DMF	61	1.5

[a] Weight percent left after TGA to 800 °C under nitrogen. [b] From AFM height images. [c] Carbon Nanotechnologies, Inc. [d] Southwest Nanotechnologies, Inc.

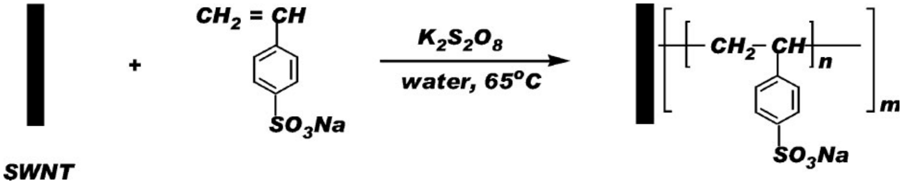


Scheme 2.
Grafting polymer brushes from SWCNT.

ATRP, grafted a larger number of chains to SWCNT, according to Raman and NIR spectra. Fewer PS chains were grafted from, and the M_n reached 40,000. The fewer grafted chains of higher molecular weight is due to their much larger hydrodynamic volume.

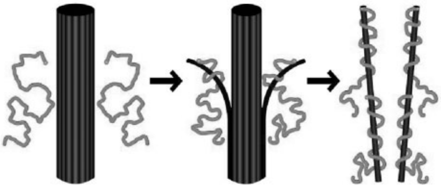
Our preferred *grafting to* method is in situ radical polymerization, during which polymer radicals add to SWCNT sidewall and end cap strained double bonds. In principle *grafting to* should work on SWCNT as received with no further purification. The rate of radical addition should be proportional to the concentration of polymer radicals in solution and to the surface area of dispersed nanotubes available. In practice *grafting to* may require that the SWCNT be oxidized to low conversion, because the amount of starting nanotube bundles that can be dispersed in the reaction solvent is much greater after gentle oxidation.

The most thoroughly characterized *grafted to* material made by polymer radical addition is SWCNT/poly(sodium 4-styrenesulfonate) (PSS).[15] The method is shown in Scheme 3. The *grafting to* experiments were performed with HiPco SWCNT as received from Carbon Nanotechnologies, Inc. The starting SWCNT left 12% or more of residue after TGA in air. The residue is assumed to be Fe_2O_3 from the catalyst used to produce the SWCNT. To prepare SWCNT/PSS, sodium 4-styrenesulfonate (NaSS) and SWCNT in a 100/1 weight ratio were stirred in water, degassed, and polymerized with potassium persulfate as initiator. The product dispersion was centrifuged gently to remove catalyst residues, ultrafiltered and washed to separate nanotube solids from polymer



Scheme 3.
In situ grafting of PSS to SWCNT.

solution, and finally ultracentrifuged to precipitate the nanotubes and leave amorphous carbon material in the supernatant liquid. The precipitated nanotubes were redispersed in water and analyzed by AFM, TEM, Raman spectroscopy, visible-NIR absorption, and fluorescence spectroscopy. Nanotubes did not precipitate from the aqueous dispersion for at least 8 months. The S/C atom ratio from elemental analysis of a dried sample indicated a 55/45 weight ratio of SWCNT/PSS. The AFM height image showed an average tube diameter of 1.2 nm, corresponding to individual tubes. Most importantly, the fluorescence spectrum showed a series of NIR peaks that were different from those of the starting SWCNT and different from those of SWCNT suspended in water by excess ungrafted PSS. Fluorescence detects only individual or small bundles of semiconducting SWCNT because metallic SWCNT, which comprise about 1/3 of HiPco samples, quench fluorescence. HiPco samples are estimated to contain about 50 isomers of SWCNT. When SWCNT were dispersed in water with independently prepared PSS, addition of sodium dodecyl sulfate (SDS) displaced the PSS from the nanotubes, whereas the PSS in the grafted sample was not displaced by SDS, indicating that the grafted PSS was covalently bound, not just adsorbed. A pictorial drawing in Scheme 4 shows a likely mechanism of the process: Growing radical PSS in solution adds to the outer nanotubes of bundles, and by osmotic force strips individual PSS-grafted SWCNT away from the bundles. In summary, this procedure for *grafting to* by in situ polymerization transformed commercial SWCNT that were contaminated with catalyst residues and amorphous carbon material into individually dispersed polyelectrolyte-grafted SWCNT. The contaminants were removed during isolation of the SWCNT/PSS. Most other reported procedures require oxidation/purification of the commercial SWCNT before polymer grafting.



Scheme 4.
Proposed mechanism of grafting to and break bundles down to individual SWCNT.

SWCNT grafted with the cationic polyelectrolyte, poly[(vinylbenzyl)trimethylammonium chloride] (PVBTMAC) were synthesized from CoMoCat SWCNT by almost the same procedure.[16] CoMoCat SWCNT differ from HiPco SWCNT by having narrower diameters (0.6-1.0 nm), fewer isomers, and a smaller fraction of metallic SWCNT.[17] More than 90% of the semiconducting CoMoCat SWCNT consist of only five isomers. The polycation-grafted SWNT were 62/38 SWCNT/PVBTMAC by weight and were individual tubes from AFM height analyses.

Poly(4-vinylpyridine) (PVP) was *grafted to* HiPco SWCNT by AIBN-initiated polymerization in DMF dispersions.[18] Purification by methods similar to those used for the aqueous polyelectrolyte-grafted SWCNT gave grafted materials containing a 61/39 weight ratio of SWCNT/PVP. The grafted materials gave stable dispersions in DMF, methanol, and 2-propanol. AFM showed individual tubes and small bundles with average diameter 1.5 nm. Raman spectra and NIR absorption spectra indicated a low degree of functionalization of the SWCNT. Thin films of the SWCNT/PVP were prepared by layer-by-layer deposition alternating with poly(acrylic acid) (PAA) up to six regular hydrogen-bonded bilayers.

Photovoltaic Materials

The polyanion-grafted and polycation-grafted SWCNT were investigated as electron acceptors in aqueous solutions and in thin films. Oppositely-charged porphyrins were the electron donors. Visible absorption spectra of the porphyrins underwent frequency shifts, and the porphyrin emission spectra were quenched as SWCNT were titrated into the solution, indicating that SWCNT and porphyrin were strongly attracted to one another electrostatically. The SWCNT-porphyrin nanohybrids were characterized by transient absorption spectra and photoelectrochemical measurements. Photoexitation in solution gave radical ion pairs with lifetimes as long as 2.2 μs. Photoelectrodes were constructed by layer-by-layer deposition of SWCNT and porphyrins on indium tin oxide coated glass. The electrodes gave internal photon-to-current efficiencies of 3.8% for the SWCNT/PVBTMAC and 9.9% for a mixture of SWCNT and unbound PVBTMAC when a potential of 0.5 V was applied.[16] Aqueous solutions of the polyanionic SWCNT/PSS and cationic porphyrins showed the same kind of spectroscopic behavior with emission lifetimes of tens of μs and solar energy conversion potential.[19,20] Similarly SWCNT/PVP-ZnPor hybrids in DMF solutions gave photoexcited radical-ion-pair states consisting of oxidized porphyrin and reduced SWCNT, and the photoexcited states had μs lifetimes.[21]

Polystyrene Composites

Well dispersed SWCNT in polymer composites should increase electrical conductivity, tensile modulus, and tensile strength at very low loading of nanotubes. In theory a dispersion of individual nanotubes having an aspect ratio of 1000 should have a percolation threshold of electrical conductivity at approximately 0.05 vol %.[22] In practice with many different polymers and many methods of dispersion the percolation threshold of electrical conductivity appears in most cases at about 0.1-1.0 vol % of nanotubes.[23] None of these composite materials has been shown to consist primarily of individual SWCNT rather than bundles. Although it might possible be acceptable to manufacture a photovoltaic material from individual SWCNT that comprise only a small fraction of the starting SWCNT, the lower market value of polymer composites requires efficient use of the nanotubes. Our method of preparation of polystyrene composites is to disperse the nanotubes into a DMF or N-methylpyrrolidinone (NMP) solution of polystyrene and precipitate the composite by pouring the solution into water.[8] Maximum use of commercial SWCNT and percolation threshold of electrical conductivity at 0.4-0.5% SWCNT were attained by gently oxidizing the SWCNT to improve dispersion in DMF before precipitating the composite. Gravimetric analyses proved that no nanotubes were lost during the oxidation procedure. AFM analyses showed that most of the nanotubes in the dispersions were in bundles 3-6 nm in diameter. Similar results were obtained with three different types of SWCNT: HiPco, CoMoCat, and SWCNT prepared by laser desorption. Recently we grafted polystyrene of different average molecular weights to SWCNT by use of stable free radical (TEMPO) capped polystyrene and prepared composites by the same method using NMP as the solvent.[24] The weight fraction of polystyrene grafted was approximately the same regardless of the molecular weight (3,000, 15,000, or 50,000) of the polystyrene, which suggests that the amount of PS grafted is limited by the amount of space available for solvated PS chains on the surface of the nanotubes. Similar results were reported for grafting of a different nitroxyl-terminated PS to SWCNT.[25] The percolation threshold of electrical conductivity of PS-grafted SWCNT in PS composites was about the same as SWCNT dispersed in PS composites, but the absolute conductivities of the grafted composites at nanotube contents above the threshold were less than those of the composites prepared with ungrafted polystyrene. We attribute the lower conductivities to an insulating barrier of the grafted polystyrene between SWCNT when the nanotubes are in percolation contact.

Conclusion

Polymers can be grafted both to and from SWCNT by living and by conventional radical polymerization methods. The hybrid materials are soluble indefinitely in good solvents for the polymers. The *grafting from* method requires prior chemical modification of the nanotube surface with an initiator. The *grafting to* method has been performed without prior purification of the SWCNT, with separation of catalyst residues and carbonaceous impurities after grafting. A drawback of the *grafting to* method is the simultaneous formation of a large amount of ungrafted polymer, which must be separated from the SWCNT for some applications. The grafted materials have been applied as components of photovoltaic thin films and as electrically conducting filler in polystyrene composites.

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