Surface Modification of Multiwalled Carbon Nanotubes by Poly(2-vinylpyridine): Dispersion, Selective Deposition, and Decoration of the Nanotubes

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Surface Modification of Multiwalled Carbon Nanotubes by Poly(2-vinylpyridine): Dispersion, Selective Deposition, and Decoration of the Nanotubes**

By *Xudong Lou, Christophe Detrembleur, Christophe Pagnoulle, Robert Jérôme,* Vera Bocharova, Anton Kiriy,* and Manfred Stamm*

Carbon nanotubes (CNTs) have unique electronic, mechanical, thermal, and chemical properties that justify the steadily increasing attention paid to them.[1] For a number of applications, the spatial organization of CNTs and their intimate and robust association with nanometer-sized objects of a well-defined functionality are of prime importance. Nevertheless, the problem of processability remains a severe limitation to the extensive use of CNTs, which explains the recent interest in making the surfaces of CNTs organophilic. Several strategies have been reported recently, based on the non-covalent and covalent bonding of organic molecules to CNTs.[2–4] Other than small molecules, polymer chains have been chemically attached to the tubes, with the purpose of making them dis-

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persible in organic solvents and within polymer matrices. In this respect, "grafting-from" and "grafting-to" methods have been proposed.[5–7] The "grafting-from" approach relies on the immobilization of initiators for the living/controlled polymerization of various monomers, followed by chain growth from the surface and formation of polymer brushes of possibly high grafting density. The anionic grafting of polystyrene is one example,[5] whereas initiators for the controlled radical polymerization of butyl methacrylate, methyl methacrylate, and styrene by atom transfer radical polymerization (ATRP) have also been attached to CNT surfaces and used in "grafting-from" processes.[6,7] However, contamination of the final product by metal residues may be a concern. The "grafting-to" method is based on the reaction of preformed polymer chains with the substrate to be modified,[8] as illustrated recently by Qin et al.[7] in the covalent grafting of polystyrene to CNTs by a multistep process via the cycloaddition of azide end-capped polystyrene.

This paper aims at reporting on the reaction of sp^2-hybridized carbons of CNTs with poly(2-vinylpyridine) (poly2VP) chains terminated with the 2,2,6,6-tetramethylpiperidinyl-1-oxyl (TEMPO) radical-stabilizing group. Upon heating, polymeric radicals that are reactive towards the surface are released, as shown in Scheme 1.

There are several reasons for choosing poly2VP. First of all, its solution behavior can be changed significantly, being a hydrophobic polymer in apolar solvents and a cationic polyelectrolyte in water at low pH.[9] Moreover, poly2VP has inorganic-ion complexing properties,[10] which are precursors to nanometer-scale semiconducting particles. Finally, the positively charged polymer interacts spontaneously with oppositely charged solid surfaces.

Poly2VP of controlled molecular weight (3–5 kg mol⁻¹), narrow molecular-weight distribution (polydispersity index of 1.25) and end-capped by TEMPO (poly2VP-TEMPO) was prepared by the controlled-radical polymerization of 2-vinylpyridine in the presence of benzoyl peroxide and TEMPO (Table 1).[11] A 0.3 wt.-% dispersion of CNTs in dry toluene

was stirred with a one-hundred-fold weight excess of poly2VP-TEMPO at 120 °C for 7–48 h (Table 1).

Table 1. Molecular characteristics of TEMPO end-capped poly(2-vinylpyridine) and grafting ratios of the CNTs. In the grafting reactions, 2.0 g of (co)polymer and 20 mg of CNTs were mixed in 6 ml of toluene at 120 °C.

Sample	M_n[a] [kg mol⁻¹]	M_w/M_n [a]	Reaction Time [h]	Grafting Ratio [b] [%]
a	3.0	1.25	24	10
b	5.0	1.30	7	6.0
c	5.0	1.30	24	12
d	5.0	1.30	48	11.5

[a] Number-average molecular weight (M_n) and weight-average molecular weight (M_w) were determined by size-exclusion chromatography (SEC) using polystyrene standards. [b] The grafting ratio (wt.-% of poly2VP with respect to the modified CNTs) was determined by thermal gravimetric analysis (TGA).

After reaction, the modified CNTs (CNT-*g*-P2VP) were recovered by filtration through a 0.2 μm Teflon membrane. They were re-dispersed in tetrahydrofuran (THF) and filtered again. This procedure was repeated at least four times until no more polymer was extracted. In order to completely remove possible traces of non-grafted poly2VP chains, CNT-*g*-P2VP was dispersed in acidic water (HCl, pH 2) and recovered by centrifugation (4000 g, 1 h).

In contrast to neat CNTs, the CNT-*g*-P2VP tubes were easily dispersed in organic solvents and acidic water. Figure 1a compares the stability of 0.05 wt.-% dispersions of CNT-*g*-P2VP and pristine CNTs in water at different pHs 3 h after ultrasonication. The visual appearance of the dispersions is drastically different, depending on pH and whether the CNTs were surface modified or not. In order to confirm that the dispersion stability does not merely result from physisorption of poly2VP to the nanotube surface, CNTs were treated with poly2VP ($M_n = 5$ kg mol⁻¹) under the same experimental conditions, except that the chains did not contain the TEMPO
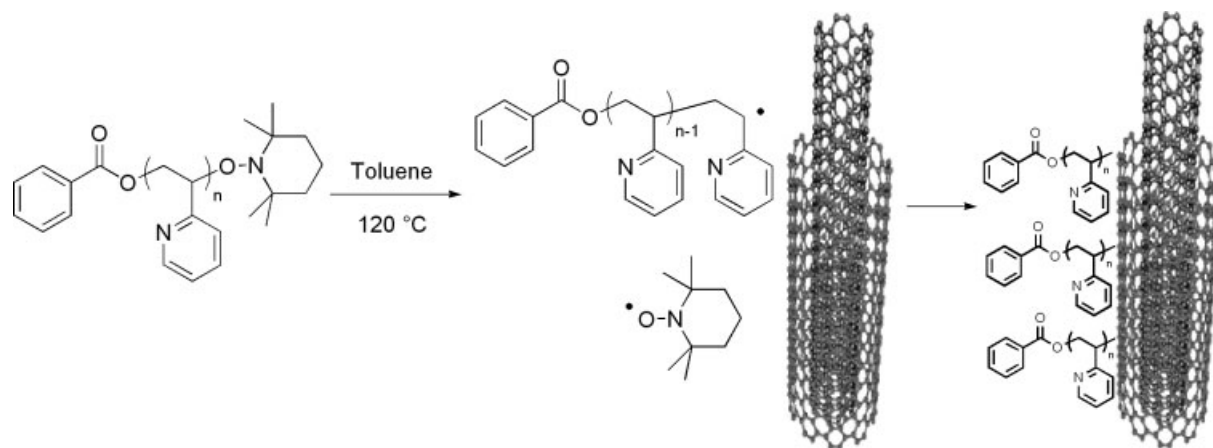
Scheme 1. Heating of TEMPO-terminated poly2VP chains causes the TEMPO group to dissociate, resulting in radical-terminated chains which are grafted to CNTs.
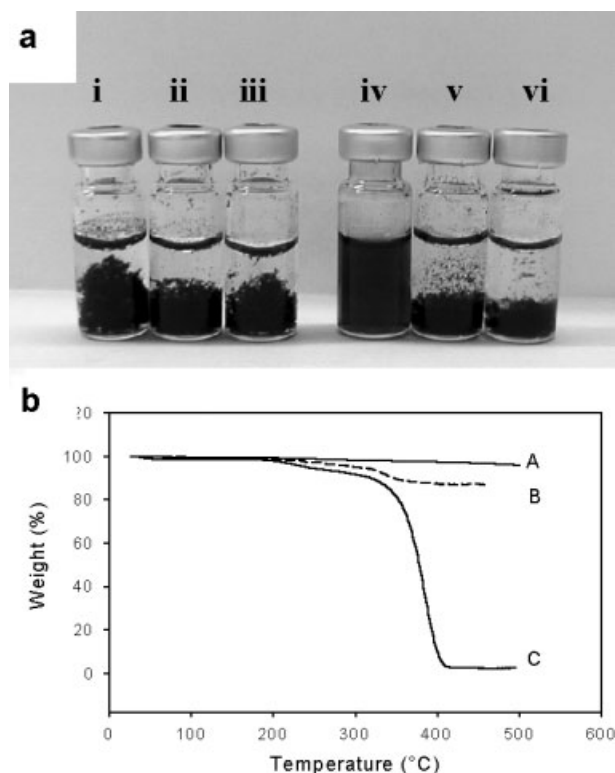
Figure 1. a) CNT dispersions in different aqueous solutions 3 h after ultrasonication. Pristine CNTs in: i) acidic water (HCl, pH 2.0); ii) neutral water; iii) basic water (NaOH, pH 12); and CNT-*g*-P2VP nanotubes in: iv) acidic water (HCl, pH 2.0); v) neutral water; and vi) basic water (NaOH, pH 12). b) Thermogravimetric analysis (TGA) under nitrogen at a heating rate of $10\,°C\,min^{-1}$: A) pristine CNTs; B) CNT-*g*-P2VP; C) P2VP-TEMPO ($M_n = 5000$).

Figure 2. TEM micrographs of a) pristine CNTs; and b) CNT-*g*-P2VP in HCl solution (scale bar: 50 nm). Atomic force microscopy (AFM) images of c) CNT-*g*-P2VP deposited onto a Si-wafer from acidic water (pH 2, HCl); d) CNT-*g*-P2VP as in (c), but after decoration of the poly2VP shell by Prussian Blue (PB) nanoclusters; e,f) cross-sections taken along the pristine and the modified tubes shown in (c) and (d), respectively.

end group (the poly2VP was synthesized by anionic polymerization). In sharp contrast to CNT-*g*-P2VP, the carbon nanotubes did not form any stable dispersion in THF.

The absorbance of CNT-*g*-P2VP dispersions in 0.5 M HCl decreased gradually from the UV to near-IR regions, similar to previously reported spectra of other surface-modified CNTs.[12] The poly2VP chains grafted to CNTs were selectively degraded by heating at a rate of $10\,°C\,min^{-1}$ under nitrogen. Figure 1b compares the thermal gravimetric analysis (TGA) curves for pristine CNTs, poly2VP, and CNT-*g*-P2VP. Curve B shows that the poly2VP chains grafted onto CNTs were degraded at the same temperature as poly2VP (curve C), whereas neat CNTs (curve A) were stable in the same temperature range. Therefore, the grafting ratio, defined as the weight percent of the grafted polymer with respect to the nanotubes, can be determined by TGA. It is found to be in the 6–12 % range, as listed in Table 1.

Direct observation of the CNTs confirmed the impact of poly2VP grafting on the disentanglement of the tubes after dispersion in water at low pH. Upon casting of the dispersion onto a carbon-coated copper grid, transmission electron microscopy (TEM) shows a (locally) densely entangled network of pristine CNTs (Fig. 2a). In contrast, a very loose network
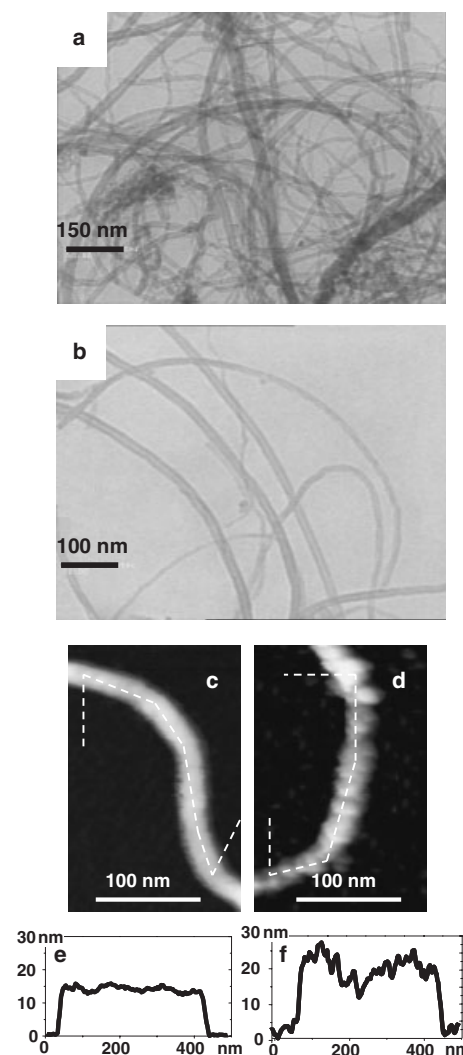
of CNTs is observed after surface modification, in line with a homogeneous dispersion in water and a homogeneous deposition on the grid, which accounts for the lower number of tubes per surface area (Fig. 2b). Because of the limited resolution of TEM, the shell of poly2VP chains cannot be directly observed. In order to overcome this limitation, observations by atomic force microscopy (AFM) were carried out. Because of the extensive disentanglement of the CNT bundles by poly2VP grafting, individual nanotubes could indeed be deposited onto a solid support and directly observed. Figure 2c and Figure S1a Supporting Information) show representative AFM images of an isolated CNT-*g*-P2VP tube, 10–20 nm in diameter, with smooth sidewalls. Once again, the poly2VP shell is unobserved. However, we recently reported a simple and efficient method to decorate positively charged polymer

chains, even on rough surfaces. Water-soluble Prussian Blue (PB) nanoclusters interact with these cationic chains all along their backbone.[13] Therefore, CNT-*g*-P2VP nanotubes deposited onto a Si-wafer were immersed in an aqueous solution of PB nanoclusters at pH 2 for several minutes. As shown by Figures 2d,S1b, after careful washing of the sample by acidic water, particles several nanometers in height clearly impart roughness to the sidewall of the nanotubes as a result of the decoration of positively charged chains on their surface. This is not seen in the case of pristine CNTs. Of course, the amount of material deposited at the periphery of CNTs could be modulated by the molecular weight and the grafting density of the poly2VP chains. This selective-deposition technique, by complexation of metal derivatives, raises promising prospects for the in-situ formation of Pd,[10] Au, CdS, and CdSe clusters by standard chemistry,[14] thereby modifying the CNTs with novel components, e.g., for optoelectronic devices.[15]

For various applications, CNTs must be deposited as individual objects on a surface, but more importantly, one should be able to deposit them very selectively on a particular spot of a multicomponent surface. In order to illustrate that such an achievement is feasible, positively charged CNT-*g*-P2VP dispersed in acidic water was deposited onto a (macroscopically) patterned surface, consisting of oppositely charged surface areas. For this purpose, a freshly cleaned Si wafer was completely immersed in an aqueous solution of poly(diallyldimethylammonium chloride) (PDADMAC) for 10 min, thereby charging the *whole* surface positively. After thorough washing with water, *half* of the wafer was vertically dipped into an aqueous solution of polystyrene sulfonic acid (PSA) (0.1 g L^{-1}) for a few seconds followed by repeated washing. *Half* of the Si-wafer surface area is thus *positively charged* due to the adsorbed PDADMAC layer, and the other half is *negatively charged*, being covered by PSA. This two-component surface was then completely immersed in a dispersion of CNT-*g*-P2VP in acidic water (HCl, pH 2) for 30 s, and washed with water again. Figure 3 is the AFM image of the boundary area of the substrate after deposition of the carbon nanotubes. A sharp boundary between the positive PDADMAC layer and PDADMAC–PSA bilayer is observed as a 1 nm high step (marked by the solid arrow). The upper part of the image is coated by PDADMAC and only one nanotube can be observed (marked by the dashed arrow). In sharp contrast, a rather homogeneous deposition of CNTs is observed on the PSA layer, which is strong evidence that tube deposition can be highly selective on a chemically heterogeneous surface.

In conclusion, an alternative "grafting-to" technique has been successfully tested for the polymer modification of carbon nanotubes. The direct covalent bonding of polymeric radicals, released by the thermolysis of TEMPO-end-capped poly2VP, to pristine nanotubes resulted in the extensive disentanglement of the original CNTs bundles. The poly2VP-grafted chains form a shell covering the CNTs, and their amount can be controlled to some extent. This shell makes the CNTs dispersible in organic solvents as well as in acidic water, and is an ideal support for the immobilization of (met-
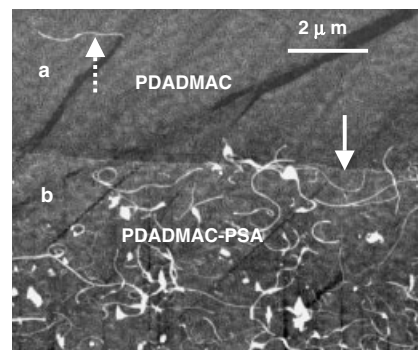

Figure 3. AFM image of a macroscopically patterned Si-wafer, after dipping into a dispersion of CNT-*g*-P2VP in acidic water. The upper part (a) was covered by a positively charged PDADMAC layer, and the lower part (b) by a negatively charged PDADMAC–PSA bilayer. The high selectivity of the CNT-*g*-P2VP is thus demonstrated.

al) nanoclusters on the CNT surfaces. The positively charged poly2VP shell is responsible for the selective deposition of CNTs onto oppositely charged surfaces. These results open the way to novel nanometer-scale systems where CNTs and nano-objects with specific properties can be integrated.

Experimental

Commercially available carbon nanotubes (CNTs) (Nanocyl S.A., Belgium, 50 μm long, average inner diameter 6 nm, outer diameter 25 nm, and purity higher than 95 wt.-%) were used without further purification. 2,2,6,6-Tetramethylpiperidinyl-1-oxyl (TEMPO) end-capped poly(2-vinylpyridine) (poly2VP) was synthesized as reported elsewhere [11]. Si wafers (from Wacker Chemitronics) were repeatedly cleaned (at least three times) in a ultrasonic bath with dichloromethane for 5 min, and then treated by a cleaning solution of NH$_4$OH and H$_2$O$_2$ at 60 °C for 1 h.

Poly2VP Covered by Prussian Blue (PB) Clusters: A K$_4$Fe(CN)$_6$· 3H$_2$O solution (0.5 g L^{-1}, 1.18 mmol L^{-1}) in acidic water (HCl, pH 2.0) and a FeCl$_3$ solution (0.024 g L^{-1}, 0.148 mol L^{-1}), also in pH 2.0 water, were extensively mixed for several minutes. The substrate covered with poly2VP-grafted CNTs (CNT-*g*-P2VP) was dipped into the freshly prepared dispersion of PB clusters at ambient temperature for 3 min, and then washed with water. Finally, the substrate was dried under an argon flux.

Size-Exclusion Chromatography (SEC): SEC was performed in tetrahydrofuran at a flow rate of 1.0 mL min^{-1} at 40 °C using a SFD S5200 liquid chromatograph equipped with a RI2000 refractive index and a S3240 UV-vis detector, and calibrated with polystyrene standards.

Thermogravimetric Analysis (TGA): A TA Instruments TGA Q500 thermal analyzer was used in the 25–500 °C range, with a heating rate of 10 °C min^{-1} under nitrogen.

Atomic Force Microscopy (AFM) Measurements: A Multimode AFM instrument (Digital Instruments, Santa Barbara) was operated in tapping mode. Silicon tips with 10–20 nm radius, a spring constant of 30 N m^{-1}, and a resonance frequency of 250–300 kHz were used.

Transmission Electron Microscopy (TEM) Measurements: A Philips CM 100 apparatus, equipped with a Gatan 675 charge-coupled device (CCD) camera for digital imaging, was used at an accelerating voltage of 100 kV.

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Collective Optical Behavior of Cationic Water-Soluble Dendrimers**

By *Shu Wang*, *Brent S. Gaylord*, and *Guillermo C. Bazan**

Dendrimers are hyperbranched macromolecules with well-defined three-dimensional architectures and a large number of terminal (external) groups that can be used to control prop-

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erties such as size, molecular weight, topology, and surface functionality.[1,2] Dendrimers containing optically active components have properties similar to natural photosynthetic systems, which harvest light and channel multiple excitations to defined low-energy sites.[3–6] Recent interest has grown in utilizing the light-harvesting (or antenna-like) properties of dendrimers to achieve sensory signal amplification in the presence of suitable energy or electron acceptors.[7–10]

Water-soluble conjugated polymers display an analogous ability to collect excitations and deliver them to focal points by energy-transfer mechanisms. Cationic versions have been used for strand-specific DNA or RNA detection[11–14] via a mechanism that involves cooperative electrostatic interactions.[15–18] Because of the problems intrinsic to statistical polymerization reactions, the ill-defined nature of conjugated polymers (i.e., polydispersity and molecular weight variations) makes detailed structure–property determination difficult. Furthermore, structural rigidity limits their ability to conform effectively with various secondary structures presented by biological macromolecules.[19] The precise molecular structures of dendrimers[20,21] make them attractive fluorescence donor substitutes for DNA assays. Also of relevance is that the flexibility of polyamidoamine (PAMAM) dendrimers and favorable electrostatic interactions between negatively charged nucleic acids and positively charged surfaces has led to their use as tools in gene-transfer studies.[22–24]

In this contribution we provide a series of cationic PAMAM dendrimers functionalized with optical units (Scheme 1), which serve to examine how variations in molecular size, charge, and terminal surface groups may be used to optimize fluorescence-based sensory processes. The chemical structure of the surface groups and the number of charged groups can be varied to regulate optical properties and net macromolecular charge. The overall size of the macromolecule and the number of optical units are determined by the dendrimer generation.

Four generations of phenylene-fluorene-functionalized polyamidoamine (PAMAM) dendrimers were synthesized via the route depicted in Scheme 2. Each family was synthesized by coupling pentafluorophenol 4-[9′,9′-bis(6″-*tert*-butoxycarbonylaminohexyl)-2′-fluorenyl]-benzoate or pentafluorophenol 4-[9′,9′,9″,9″-tetra(6‴-*tert*-butoxycarbonylaminohexyl)-7′,2″-bisfluoren-2′-yl]-benzoate with commercially available amine-terminated PAMAM dendrimers. The dendrimers and all intermediates were characterized by ^{1}H NMR and ^{13}C NMR spectroscopy, high-performance liquid chromatography (HPLC), and electrospray mass spectrometry (for G_0 and G_2 only). The ^{1}H NMR spectra of the *t*-butoxycarbonyl (Boc)-protected dendrimers in CDCl$_3$ were used to calculate the degree of surface functionalization. Specifically, the ethylene signals, with peaks from 3.2 to 3.6 ppm and from 2.3 to 2.7 ppm, are representative of the dendrimer interior. Peaks from 7.2 to 8.0 ppm correspond to the aromatic signals, which are unique to the oligofluorene units. The ratio of integrated aromatic/CH$_2$ proton signals indicates greater than 95 % surface functionalization for the smaller dendrimers. For example, in Boc-G_0-1F, there are 44 aromatic and 36 CH$_2$ protons, which

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