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Synthesis of Pyrene-Containing Polymers and Noncovalent Sidewall Functionalization of Multiwalled Carbon Nanotubes

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Pyrene-containing polymers have been prepared for noncovalent sidewall functionalization of multiwalled carbon nanotubes (MWNTs). (1-Pyrene)methyl 2-methyl-2-propenoate (PyMMP) has been synthesized and copolymerized with methyl methacrylate (MMA). Poly(ethylene-*co*-butylene)-*b*-poly(MMA-*co*-PyMMP) diblocks have also been synthesized. The surface of MWNTs, produced by both the CCVD and arc discharge methods, has been modified by these copolymers for making them dispersible in a variety of organic solvents. The modified MWNTs have been characterized by thermogravimetric analysis, transmission electron microscopy, and atomic force microscopy.

Introduction

Since their discovery in 1991,[1] carbon nanotubes (CNTs) are receiving steadily increasing attention because of their unique structural and electrical properties.[2] Moreover, they are potential modifiers for polymer matrixes to improve their mechanical properties and electrical conductivity.[3] However, preparation of valuable polymer−CNTs nanocomposites strongly depends on the extent of the CNTs dispersion and the strength of the interfacial adhesion. Although polymer−CNTs nanocomposites can be prepared by merely mixing CNTs with the polymer in the melt,[4] an appropriate chemical treatment of the nanotube surfaces or the use of a compatibilizer is needed for a fine dispersion to be observed. It is the reason why surface properties of CNTs have been modified by grafting of organic molecules, including polymer chains.[5] "Grafting from" and "grafting to" methods have been reported for the covalent bonding of polymers onto CNTs. The grafting from technique relies on the immobilization of initiators onto the tubes followed by surface-initiated polymerization and formation of possibly dense polymer brushes. For instance, carbanions have been generated at the CNTs' surface by reaction with an anionic compound (*sec*-butyllithium), followed by the surface-initiated polymerization of styrene.[6] According to a similar strategy, ATRP initiators have been attached to CNTs and poly(*n*-butyl methacrylate), poly(methyl methacrylate), and polystyrene chains have been grown from the surface.[7,8] These techniques are, however, time-consuming. As example of the grafting to technique, Qin et al.[8] have reported on the cycloaddition reaction of polystyrene-N_3 onto CNTs. A multistep process is required for the synthesis of the azide end-capped polystyrene, and a long reaction time is an additional drawback. Although the covalent bondings of (macro)molecules to CNTs improve their solubility and processability, they alter their structure and electronic properties.

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CNTs have also been solubilized in organic solvents and water by polymer wrapping[9−13] with, for example, poly(vinylpyrrolidone),[9] polystyrene sulfonate,[9] and poly(arylene ethynylene)s.[11] This technique that keeps the nanotube structure and electronic properties unmodified has also been implemented with pyrene derivatives because of $\pi-\pi$ stacking interactions with the graphitic surface of CNTs.[11−13] Substituents of pyrene have been selected and used to link, for example, natural proteins[12] or initiators of ring-opening metathesis polymerization[14] to CNTs. Noncovalent immobilization of proteins and other biopolymers on CNTs[12] opens new fields of application, such as biosensoring and antibody binding.[15] On the basis of the affinity of pyrene for CNTs, some of us have reported on the solubilization of CNTs in water and various organic solvents by noncovalent sidewall modification with pyrene-containing polymers of different nature and molecular architecture.[16]

This paper aims at reporting on a simple and versatile nondestructive strategy for the noncovalent functionalization of multiwalled carbon nanotubes (MWNTs) by polymers containing pendant pyrene groups. (1-Pyrene)-methyl 2-methyl-2-propenoate (PyMMP) has been prepared in high yield and copolymerized with methyl methacrylate (MMA) by a radical initiator. Diblock copolymer consisting of this random copolymer and a preformed poly(ethylene-*co*-butylene) chain have also been synthesized. Pyrene-containing random and block copolymers have been used to modify MWNTs that have been characterized by TGA, TEM, and AFM.

Experimental Section

Materials. Commercially available thick MWNTs produced by Catalytic Carbon Vapor Deposition (CCVD) were supplied by “Nanocyl S. A.” Belgium (50-μm long with an average inner diameter of 6 nm, an outer diameter of 25 nm, and a purity higher than 95 wt %). Arc discharge MWNTs were obtained from “Materials and Electrochemical Research Corporation” (MER) in Tucson, Arizona. This raw material contained 10−40% nanotubes with 5−20 graphitic layers, a 2−15-nm diameter, and a 1−10-μm length. These MWNTs were used without further purification. 1-Pyrenemethanol, methacryloyl chloride, 1,14,7,10,10-hexamethyltriethylenetetramine (HMTETA), and triethylamine were purchased from Aldrich. Kraton Liquid 1203 (hydroxyl terminated copolymer of ethylene and butylene, PEB, $M_n = 4200$) was supplied by Shell Chemical Company. α,α'-Azoisobutyronitrile (AIBN, 98%) was supplied by Fluka. Methyl methacrylate was dried over calcium hydride and distilled under reduced pressure just before use. Commercial grade PMMA was supplied by ICI with a number average molecular weight of 42 000.

Synthesis of (1-Pyrene)methyl 2-methyl-2-propenoate (PyMMP). 1-Pyrenemethanol (5 g; 0.022 mol) was added to a solution of triethylamine (9.0 mL; 0.065 mol) in 250 mL of dried THF. Methacryloyl chloride (6.3 mL; 0.065 mol) was added dropwise under stirring at 0 °C. The reaction was conducted at room temperature overnight. The reaction medium was filtered, THF was evaporated, and the solid residue was dissolved in methylene chloride (300 mL). This solution was washed with 1.0 M HCl solution, then with an aqueous solution of sodium hydrogen carbonate, and finally with water. After drying over magnesium sulfate ($MgSO_4$), the organic solution was filtered, and the solvent was evaporated under reduced pressure. A yellow solid was collected, dissolved in 5 mL of THF, and precipitated by addition of 10 mL of methanol. After one night at −20 °C, the product was collected by filtration. The THF/methanol solution was evaporated again, and the residue purified by the same procedure (total yield: 77%).

^{1}H NMR($CDCl_3$, δ): 7.99−8.19 (m, 9H, aromatic H), δ 6.15 (s, 1H, $CH_2{=}C$), δ 5.89 (s, 2H, CH_2O), δ 5.56 (s, 1H, $CH_2{=}C$), δ 1.97 (s, 3H, CH_3).

Synthesis of Poly(MMA-*co*-PyMMP). In a typical experiment, 0.5 g of PyMMP (1.7 mmol) and 0.04 g of AIBN (0.24 mmol) were added into a glass reactor and degassed by vacuum-nitrogen cycles (three times). Then, 4 mL of MMA (37 mmol) and 5 mL of degassed toluene were added, and the mixture was heated at 60 °C under stirring for 24 h. After cooling to 25 °C, 10 mL of toluene was added, and the polymer was recovered by precipitation in methanol and dried.

Synthesis of Poly(ethylene-*co*-butylene) Macroinitiator (PEB−Br). Thirty grams (7.1 mmol) of poly(ethylene-*co*-butylene) (Kraton Liquid 1203) was added into a solution of 1.54 g (15.3 mmol) of triethylamine in 300 mL of dry and degassed methylene chloride. A solution of 1.9 mL of 2-bromoisobutyryl bromide (15.5 mmol) in 150 mL of dried methylene chloride was added dropwise under stirring at 0 °C. Temperature was allowed to increase up to room temperature, the reaction medium was kept under stirring overnight, and half the volume of methylene chloride was evaporated and replaced by toluene. This solution was filtered, and the polymer was precipitated in methanol. After two additional reprecipitations from toluene to methanol, the macroinitiator was dried under reduced pressure.

Synthesis of Copolymer PEB-*b*-Poly(MMA-*co*-PyMMP). Fourteen grams of PEB−Br (3.4 mmol), 4.0 g of PyMMP (13 mmol), and 0.48 g of CuBr (3.4 mmol) were added into a glass reactor and degassed by vacuum-nitrogen cycles (three times). Sixty milliliters of degassed toluene, 7.1 mL of MMA, and 0.77 g of HMTETA (3.4 mmol) were then added, and the mixture was heated at 85 °C under stirring overnight. After cooling to 25 °C, 50 mL of toluene was added, and the solution was filtered through silica gel to eliminate the metal residue. The copolymer was recovered by precipitation in methanol and dried.

Noncovalent Functionalization of MWNTs. In a typical experiment, 20 mg of pyrene-containing copolymer and 20 mg of MWNTs were added into 250 mL of THF and stirred at room temperature overnight. After sonication for 30 min, the solution was used for TEM analysis. To remove the unattached copolymer, MWNTs were collected by filtration with a 0.2-μm Teflon membrane and washed with THF, a good solvent for the copolymer. The nanotubes were dispersed again in 150 mL of THF by sonication for 15 min and filtered. This procedure was repeated three times.

Characterization. Thermogravimetric analysis (TGA) was carried out with a TA Instruments TGA Q500 thermal analyzer in the 25−600 °C range, at a 20 °C/min rate, under nitrogen. ^{1}H NMR spectrum was recorded in $CDCl_3$ at 400 MHz in the FT mode with a Bruker AN 400 apparatus at 25 °C. Size exclusion chromatography (SEC) was performed in THF at a flow rate of 1.0 mL/min at 40 °C using an SFD S5200 liquid chromatograph equipped with an RI2000 refractive index and an S3240 UV/vis detector and calibrated with polystyrene standards. TEM was performed with a Philips CM 100 apparatus, equipped with a Gatan 675 CCD camera for digital imaging, at an accelerating voltage of 100 kV. A drop

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Table 1. Molecular Characteristics of Statistical Copolymers of (1-Pyrene)methyl 2-methyl-2-propenoate (PyMMP) and Methyl Methacrylate (MMA)[e]

entry	F[a]	AIBN (%)	F[b]	$M_n{}^c \times 10^{-4}$	M_w/M_n	n[d]
1a	0.045	1.0	0.02	12	1.80	23
1b	0.045	10	0.02	1.6	2.0	3.0

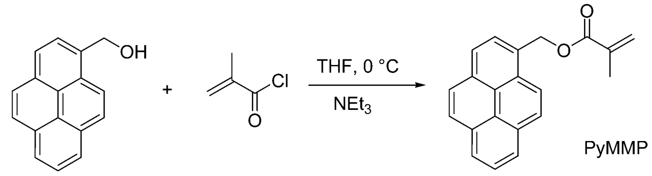
[a] Molar fraction of PyMMP in the comonomer feed. [b] Molar fraction of PyMMP in the copolymer (determined by ^{1}H NMR in $CDCl_3$). [c] Measured by SEC in THF, with polystyrene standards. [d] Average pyrene content (groups/chain). [e] Conditions: toluene, 60 °C, 24 h.

of MWNTs dispersion was deposited on a TEM carbon-covered grid, and the solvent was allowed to evaporate. High-resolution TEM was performed on a LEO 922 OMEGA operating at 200 kV in zero-loss energy mode. MWNTs were deposited from a dilute suspension in toluene onto copper grids coated with a carbon film. The nanotube surface was imaged by atomic force microscopy in the lateral force mode. The frictional contrast in the images arises not only arises from the topography, but also from changes in the material composition. Reliable information on the chemical composition of the surface can be drawn from the proper control of the chemical species at the tip surface.[17] The tips were treated by UV-ozone to remove any organic contaminent and to generate oxygenated functions on the surface. The tips obtained by this treatment are highly hydrophilic.[18] Lateral force measurements were carried out with an Autoprobe CP microscope (Thermomicroscopes, Sunnyvale, CA) operating in air with a 100-μm scanner equipped with ScanMaster detectors for correction of nonlinearity and hysteresis effects. Cantilevers were standard Si_3N_4 microlevers with pyramidal tips. Hydrophilic tips were prepared by UV-ozone treatment of silicon nitride (Thermomicroscopes, Sunnyvale, CA) tips.

Results and Discussion

Synthesis of Pyrene-Containing Polymers. (1-Pyrene)methyl 2-methyl-2-propenoate (PyMMP) was synthesized by reaction of 1-pyrenemethanol with methylacryloyl chloride in THF, as shown in Scheme 1. This

Scheme 1



yellow solid has been purified by recrystallization in a mixture of methanol/THF (yield = 77%). Primary experiments have shown that copolymerization of PyMMP with MMA was controlled when initiated by 2-bromopropionate in the presence of the CuBr/1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) catalyst, in toluene at 85 °C. Not only molecular weight is predictable, but molecular weight distribution is narrow.[16] However, traditional free-radical copolymerization initiated by α,α′-azoisobutyronitrile (AIBN) in toluene at 60 °C has been used in this study, so avoiding contamination of the copolymer by metal residues. As reported in Table 1, two copolymers of same composition (2 mol % PyMMP) have been prepared, with a different molecular weight, that is, 1.2×10^5 and 1.6×10^4, respectively. Figure 1 shows the typical ^{1}H NMR spectrum of the poly(MMA-*co*-PyMMP) copolymers. These major peaks can be assigned to the methylene protons of the backbone ($\delta = 0.8-1.1$ ppm) and the methyl protons of the backbone ($\delta = 1.9$ ppm) and of the ester ($\delta = 3.7$ ppm), respectively. Resonances for the methylene protons adjacent to pyrene ($\delta = 5.8$ ppm) and pyrene protons ($\delta = 8.0-8.3$ ppm) are observed with a low intensity. Figure 2 compares the SEC traces of the same copolymer recorded by the dual refractive index and the ultraviolet detector (254 and 366 nm). The elution peaks are monomodal and detected at the same elution time, which confirms that the pyrene-containing units are incorporated into the copolymer chains.

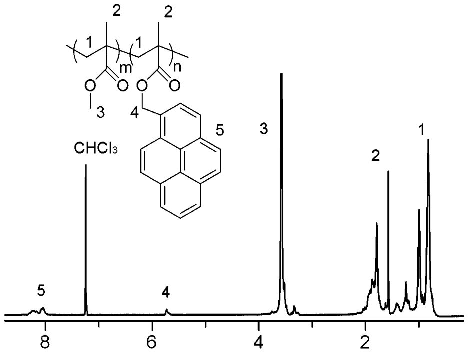


Figure 1. ^{1}H NMR spectrum for a statistical copolymer of MMA and PyMMP in $CDCl_3$ (copolymer 1b, Table 1).

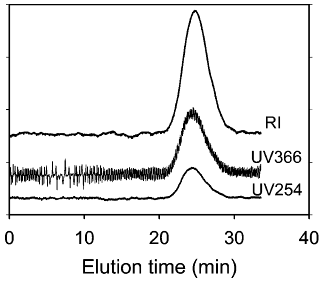
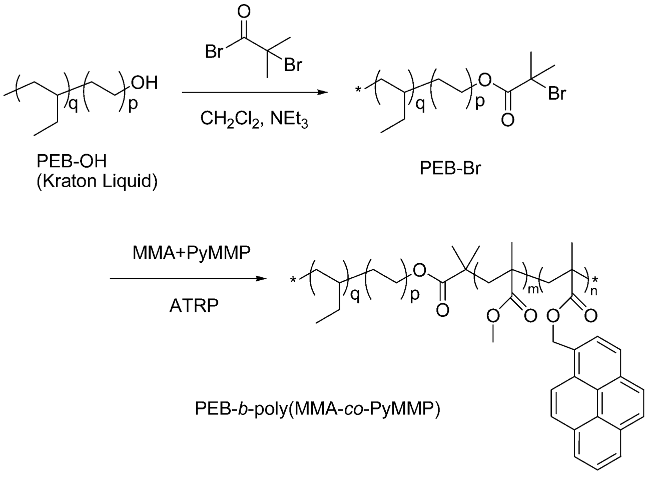


Figure 2. SEC chromatograms for a statistical copolymer (copolymer 1b, Table 1) of MMA and PyMMP with refractive index (RI) and ultraviolet detectors (at 366 nm and UV254 at 254 nm).

Scheme 2



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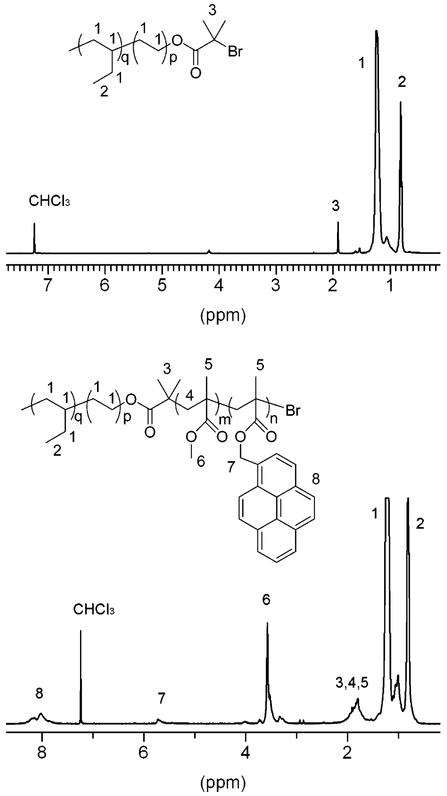
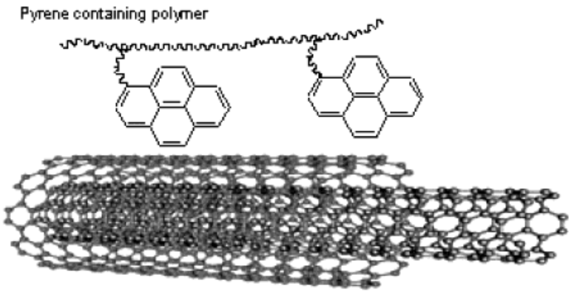


Figure 3. ^{1}H NMR spectrum for the PEB−Br macroinitiator and the PEB-*b*-PMMAPyMMP diblock in $CDCl_3$.

Poly(MMA-*co*-PyMMP) has also been associated to a poly(ethylene-*co*-butylene) chain (PEB) in a diblock structure (Scheme 2). A hydroxyl terminated PEB was reacted with 2-bromoisobutyryl bromide in CH_2Cl_2, with formation of a PEB macroinitiator (PEB−Br). Figure 3 (top) shows the ^{1}H NMR spectrum and the assignment of the signals for PEB−Br. The peak at $\delta = 1.9$ ppm is characteristic of the protons of the methyl groups at the chain end. The disappearance of the peak at 3.6 ppm for the hydroxyl end-group is consistent with the completeness of the reaction. ATRP of PyMMP and MMA initiated by PEB−Br in the presence of the CuBr/HMTETA catalyst, in toluene at 85 °C, leads to the expected copolymer, PEB-*b*-PMMAPyMMP, with controlled molecular weight ($M_{n,SEC} = 2.1 \times 10^4$, polystyrene standards) and narrow molecular weight distribution ($M_w/M_n = 1.20$). The ^{1}H NMR spectrum in Figure 3 (bottom) shows clearly the comonomer units of the PEB block, and the MMA and PyMMP units of the copolymer chain. From the integration of these peaks, the degree of polymerization for MMA is calculated as 25.6 and that of PyMMP as 3.2. Furthermore, multidetector SEC analysis confirms that the pyrene units are part of the copolymer chain.

Noncovalent Surface Modification of Nanocyl MWNTs by Poly(MMA-*co*-PyMMP). Pyrene-containing organic molecules interact with carbon nanotubes surface by $\pi\angle\pi$ stacking.[11−13,15] Therefore, pyrene-containing polymers are expected to interact with MWNTs as shown in Scheme 3 and to increase the stability of MWNTs dispersion in good solvents for PMMA. In dispersion of the surface-modified MWNTs within PMMA, the MWNTs/PMMA interaction should be improved and the load transferred from the polymer to the nanofiller, as well. Nanocyl MWNTs (produced by CCVD method) and poly(MMA-*co*-PyMMP) have been mixed in THF by sonication (30 min) at room temperature, the copolymer to MWNTs weight ratio ($R_{initial}$) being in the 0.5−10 range. In contrast to neat MWNTs dispersion, that settles down within seconds, a stable carbon nanotubes dispersion is observed in THF when $R_{initial}$ is higher than 2. To confirm that the dispersion stability does not merely result from interaction between carbon nanotubes and PMMA, MWNTs dispersion was prepared under the same experimental conditions, except that poly(MMA-*co*-PyMMP) was replaced by PMMA. No stable dispersion is observed. A few drops of an MWNTs dispersion with $R_{initial} = 5$, in a THF solution of poly(MMA-*co*-PyMMP) (0.5 g/L) and

Scheme 3



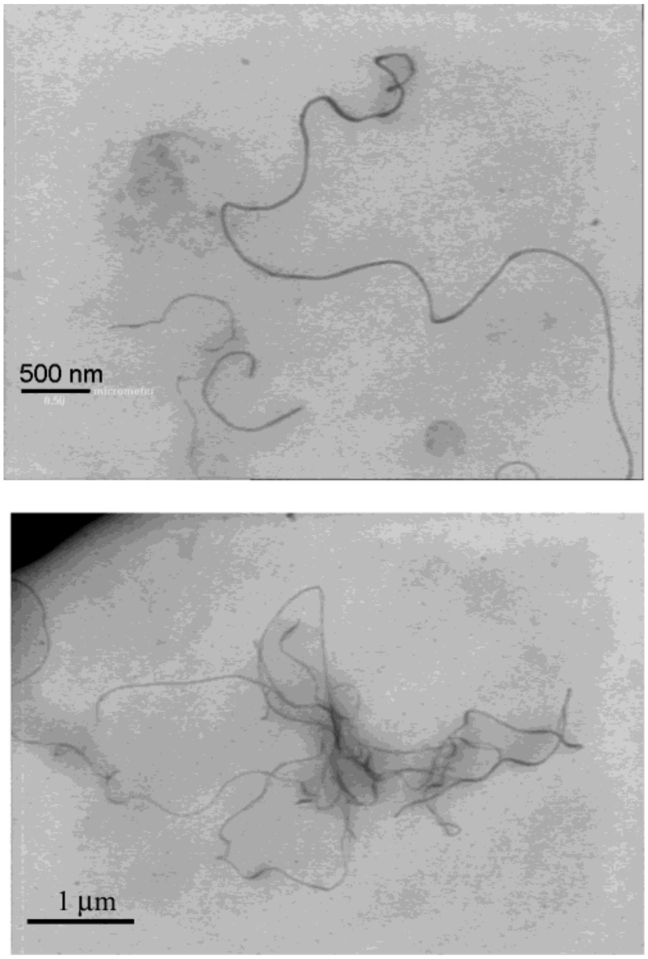


Figure 4. TEM images at two different magnifications for nanocyl MWNTs after dispersion in a THF solution of poly(MMA-*co*-PyMMP) ($R_{initial} = 5$).

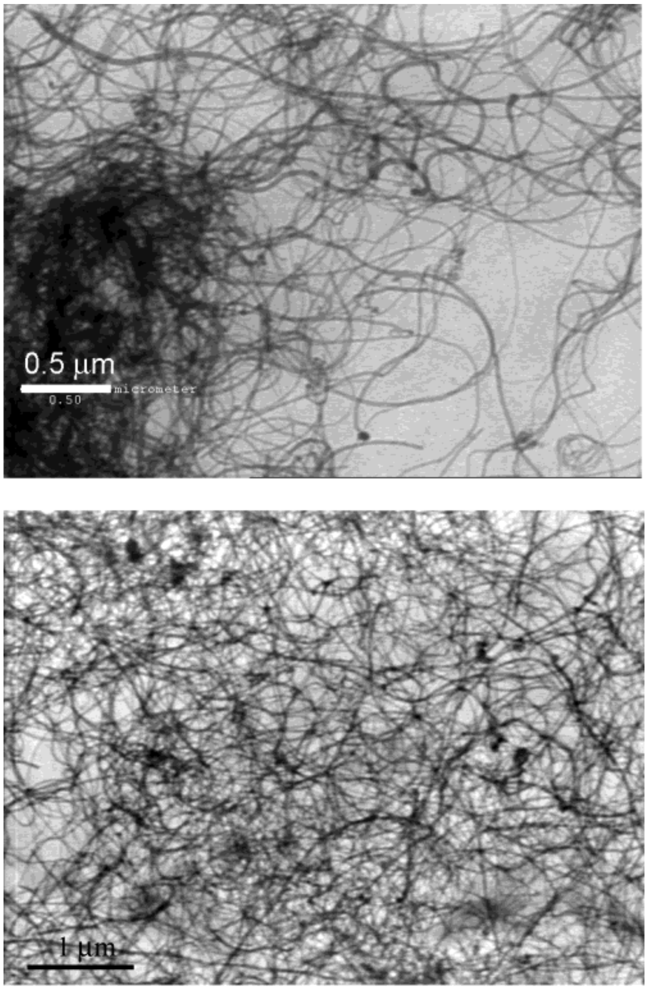


Figure 5. TEM images at two different magnifications for nanocyl MWNTs after dispersion in a THF solution of PMMA ($R_{\mathrm{initial}} = 5$).

PMMA (0.5 g/L), respectively, were deposited onto carbon-coated copper grids, and the solvent was let to evaporate. Figure 4 shows typical TEM images of MWNTs modified by poly(MMA-*co*-PyMMP) (copolymer 1b, in Table 1). Very well separated nanotubes are observed in contrast to densely entangled nanotubes that persist with PMMA (Figure 5). This indicates that the poly(MMA-*co*-PyMMP) chains immobilized at the surface of the MWNTs form an effective steric barrier against agglomeration.

MWNTs dispersed in a solution of poly(MMA-*co*-PyMMP) were recovered by filtration and washed with THF. Dispersion in THF, followed by filtration and washing, was repeated two more times to eliminate the copolymer excess. The grafting ratio (GR) of the copolymer, defined as the mass ratio of the immobilized copolymer to modified MWNTs, was estimated by thermogravimetric analysis (TGA). For sake of comparison, dispersion of MWNTs in THF was sonicated, and the nanotubes were collected by filtration, dried, and analyzed by TGA. Trace A in Figure 6 was recorded for the control MWNTs, which are stable until 600 °C with negligible weight loss, whereas trace D shows that the poly(MMA-*co*-PyMMP) copolymer ($M_{\mathrm{n}} = 1.2 \times 10^5$) is completely degraded at 400 °C range. The surface-modified MWNTs ($R_{\mathrm{initial}} = 5$) show a 23% weight loss (GR = 0.23) at the same temperature as poly(MMA-*co*-PyMMP) (trace C, Figure 6), leaving behind the thermally stable MWNTs. To confirm that $\pi-\pi$ stacking results in the irreversible adsorption of copolymer chains, these surface-modified MWNTs were redispersed in THF, recovered by filtration, and washed with THF. TGA was repeated and shows that the GR remains unchanged (traces C and E, Figure 6). After dispersion in a PMMA solution, filtration, and washing, no polymer is immobilized at the surface of the MWNTs as assessed by trace curve B in Figure 6. This observation confirms, if necessary, that the interaction of the carbon nanotubes with PMMA is quite weak, compared to poly(MMA-*co*-PyMMP).

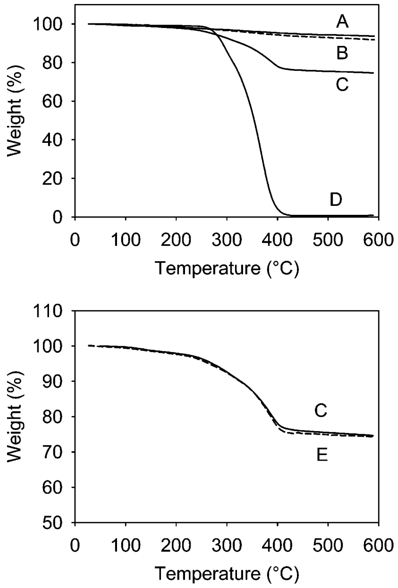


Figure 6. TGA traces for (A) MWNTs dispersed in THF under sonication (solid line); (B) MWNTs dispersed in a THF solution of PMMA under sonication (dashed line); (C) MWNTs modified by poly(MMA-*co*-PyMMP) ($M_{\mathrm{n}} = 1.2 \times 10^5$, $R_{\mathrm{initial}} = 5$); (D) pure poly(MMA-*co*-PyMMP); (E) same sample as C, after redispersion in THF and filtration and washing with THF (dashed line).

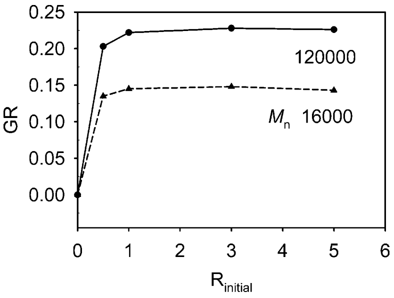


Figure 7. Dependence of GR (grafting ratio) on R_{initial} for poly(MMA-*co*-PyMMP) of different molecular weight.

Figure 7 illustrates the dependence of GR on R_{initial} for two poly(MMA-*co*-PyMMP) copolymers of different molecular weight. For both the copolymers, GR increases first and levels off when R_{initial} is higher than 1. This observation strongly suggests that the surface of MWNTs is totally covered by the copolymer at $R_{\mathrm{initial}} = 1$. The maximum GR value increases with the molecular weight of the copolymer, which means that the average thickness of the copolymer layer is as high as the molecular weight copolymer is high, which makes

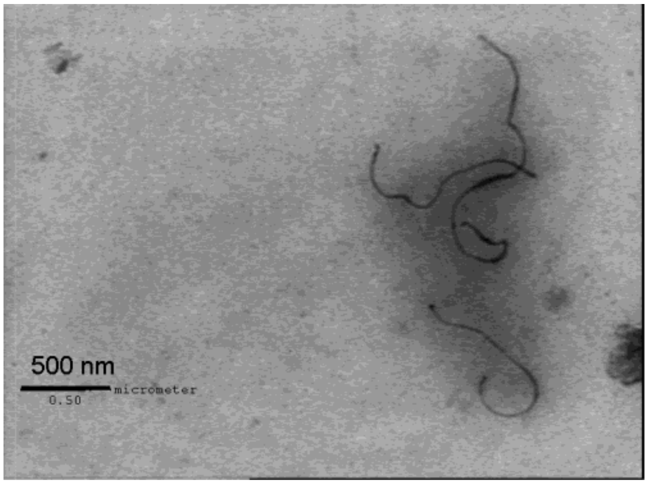


Figure 8. TEM image for nanocyl MWNTs modified by PEB-*b*-PMMAPyMMP ($R_{\mathrm{initial}} = 2$).

it possible to change the amount of copolymer adsorbed onto the carbon nanotubes surface, at least to some extent.

Noncovalent Surface Modification of MWNTs by PEB-*b*-PMMAPyMMP. The surface of the nanocyl MWNTs was also modified by the PEB-*b*-PMMA-PyMMP diblock according to the same procedure. Dispersion of the modified MWNTs ($R_{\mathrm{initial}} > 2$) is stable in toluene, THF, and chloroform. Figure 8 shows the TEM image after deposition of a few drops of this dispersion in THF ($R_{\mathrm{initial}} = 2$) on a carbon-covered grid. Similar to Figure 4, carbon nanotubes are well separated from each other. After filtration and careful washing with THF, the MWNTs were analyzed by TGA, and the maximum GR was estimated at 0.11.

HRTEM was used to observe the polymer layer deposited on arc discharge MER MWNTs before and after modification by the PEB-*b*-PMMAPyMMP copolymer (Figure 9). The pristine MER nanotubes have a well-defined graphitic structure and a very smooth surface as shown in Figure 9C. After polymer deposition, a disorganized polymer layer is clearly observed on top of the graphitic surface (Figure 9A and 9B). In contrast, there is a large number of defects (defective and incomplete graphene layers) at the surface of the pristine CVD MWNTs. It is therefore a problem to identify unambiguously the layer deposited on this type of nanotubes (Figure 10).

The surface of MWNTs was also investigated by AFM operating in lateral force mode with hydrophilic tips. In a first step, lateral force images have been realized on pristine MER MWNTs (Figure 11A), which were dispersed on silicon substrate. These images clearly show that the nanotube surface is very smooth without any topographical defects, and they confirm the TEM analysis. As expected, the friction force measured with the hydrophilic tip is higher on the silicon substrate than on the carbon nanotube, as assessed by a brighter shade on the substrate for the trace image (and a reverse contrast for the retrace image, proving the chemical origin of the contrast). This observation indicates that the nanotube surface is hydrophobic. In a second step, lateral force measurements on modified MWNTs (Figure 11B) have shown that the polymer layer is homogeneously deposited along the nanotube. However, slight differences observed in the friction at the nanotube surface, which can be seen by some color differences on the coated tubes, tend to show that the polymer layer thickness is not completely uniform, as revealed by TEM (Figure 10B). This thickness cannot be measured by AFM. As the contrast observed for the pristine and modified MWNTs is rather similar, we can conclude that the polymer modification does not change significantly the surface hydrophobicity. This might indicate that PEB is preferentially at the top surface rather than PMMA (more hydrophilic).

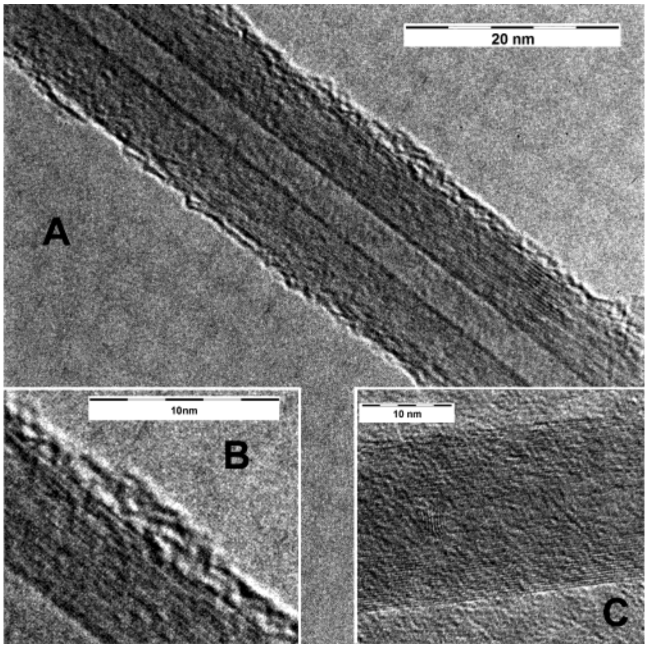


Figure 9. High-resolution TEM of (A) MER MWNTs modified by PEB-*b*-PMMAPyMMP; (B) same as A, at higher magnification; (C) pristine MER MWNTs.

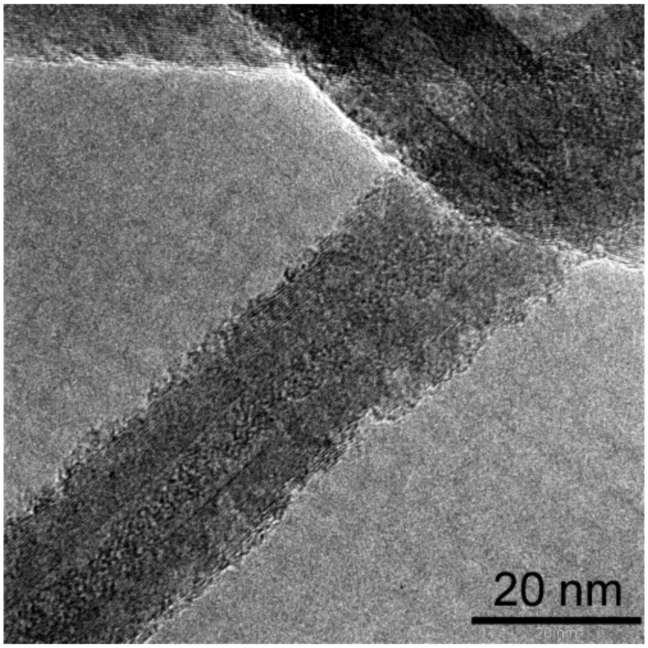


Figure 10. High-resolution TEM of nanocyl MWNTs modified by PEB-*b*-PMMAPyMMP.

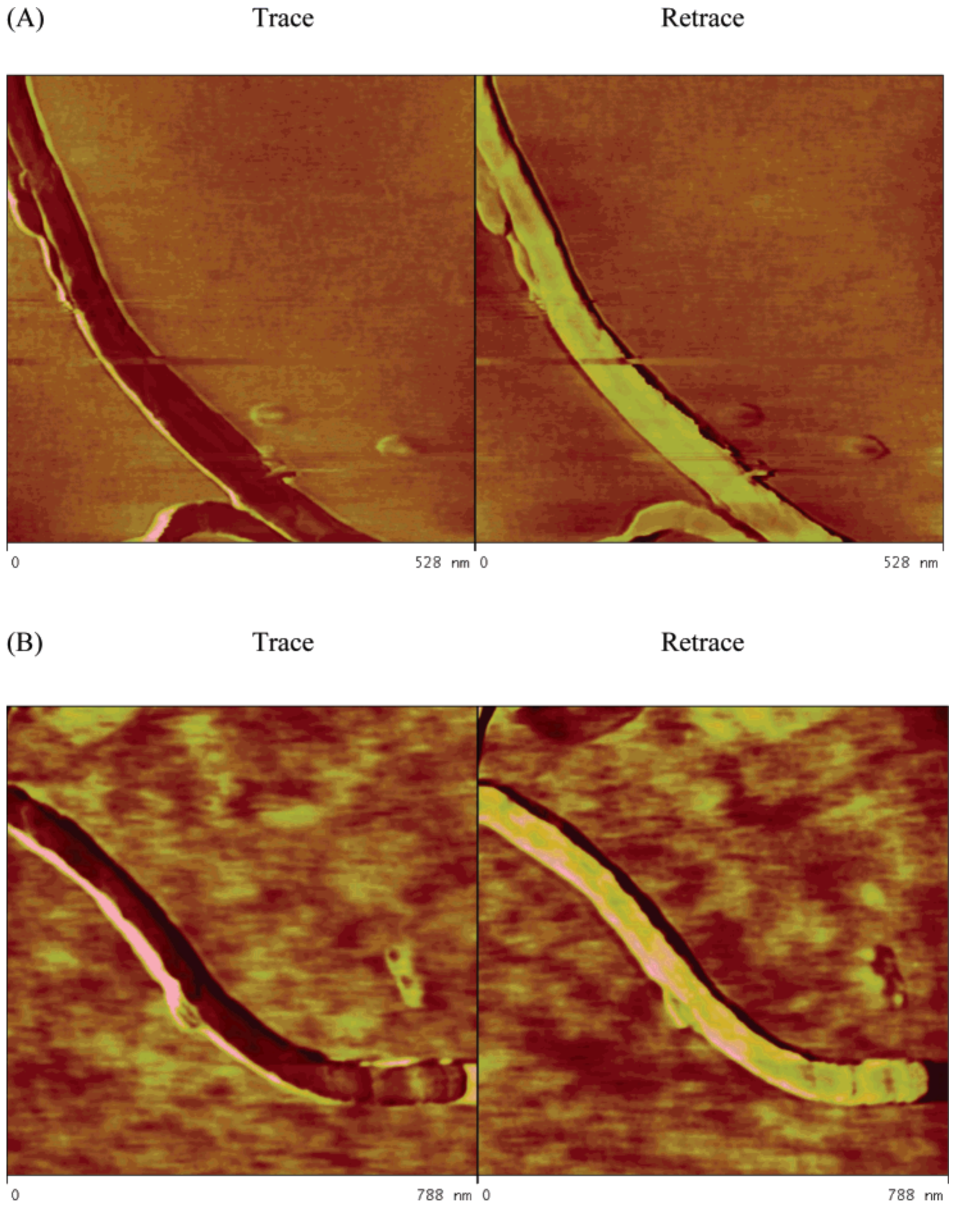


Figure 11. Trace-retrace lateral force microscopy of (A) pristine MER MWNTs and (B) PEB-*b*-PMMAPyMMP modified MER MWNTs with a hydrophilic tip.

Conclusions

The surface modification of MWNTs by pyrene-containing polymers, including poly(MMA-*co*-PyMMP) and PEB-*b*-PMMAPyMMP, is a very straightforward and efficient method for making them dispersible in a variety of organic solvents. These copolymers are strongly adsorbed onto MWNTs, prepared by either CCVD or arc discharge, even after extensive washing by good solvents for them. The adsorbed copolymer has been quantitatively analyzed by TGA and observed by TEM and AFM. These microscopy techniques reveal that the grafted polymer layer is homogeneously deposited along the nanotube. The pyrene-containing methacrylate, PyMMP, can be copolymerized with a series of comonomers, for example, 2-(dimethylamino)ethyl methacrylate.[16] The method reported in this paper is very general and can impart a large range of properties to the CNTs surface, such as polarity, affinity for solvents, reactivity, and so forth.

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