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# Controlled Functionalization of Multiwalled Carbon Nanotubes by in Situ Atom Transfer Radical Polymerization

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Functionalization or modification of carbon nanotubes (CNT) has attracted increasing attention over the past years.[1-3] Up to now, synthetic polymers and biomacromolecules have been grafted or assembled onto the convex surface of CNT via covalent bonds[4,5] or "chemisorption".[6,7] However, to fabricate functionalized CNT with well-controlled thickness of the functional layers is still a dream. To meet the challenge, this work presents a novel in situ atom transfer radical polymerization (ATRP) "grafting from" approach to functionalize multiwalled carbon nanotubes (MWNT). In comparison with the anionic polymerization approach reported in the literature,[8] the living "radical polymerization" approach displays at least three merits: (1) both styrene and acrylate/acrylamide monomers can be directly used as the raw materials; (2) the initiating sites in the reaction system remain constant after the graft polymerization and purification of the products, so it is convenient to further perform block copolymerization and chain extension; and (3) it presents an access to prepare the polymers with a functional group in each repeating unit such as poly-(hydroxyethyl methacrylate) (PHEMA).[9,10]

The general strategy for grafting polymers from the multiwalled carbon nanotubes (MWNT) via ATRP is described in Scheme 1. Four steps are included: (1) carbonyl chloride groups functionalized MWNT (MWNT-COCl) was prepared via reaction of thionyl chloride with carboxyl-contained MWNT (MWNT-COOH) previously made by oxidation of the crude MWNT with 60% HNO$_3$,[3a] (2) hydroxyl groups were introduced onto the surface of MWNT by reaction of MWNT-COCl with glycol, generating MWNT-OH, (3) initiating sites (MWNT-Br) for ATRP were formed by reacting MWNT-OH with 2-bromo-2-methylpropionyl bromide, and (4) grafting polymerization of methyl methacrylate (MMA) from MWNT-Br was carried out by means of in situ ATRP, resulting in MWNT-PMMA. The thickness of the polymer layer in the functionalized MWNT can be well-controlled by the feed ratio (in weight) of MMA to MWNT-Br ($R_{wt}$) (Table 1).

To prove the covalent linkage of PMMA onto MWNT, two parallel experiments were conducted. The first one was ATRP of MMA initiated by free ethyl 2-bromoisobutyrate in the presence of MWNT-COOH, giving the filtered black solid after sufficient filtration, dispersing, and washing (sample CM1). The second one was mechanical blending of PMMA with MWNT-COOH, affording two mixtures with 33.3 wt % PMMA (sample CM2) and 66.7 wt % PMMA (sample CM3), respectively (see Supporting Information S1).

The MWNT-PMMA shows a relatively good solubility in non- or weakly polar solvents such as THF and CHCl$_3$, and a poor solubility in strong polar solvents such as DMF and DMSO. The solubility of CM1 and CM3 is very similar to that of MWNT-COOH, and completely different from that of MWNT-PMMA. Measurements of UV−vis spectra showed that the absorbance of MWNT-Br in CHCl$_3$ is much higher than that of MWNT-OH or
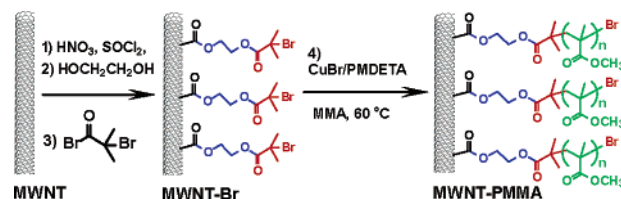
**Scheme 1**

**Table 1.** The Reaction Conditions and Some Results

| code | $R_{wt}{}^a$ | $r^b$ | temp/°C | time/h | $f_{wt}$/%$^c$ | $\bar{d}$/nm$^d$ |
|------|------|------|---------|--------|--------|--------|
| CP1 | 1:1 | 5:1:1 | 60 | 20.0 | 31.9 | 3.8 |
| CP2 | 2:1 | 10:1:1 | 60 | 20.0 | 50.0 | 5.3 |
| CP3 | 5:1 | 25:1:1 | 60 | 25.0 | 70.0 | 8.0 |
| CP4 | 10:1 | 50:1:1 | 60 | 30.0 | 82.0 | 14.0 |
| CP5$^e$ | 1:1 | 5:1:1 | 60 | 20.0 | 54.5 | 7.8 |

$^a$ $R_{wt}$ = monomer:MWNT-Br (wt:wt). $^b$ $r$ = momoner:CuBr:$N,N,N',N'',N''$-pentmethyldiethylenetriamine (PMDETA) (mol:mol:mol). $^c$ $f_{wt}$, the loss-weight fraction of polymer calculated from TGA. $^d$ $\bar{d}$ = the average thickness of grafted polymer layers measured from TEM images. $^e$ The monomer is HEMA; $R_{wt}$ = HEMA:CP1 (wt:wt).

MWNT-COOH, and the absorbance of MWNT-PMMA is significantly greater than that of CM1, CM3, or MWNT-COOH, while the absorbance of CM1 or CM3 is almost equal to that of MWNT-COOH (see Supporting Information S2). The different solubility and absorbance of the samples give direct evidence for the conclusion that the ATRP initiator is covalently linked to the MWNT and then PMMA is covalently grafted onto the MWNT in the MWNT-PMMA samples.

The structure of the resultant samples was detected with transmission electron microscopy (TEM) and scanning electron microscopy (SEM) (see Figure 1 and Supporting Information S3). Figure 1A shows the image of a part of crude MWNT. It is notable that the diameters and the numbers of walls of MWNT are not completely identical with one another in our observation. Figure 1B−E displays the images of modified MWNT with various thicknesses of the polymer layers having somewhat shallower and more transparent color. The average thicknesses ($\bar{d}$'s) of the enwrapped polymer layers are ∼3.8, ∼5.3, ∼8, and ∼14 nm, respectively (measured from 8 to 10 tubes). It is found that the average thickness of the polymer layer increases with an increase in the feed ratio $R_{wt}$. Therefore, the thickness of polymer layer can be well controlled through the in situ ATRP approach presented here. As a comparison, no polymer layers were observed in the image of CM1. In the image of CM3, the structure of MWNT enwrapped by the polymer layer similar to that of MWNT-PMMA was hardly found.

Furthermore, the outcome obtained from TEM well accords with that resulting from thermal gravimetric analysis (TGA) (Supporting Information S4). The onset of the weight loss for the grafted PMMA is at 280−330 °C, while that of pure MWNT is higher than 600
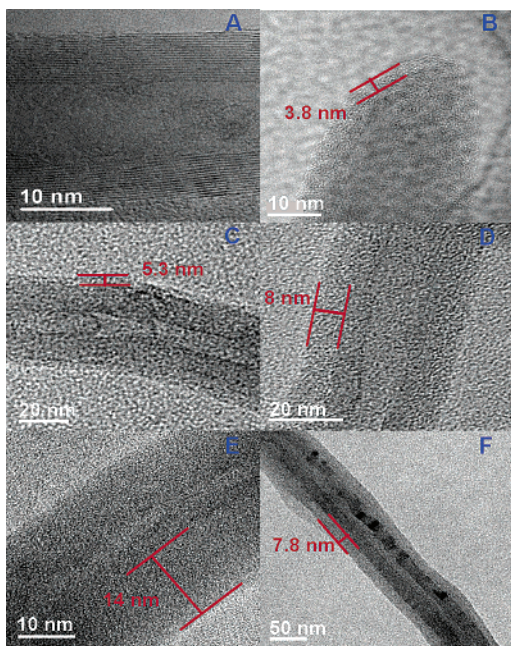
**Figure 1.** TEM images of MWNT (A), CP1 (B), CP2 (C), CP3 (D), CP4 (E), and CP5 (F).

°C. The loss-weight fraction of the polymer layers for the MWNT-PMMAs ranges from 31.9% to 82.0% (Table 1) and increases with increasing $R_{wt}$, indicating that the content of the polymer in the functionalized MWNT can be adjusted by $R_{wt}$. For MWNT-OH and MWNT-Br, the relatively high onset temperatures (311 and 275 °C, respectively) assigned to the decomposition of the functionalized moieties of MWNT-OH and MWNT-Br indicate that glycol and 2-bromo-2-methylpropionyl bromide were covalently linked to MWNT; otherwise, the weight loss temperature would be much lower because the boiling points (bp) of glycol and 2-bromo-2-methylpropionyl bromide are only 196 and 162 °C, respectively. In addition, the TGA curve of CM1 is very similar to that of MWNT-COOH, and no polymer weight loss region can be detected, which demonstrates that the possible absorbed polymer can be predominantly removed from the system of CM1 by washing.

The other question we are concerned with is whether the approach can be extended to copolymerization. To answer this question, the ATRP of hydroxyethyl methacrylate (HEMA) using MWNT-PMMA (CP1) as the macroinitiator was performed (see Supporting Information S1). The reaction conditions and results are also illustrated in Table 1 (CP5), Figure 1 (F), and the Supporting Information. The structure of the copolymer-anchored MWNT was confirmed with FTIR and ^{1}H NMR. The molar ratio of PHEMA to PMMA calculated from ^{1}H NMR is 2.1/1 (see Supporting Information S5), while the ratio calculated from the TGA data is only 0.55/1. The difference may be caused by the poor solubility of PMMA blocks in DMSO. In the TEM image of CP5, $\bar{d}$ of the polymer layer is ~7.8 nm, and about 2-fold of its precursor CP1. CP5 exhibited a relatively good solubility in DMF and DMSO, but a very poor solubility in CHCl$_3$ and THF. All of the characteristics indicate that the in situ polymerization presented here is still a living polymerization, and PMMA-*block*-PHEMA grafted MWNT are obtained. As the result, carbon nanotubes coated with coaxial nonpolar and polar amphiphilic polymer brushes are realized (the cartoon of the novel nanoobject is shown below). The in situ ATRP approach can be extended to other vinyl monomer systems and will be published elsewhere.
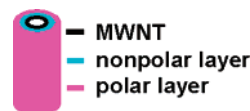
In conclusion, an in situ ATRP "grafting from" approach is presented and successfully applied to functionalize MWNT, resulting in MWNT grafted with various contents of polymer layers. Significantly, the approach can be extended to the copolymerization system, which may open an avenue for exploring and preparing novel CNT-based nanomaterials and molecular devices with tailor-made structures and properties.

**Supporting Information Available:** (S1) Experiments details, (S2) solubility, (S3) SEM and TEM images, (S4) TGA curves, (S5) ^{1}H NMR and FTIR spectra (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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