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A tailored RAFT copolymer for the dispersion of single walled carbon nanotubes in aqueous media

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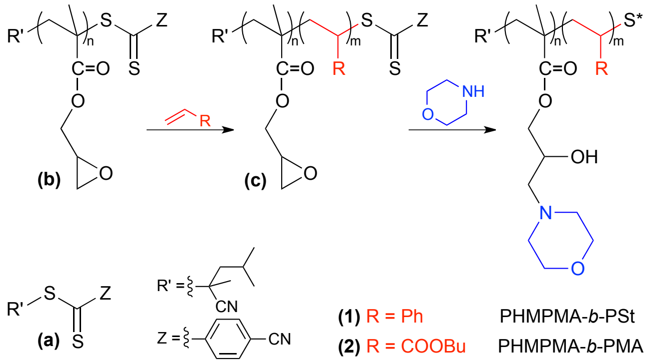
The reversible addition-fragmentation chain-transfer (RAFT) synthesis of poly(glycidyl methacrylate) (PGMA) copolymers followed by the post-polymerisation treatment with morpholine allows the rational design of amphiphilic block copolymers that are capable of efficiently dispersing single walled carbon nanotubes (SWCNTs) in aqueous media, as shown by comparative photophysical characterization and AFM analysis.

The technological implementation of single walled carbon nanotubes (SWCNTs) in the area of materials science and electronics is still largely hampered by their insolubility, which ultimately prevents easy manipulation.[1] The dispersion of SWCNTs in water as well as organic solvents has been accomplished with a variety of amphiphilic molecules that wrap around the carbon scaffold through hydrophobic interactions.[2,3,4] However, a rational synthetic strategy to build up tailored materials able to debundle CNT in polar media through non-covalent interactions and provide them specific properties has been only rarely pursued.[5]

The reversible-addition fragmentation chain-transfer (RAFT) process is a versatile and powerful tool for the design of polymers with a specific architecture and a restricted distribution of molecular weights.[6] The combination of this technique with post-polymerisation modifications of poly(glycidyl methacrylate) (PGMA) represents an optimal strategy for obtaining amphiphilic block copolymers.[7] In particular, we can convert poly(glycidyl methacrylate)-*b*-polystyrene (PGMA-*b*-PSt) and poly(glycidyl methacrylate)-*b*-poly(butyl acrylate) (PGMA-*b*-PBA) (^{1}H NMR spectra and GPC traces reported in the ESI) into the amphiphilic block copolymers Poly(2-hydroxy-3-morpholinopropyl methacrylate)-*b*-polystyrene (PHMPMA-*b*-PSt) **1** and Poly(2-hydroxy-3-morpholinopropyl methacrylate)-*b*-poly(butyl acrylate) (PHMPMA-*b*-PBA) **2**.

Herein we show that the copolymer **1**, which contains polystyrene units, is substantially more effective in dispersing SWCNTs in water when compared to the copolymer analogue **2** that lacks the polystyrene fragments, and hence exhibits a weaker interaction with the carbon nanomaterial. The dispersion procedure consists of a few highly reproducible steps and the final products are investigated by UV-Vis-NIR absorption, fluorescence mapping, and AFM microscopy. The π-π and van der Waals non-covalent interaction of the copolymer with SWCNTs allows the preservation of the nanotube sp^2 carbons and hence the electronic properties of the carbon nanomaterial.[8] We wish to emphasize that RAFT polymers have been previously used in connection with carbon nanotubes for instance in (i) the study of the interactions between CNTs and RAFT polymers containing pyrene,[5] (ii) cholesterol-containing polymers for solubilization of CNTs in apolar organic solvents,[9] (iii) polystyrene chains grafted on the surface of MWCNTs by using a RAFT agent immobilized on the carbon scaffold.[10] However, to the best of our knowledge, the present work is the first example of the use of tailored amphiphilic RAFT block copolymer for dispersion of CNTs in aqueous media via non-covalent interactions.



Scheme 1. Schematic description of the synthesis of the amphiphilic block copolymers. **(a)** RAFT agent 2-cyano-4-methylpent-2-yl 4-cyanodithiobenzoate. **(b)** PGMA macro RAFT. **(c)** PGMA-*b*-PSt (R = Ph), PGMA-*b*-PBA (R = COOBu). (1) PHMPMA-*b*-PSt. (2) PHMPMA-*b*-PMA.[7]

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PHMPMA-*b*-PSt **1** and PHMPMA-*b*-PBA **2** were synthesized as previously described[7] starting from the poly(glycidyl methacrylate) (PGMA) macroRAFT (**b**, Scheme 1), which was chain extended with styrene or butyl acrylate. Amphiphilicity is attained upon treatment with morpholine, which makes the resulting PHMPMA soluble in a range of solvents from chloroform to water. Solubility in organic polar solvents like dimethylformamide (DMF) allows the dispersion in water of the self-assembled material consisting of the wrapped amphiphilic block copolymers and SWCNTs. The preparation of the copolymer is described in Scheme 1.

The procedure for preparing dispersions of SWCNTs consists of a few simple steps. First the polymer (≈ 0.2 mg) and the SWCNTs (≈ 0.1 mg) undergo bath sonication in 1 mL of DMF for 30 min. After this treatment, the sample is a transparent liquid with black solid material floating on top. In the second step, deionized water (1 mL) was added to the mixture at uniform dropwise rate (1 mL/min), followed by sonication (30 min). The latter step is further repeated twice to increase the amount of water from 1 to 3 mL and get a DMF:water ratio of 1:3. At this stage, the lipophilic block of the polymer becomes insoluble and tends to form micellar particulate[11] as the amount of water is progressively increased. The hydrophilic part gets solubilised in water, while the hydrophobic portion interacts with the carbon nanotube surface, through the formation of micelles around the CNTs that enable their dispersion (see below).

Eventually, the samples are filtered through cotton to remove the largest non-dispersed residues. The dispersions, hereafter referred to as **1.SWCNT** and **2.SWCNT,** are transparent but **1.SWCNT** is dark grey and **2.SWCNT** is light grey, a preliminary indication of the different ability of the two polymers to disperse SWCNTs.[12] Finally, to remove residual non-solubilized materials and the excess of unwrapped polymer, a centrifugation step is applied (2h, 20000 rpm) and the resultant supernatant is then collected.

SWCNTs, that underwent the above described processing, were investigated by absorption and luminescence spectroscopy in the visible and near-IR (Vis-NIR) regions in order to verify the presence of the spectroscopic fingerprints of debundled SWCNTs and, consequently, to evaluate the degree of dispersion. When no separation techniques are applied (e.g. ultracentrifugation or chromatography), the absorption spectra of SWCNTs exhibit a strong background due light scattering and a high ratio of metallic tubes; moreover, spectral features are poorly resolved due to a number of closely spaced bands corresponding to the large variety (i.e., diameters) of semiconducting SWCNTs in the sample. Such bands are also broadened by electronic coupling effects due to aggregation.[13]

The Vis-NIR absorption spectrum of **1.SWCNT**, before the final centrifugation, exhibits several relatively intense and well-resolved bands, whereas the features of **2.SWCNT** are weaker and less resolved (Fig. 1a). To emphasize the enhanced dispersion power of **1**, we determined the so-called resonant area of the absorption spectra of the two samples in the NIR region (ESI, Fig. S4)**.**[14] Upon centrifugation, the two samples exhibit different behaviour. In the case of **1.SWCNT**, the supernatant shows the same optical transitions observed for the uncentrifuged sample but, as expected, with a substantially weaker background (Fig. 1b). On the contrary, the spectra of **2.SWCNT** exhibit much less pronounced differences in the resolution and absorbance between the uncentrifuged sample and the supernatant fraction of the centrifuged sample (Fig.1b). This finding suggests that most of the SWCNTs, which remain highly bundled in the presence of **2**, are removed in the preliminary filtration step.

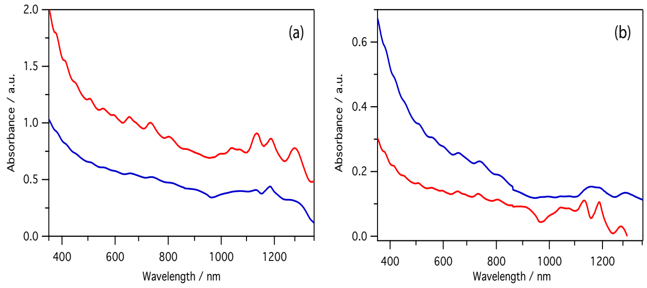

Fig. 1. Absorption spectra of **1.SWCNT** (red) and **2.SWCNT** (blue) dispersed in DMF:water 1:3: (a) before centrifugation (b) after centrifugation (supernatant fraction).

It is known that the fluorescence of semiconducting SWCNTs (s-SWCNTs) is quenched by the non-emitting metallic analogues (m-SWCNTs) in the presence of bundles; therefore fluorescence spectroscopy is a powerful tool to assess the extent of dispersion of SWCNTs.[15-18] The comparison of the fluorescence maps of the uncentrifuged **1.SWCNT** and **2.SWCNT** shows that in the former case the luminescence peaks are more numerous, intense and resolved. In **2.SWCNT**, only a limited number of weak emission bands are present with a large instrumental noise due to scattered light (Fig. 2). The centrifuged fraction preserves the emission properties in the case of **1.SWCNT** (ESI, Fig. S5), while only minor signals are detectable with a predominant contribution of scattered light in the sample **2.SWCNT**.

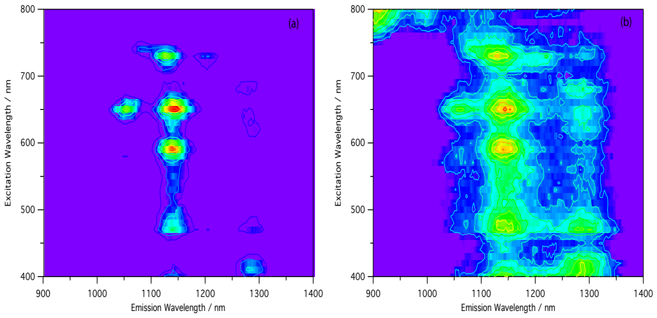

Fig. 2. Photoluminescence map of uncentrifuged (a) **1.SWCNT** and (b) **2.SWCNT** in DMF:water 1:3.

The dispersion of polymer coated SWCNTs were then analysed using atomic force microscopy (AFM), where the effective solubilisation of the nanotubes with the polymer PHMPMA-*b*-PSt is compared to PHMPMA-*b*-PBA. Films of the dispersions of **1.SWCNT** and **2.SWCNT** were prepared via spin coating onto freshly cleaved mica surfaces at three different stages of manipulation: a) before filtration, b) after filtration and c) after centrifugation (supernatant portion).

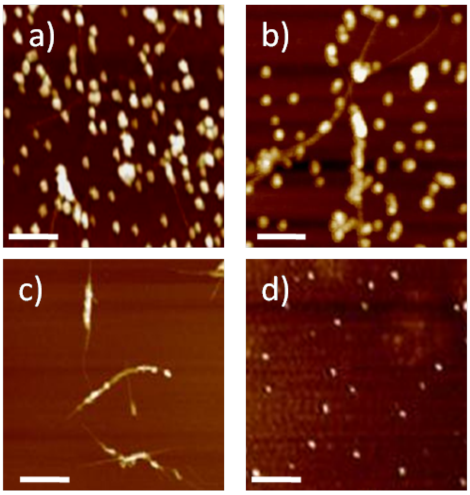

Fig. 3. Atomic Force Microscopy (AFM) images showing **1.SWCNT** deposited on mica supports a) before filtration, b) after filtration, c) after centrifugation (supernatant fraction). Image d): **2.SWCNT** after filtration, deposited on mica showing no stabilised SWCNT. Scale bars are 200 nm in length.

Analysis of the dispersion before filtration reveals large micelles both for **1.SWCNT** and **2.SWCNT** (see, for example, Fig. 3a for **1.SWCNT**) due to the large quantity of polymer in solution. A similar analysis of the dispersions after filtration shows a notable difference between **1.SWCNT** (Fig. 3b) and **2.SWCNT** (Fig. 3d). In the former case, the stabilization of the SWCNTs is evidenced by the presence of micelles along the length of the carbon nanotube, while in **2.SWCNT** almost only polymeric particles are present, suggesting that bundling of the nanotubes had occurred and they were removed via filtration. The final step of centrifugation of **1.SWCNT** enables the isolation of carbon nanotubes from the free polymer in solution, and shows that almost all of the nanotubes are coated with polymer (Fig. 3c). In particular, Fig. 3c shows the wrapping of polymer **1** along the length of the carbon nanotubes. In Fig. S6 a 5-fold larger area is provided, confirming that many polymer wrapped SWCNTs are present on the AFM scanned surface.

In conclusion, we have proposed a new rational approach to the preparation of functional copolymers targeted to the dispersion of SWCNTs in aqueous media via non-covalent interactions. Photophysical and AFM analyses have been used to monitor each single preparation and manipulation step and clarify the overall rationale of the proposed dispersion protocol. The flexibility of the RAFT technique, combined with the post-polymerisation treatment of PGMA, allows the preparation of a virtually unlimited library of polymers. This opens the way to the rational functionalization of carbon nanotubes in polar media through non covalent interactions. Moreover, the biocompatibility of the polymers, along with the possibility of their further functionalization, makes the proposed approach potentially useful for biological applications.[19]

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