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Noncovalent functionalization of multi-walled carbon nanotubes by pyrene containing polymers

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Multi-walled carbon nanotubes (MWNTs) have been solubilized in water and in various organic solvents by noncovalent side-wall functionalization by pyrene containing polymers.

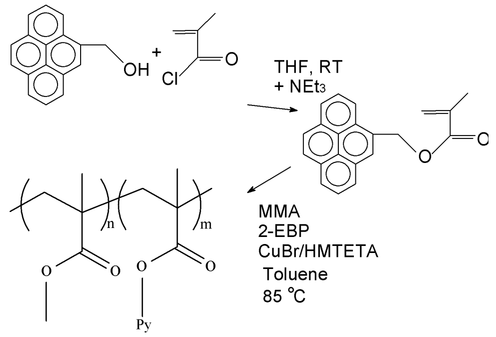
Carbon nanotubes (CNTs)[1] are produced as agglomerates of intimately intertwined long tubes that interact mutually by van der Waals forces. This characteristic feature accounts for poor dispersibility in liquids and for difficult processing. An appropriate energy input is a way to trigger the tubes' disentanglement, whereas surface modification is a possible strategy to stabilize CNTs,[2,3] in particular to prepare CNT-based nanocomposites with high performances. These performances depend indeed on the homogeneity of the dispersion and the strength of the interfacial interactions.[4,5] Moreover, water-soluble carbon nanotubes are of special interest because of possible biochemical and biomedical applications.[6] Very recently, attention has been paid to the CNTs' modification by natural products with the purpose of developing biocompatible and environmentally friendly CNT-based materials.[7–11]

This communication aims at reporting on a versatile nondestructive strategy for the noncovalent side-wall functionalization of full-length multi-walled carbon nanotubes by polymers containing pendant pyrene groups. These modified MWNTs can accordingly be made soluble in water and in a variety of organic solvents, depending on the polymer used.

The strategy for the noncovalent attachment of polymers to the CNT surface is based on the affinity of pyrene for CNTs.[12–14] Copolymers of methyl methacrylate (MMA) and (1-pyrene)methyl 2-methyl-2-propenoate (PyMMP) were synthesized by "Atom Transfer Radical Polymerization" as shown in Scheme 1. Copolymerization was initiated by ethyl 2-bromopropionate (2-EBP) in the presence of the CuBr/1,1,4,7,10,10-hexamethyltriethylenetetraamine (HMTETA) catalyst, in toluene at 85 °C. Table 1 lists the copolymers synthesized with different compositions and molecular weights.

CVD MWNTs supplied by Nanocyl S.A. (Belgium) were used with two degrees of purity, *i.e.*, MWNTs-60 (> 60% purity) and MWNTs-96 (> 96% purity).†

Noncovalent side-wall functionalization was carried out by mixing MWNTs-60 with poly(MMA-*co*-PyMMP) copolymers, according to a polymer to CNTs wt ratio (R_{initial}) in the 1–50 range. R_{initial} must be at least 2 for observing stable dispersions in toluene. A dramatic improvement in the dispersion stability is however observed when R_{initial} is higher than 10. At constant R_{initial}, the stability of the dispersions increases with the pyrene content of the copolymer chains, in contrast to the molecular weight which has no significant effect at constant pyrene content. The modified nanotubes were recovered by filtration and washed with THF in order to eliminate the copolymer excess. Poly(MMA-*co*-PyMMP)-modified MWNTs-60 form stable dispersions in THF, chloroform and toluene. The grafting ratio (GR), defined as the mass ratio of grafted polymer to nanotubes, was estimated by TGA and found to be in the 0.35–0.44 range.



Scheme 1 Synthesis of poly(methyl methacrylate-*co*-(1-pyrene)methyl 2-methyl-2-propenoate) copolymer.

In order to confirm that π–π stacking results in the irreversible adsorption of the copolymer chains, a sample of modified MWNTs-60 was redispersed in THF, recovered by filtration and washed with THF. TGA shows that GR remains unchanged (Fig. 1).

In order to confirm that the dispersion stability does not merely result from interaction between the carbon nanotubes and PMMA, MWNTs-60 dispersion was prepared under the same experimental conditions, except that poly(MMA-*co*-PyMMP) was replaced by PMMA. Stable dispersion is not

Table 1 Synthesis of poly(methyl methacrylate-*co*-(1-pyrene)methyl 2-methyl-2-propenoate). [2-EBP] : [CuBr] : [HMTETA] molar ratio = 1 : 1 : 1

Entry	MMA : PyMMP[a]	M_n/g mol^{-1}[b]	M_w/M_n	Pyrene content (groups/chain)
a	0.79 : 0.21	10100	1.4	14
b	0.94 : 0.06	15700	1.3	7
c	0.99 : 0.01	17800	1.3	2
d	0.96 : 0.04	40600	1.3	14
e	0.98 : 0.02	60800	1.3	12

[a] Molar composition determined by ^{1}H NMR in $CDCl_3$. [b] Measured by SEC in THF, with PS standards.

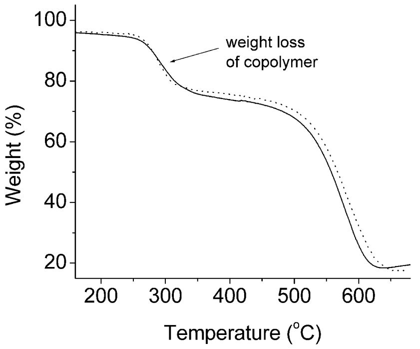


Fig. 1 TGA traces (heating rate = 5 °C min^{-1}, in air) of MWNTs-60 modified by poly(MMA-*co*-PyMMP) (Table 1-entry a): before (solid line) and after redispersion in THF, filtration and washing with THF (dotted line).

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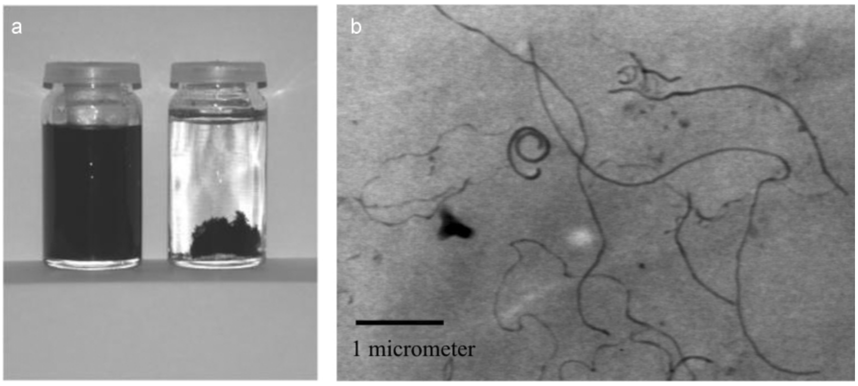


Fig. 2 a)Water-dispersions of poly(quaternized DMAEMA-*co*-PyMMP)-modified MWNTs-96 (left) and nonmodified MWNTs-96 (right); b) TEM image of water-soluble MWNTs.

observed any more and no polymer is attached to the nanotubes, after recovery by filtration and washing, as confirmed by TGA.

The purity of the MWNTs (thus substitution of MWNTs-96 for MWNTs-60) has no significant effect on the noncovalent side-wall functionalization by poly(MMA-*co*-PyMMP).

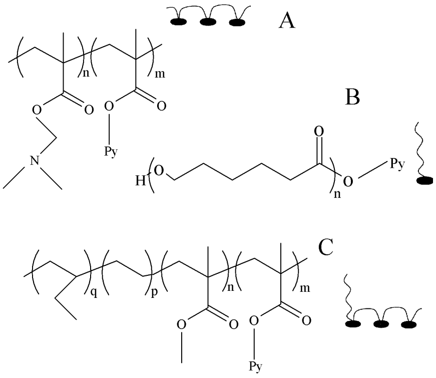
Composition and molecular structure of pyrene containing (co)polymers have been changed as shown in Scheme 2.

Firstly, 2-(dimethylamino)ethyl methacrylate (DMAEMA) has been substituted for MMA in the copolymerization with (1-pyrene)methyl 2-methyl-2-propenoate. Poly(DMAEMA-*co*-PyMMP) copolymer (Scheme 2-A) was prepared by ATRP with CuCl instead of CuBr as co-catalyst. After quaternization by ethyl bromide, this copolymer imparts high stability to a dispersion of *e.g.* MWNTs-96 in water (Fig. 2a, left). Stability for weeks is indeed observed in sharp contrast to nonmodified MWNTs-96 that reagglomerate 30 minutes after preparation (Fig. 2a, right). Fig. 2b is a typical TEM micrograph‡ of well dispersed individual MWNTs, which is evidence that the black liquid contains completely deagglomerated nanotubes.

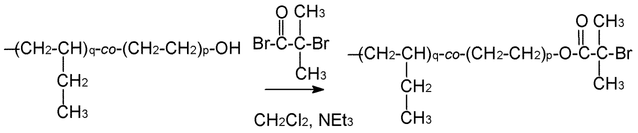
Poly(ε-caprolactone) (M_n = 2–20 K) end-capped by a pyrene group has also been synthesized (Scheme 2-B), by initiating the ring opening polymerization of ε-caprolactone by 1-pyrenemethanol in the presence of triethylaluminium. MWNTs modified by this polymer form stable dispersions for days in toluene and THF.

Finally, the poly(methyl methacrylate-*co*-(1-pyrene)methyl 2-methyl-2-propenoate) has been associated to a poly(ethylene-*co*-butylene) chain (PEB) in a diblock structure (Scheme 2-C). A hydroxyl terminated PEB (M_n = 3900), supplied by Shell Chemical Company as Kraton®, was used as a macroinitiator for the copolymerization of MMA and PyMMP by ATRP (Scheme 3). This diblock structure is efficient at stabilizing MWNTs in organic liquids (THF, toluene, chloroform) but also triggers dispersibility in polyolefins.

In conclusion, the surface modification of multi-walled carbon nanotubes by pyrene containing polymers of different nature and molecular architecture is a very straightforward and efficient method for making them dispersible in water, and in a variety of organic solvents, and for preparing homogeneous CNT-based polymer composites.



Scheme 2 Schematic representation of various pyrene bearing polymers (shaded ellipse = pyrene).



Scheme 3 Synthesis of poly(ethylene-*co*-butylene) macroinitiator for the copolymerization of methyl methacrylate and (1-pyrene)methyl 2-methyl-2-propenoate by ATRP.

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Notes and references

† MWNTs-60 – inner diameters: 2–7 nm; outer diameters: 3–15 nm; lengths: up to 50 μm; purity > 60%; MWNTs-96 – inner diameters: 4–10 nm; outer diameters: 8–50 nm; lengths: up to 50 μm; purity > 96%. MWNTs were used without further purification.

‡ A drop of dispersion was deposited on a TEM copper grid (3.05 mm 200 mesh) coated with a Formvar film, and the solvent was allowed to evaporate. A Philips CM 100 apparatus, equipped with a Gatan 675 CCD camera for digital imaging, was used, at an accelerating voltage of 100 kV.

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