

Ring opening metathesis polymerization on non-covalently functionalized single-walled carbon nanotubes†

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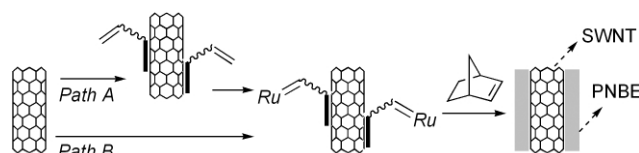
Norbornene polymerization has been initiated selectively on the surface of single-walled carbon nanotubes (SWNTs) via a specifically adsorbed pyrene-linked ROMP initiator, resulting in a homogeneous non-covalent poly(norbornene) coating.

Since their discovery in 1991,¹ carbon nanotubes (CNTs) have been the focus of numerous investigations due to their unique structural and electrical characteristics. Their outstanding sensitivity to chemical doping,^{2,3}—as is manifested in dramatic changes of resistance upon the adsorption of certain molecules in the gas phase—coupled with their diminutive size, reveals a vast potential for nanoelectronics and chemosensing applications. Key to bringing this potential to realization is a detailed investigation into the nature of association phenomena between nanotubes and various chemical environments.^{4,5} For this purpose, and in order to enhance their compatibility with various matrices and their solubility in conventional media, a series of nanotube sidewall- and end-functionalization schemes are currently under exhaustive investigation.^{6–10} Furthermore, the controlled introduction of binding sites as a tool in the tailoring of the sensing properties of CNTs while maintaining their composition essentially intact poses new challenges to the synthetic chemist. In this regard, polymer functionalization constitutes an attractive alternative to covalent modification of CNTs,^{11–15} mainly due to the unique physicochemical properties of polymers, and the possibilities inherent to the introduction of specific functional groups in their primary structure.

We have engaged in the development of functionalization strategies based on sidewall adsorption of a polymerization initiator followed by polymer growth off the nanotube sidewalls. Such an approach not only ensures selective coating with organic polymer but also provides a non-destructive modification of the nanotube structure. In this communication, we report on the preparation of polynorbornene-coated single-walled CNTs (SWNTs) using ring opening metathesis polymerization (ROMP). The variety of functional groups and macromolecular architectures amenable of ROMP have already made of it a valuable tool in the functionalization of surfaces and particles.^{16–20}

In a previous study, we demonstrated that polycyclic aromatics such as pyrene could serve as anchors for selective, non-covalent sidewall functionalization of SWNTs.⁴ With this in mind, we explored two routes towards SWNTs functionalized with ruthenium alkylidenes (Scheme 1) which make use of cross-metathesis reactions both on and off the nanotube walls. In a representative experiment (e.g. Scheme 1, Path A), a gold TEM grid or silicon oxide substrate containing as-grown SWNTs‡ was immersed in CH₂Cl₂ solutions of **4** (Scheme 2), rinsed to remove non-specific adsorption, and exposed to norbornene (NBE) solutions.

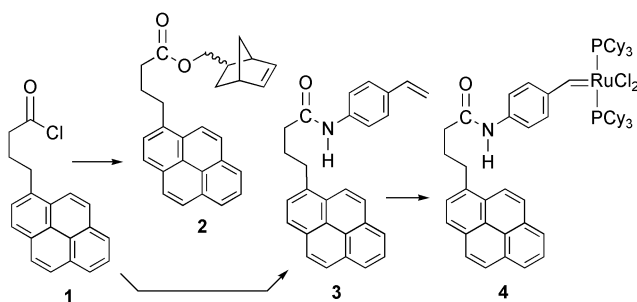
Fig. 1 shows a TEM image of SWNTs coated with polynorbornene (PNBE). As implied by microscopy, this particular sample (Table 1, entry 4) shows a PNBE-coated



Scheme 1 Complete functionalization strategy. Path A: Adsorption of organic precursors (e.g. **2** or **3**) followed by cross-metathesis with a ruthenium alkylidene. Path B: Adsorption of a pyrene-substituted ruthenium alkylidene (e.g. **4**).

nanotube of approximately 40 nm diameter (polymer coating thickness on the order of ~15 nm). A representative uncoated nanotube of ~5 nm diameter is shown in the inset.²¹ Optimum results in terms of selective functionalization were obtained with strategies involving exposure of the nanotubes to solutions of pyrene-substituted alkylidene **4** (Path B in Scheme 1): homogeneous coatings of variable thickness were obtained in almost all of the experiments which employed amide **4** and polymerization times less than 2 h (Table 1, entries 4, 10 and 11).

Initial experiments attempted to convert adsorbed organic species (e.g. **2**, **3**) *in-situ* to a ruthenium initiator employing cross-metathetical alkylidene exchange (Scheme 1, Path A). Incubation of SWNT-containing TEM grids in solutions of (isolated) norbornenylmethyl ester **2** in various solvents led to inefficient functionalization, and no clear evidence of selective PNBE coating was found after attempted alkylidene formation



Scheme 2 Synthesis of pyrene-functionalized initiators and precursors. Reagents: (a) 2-Norbornen-5-ylmethanol, Et₃N, DMAP (cat.), Et₂O; (b) 4-vinylaniline, Et₃N, CH₂Cl₂; (c) Cl₂(PCy₃)₂Ru=CHPh, CH₂Cl₂.

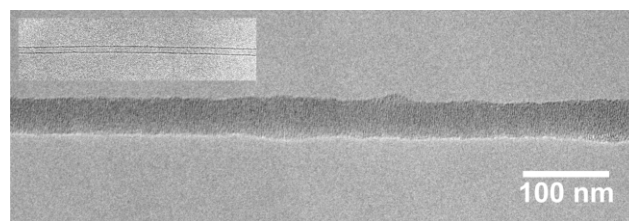


Fig. 1 Transmission electron microscopy of a single walled carbon nanotube after polymer functionalization (Table 1, entry 4). A representative as-grown tube (diameter ~5 nm) can be observed in the inset (not to scale). Note that SWNTs grown directly on our TEM grids are reproducible and appear similar in yield and structure for different batches.²¹

† Electronic supplementary information (ESI) available: full experimental details for compounds **2–4**, nanotube preparation and microscopy analysis. See <http://www.rsc.org/suppdata/cc/b2/b211194b/>

Table 1 Polynorbornene coating on SWNTs^a

| Entry | Pathway | [Norbornene]/M | Polym. time/min | Coating thickness/nm |
|-----------------|----------------|----------------|-----------------|----------------------|
| 1 | B | 0.5 | 120 | None |
| 2 | B | 0.5 | 60 | <5 |
| 3 | B | 0.5 | 20 | <5 |
| 4 | B | 0.5 | 5 | 10–20 |
| 5 | B | 0.25 | 5 | <5 |
| 6 | B | 0.10 | 5 | <5 |
| 7 | B | 0.05 | 5 | None |
| 8 | A ^b | 0.01 | 25 | None |
| 9 | A ^b | 0.5 | 25 | None |
| 10 ^c | B | 0.01 | 1 | 5–10 |
| 11 ^c | B | 0.01 | 5 | 5–10 |

^a Conditions: SWNTs on Au TEM grids. [4] ≈ 25 mM (CH₂Cl₂), 2 h incubation time, room-temperature polymerization, toluene solution. ^b 2 (5 mM); 5 (10 mM). ^c SiO₂ flat substrates.

with Cl₂(PCy₃)₂Ru=CHPh (**5**) followed by exposure to solutions of various NBE concentrations (Table 1, entries 8 and 9).

Functionalization of as-grown SWNTs (using 10 mM NBE solutions) deposited onto SiO₂ substrates utilizing ferritin-derived catalysts²² yielded samples suitable for AFM imaging (tapping mode). A representative nanotube of approximate diameter = 1.4 nm is shown in Fig. 2(a); Fig. 2(b) shows a PNBE-coated SWNT (Table 1, entry 11) of approximate diameter = 9.1 nm, corresponding to a polymer coating of ca. 7.7 nm, as determined by the respective cross-sectional height profiles. As observed in the AFM image, the SiO₂ surface was essentially free of PNBE, which provides further support for the high selectivity of the functionalization step using polycyclic aromatics.

A series of control experiments was incorporated into our study as a probe for specific physisorption of the pyrenyl group as the functionalization mechanism. For example, no polymer was observed when the SWNTs were exposed to solutions of ruthenium benzylidene **5** instead of the pyrenyl-functionalized alkylidenes. Similarly, exposure of the SWNTs-containing grids to solutions of polymer chains already grown using either **4** or **5** as initiators resulted in an almost negligible deposition of polymer on the nanotube surface.

We have begun to study the thickness dependence of the PNBE coating on the SWNT walls as a function of various polymerization variables. Such understanding, key to developing applications such as chemo- and biosensors, should also reveal interesting fundamental information regarding the geometrics (e.g. linearity) of chain growth and organization around

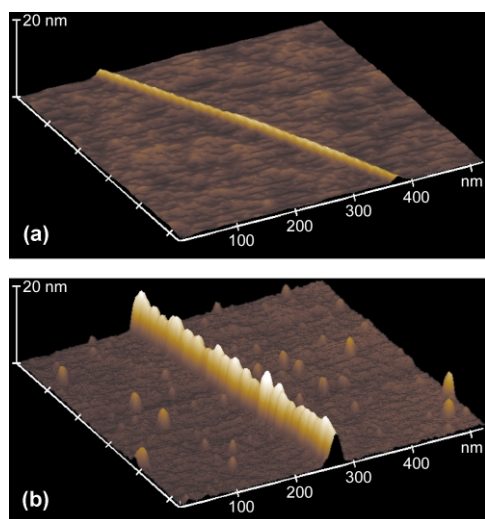


Fig. 2 Atomic force microscopy of (a) a non-functionalized SWNT and (b) a SWNT coated with polynorbornene (Table 1, entry 11).

a cylindrical object at the molecular level. While the thickness of the polynorbornene coatings on SWNTs increases with increasing monomer concentrations as predicted (Table 1, entries 4–7), it does not exhibit expected behavior with increasing polymerization time (Table 1, entries 1–4). Reaction times longer than 5–10 min, in fact, result in thinner coatings until there is virtually none at 120 min. This may be due in part to a decreasing ability of the pyrenyl group to continue to effectively anchor the polymer chain onto the SWNT while solubilization of the polymer becomes increasingly more energetically favorable as it grows longer and longer. Further efforts are directed at studying the effects that variables such as polymer desorption can have on the polymer thickness. To resolve this issue, we are currently exploring other polymerization reactions on the sidewalls of SWNTs with polymers that are less soluble in the reaction solvents.

In conclusion, we have developed a flexible methodology for the non-covalent functionalization of SWNTs with organic polymer employing ring-opening metathesis polymerization.

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Notes and references

‡ SWNTs on TEM microgrids²¹ and silicon oxide²² substrates were prepared in a manner previously described. See ESI† for a detailed experimental description.

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