

## ELECTROCHEMICAL GRAFTING OF POLYMERS ON ALIGNED MULTI-WALLED CARBON NANOTUBES

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Due to their interesting properties, carbon nanotubes (CNTs) have attracted particular attention for different application fields such as composite materials, microelectronics [1] and biology. Processing CNTs is a key point which often requires appropriate chemical modification of their surface in order to enhance their dispersability or to improve their compatibility with polymers. Regarding the numerous methods reported in the literature, chemical functionalisation is based on covalent grafting, or on molecular stacking or on wrapping of the CNTs surface with surfactants or polymers. Covalent functionalisation is usually performed chemically. More recently, methods of electrografting were reported [2, 3].

In this context, the aim of this study is to demonstrate the potentialities of electrochemical grafting of polymers on carpets of aligned CNTs. Two different methods designed to tether polymeric chains at the surface of aligned carbon nanotubes will be reported. First, grafting of BUMA (Butyl Methacrylate) by an electropolymerization method [2] will be detailed. Then, we will demonstrate that Surface-Initiated Atom Transfer Radical Polymerization (SI-ATRP) is an attractive two-step way to *graft onto* CNTs surface polymers with controlled molecular weight and thickness [4]. We have recently found that the surface “diazonium salt/ATRP” process [5a] is an effective route for carbon nanotubes functionalization with PS (PolyStyrene) and PMMA (PolyMethylMethAcrylate) [5b].

The CNTs synthesis has been performed by aerosol-assisted catalytic chemical vapour deposition (CCVD) process. Briefly, this process involves the use of solutions containing both liquid hydrocarbon and metal precursors. This method consists in producing and subsequently pyrolysing mixed liquid aerosols generated from the solutions. The starting solution is composed of ferrocene (5 wt%) dissolved in toluene and the aerosol, carried by an argon flow, is pyrolysed at 850 °C during 7 min. The resulting sample is composed of multi-walled carbon nanotubes perpendicularly aligned and attached to the substrate surface and looks like a carpet. In this case, we choose a conducting substrate (Si-n). The nanotube length reaches 130 μm, the average inter-tube spacing is around 100 nm and the external diameter of carbon nanotubes is varying between 10 and 100 nm [6, 7].

Regarding the electropolymerization process, the set-up consists in a three-electrode electrochemical cell under inert atmosphere. The working electrode was the CNTs carpet grown on Si-n, the auxiliary electrode was a graphitic carbon foil and the reference electrode was based on the Ag/Ag<sup>+</sup> couple. Finally, voltametric cycles (20 mV/s) were conducted in an electrolyte containing the monomer (BUMA). SEM images show that CNTs are mainly covered (fig 1). HRTEM observations on individual nanotubes confirm these observations showing an amorphous layer deposited on all CNTs.

For the “diazonium salt/ATRP” protocol, phenyl ethyl bromide groups were electrochemically grafted onto CNTs using the diazonium salt BF<sub>4</sub><sup>-</sup>,<sup>+</sup>N<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>CH<sub>2</sub>-Br. The as-prepared BrCH<sub>2</sub>CH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-modified CNTs (CNT-Br) served as a platform for the growth of PS and PMMA chains by ATRP. The overall synthesis process is illustrated in

figure 2. TEM images (Fig.3) show that for raw CNTs, the external surface of the nanotubes is well organized and corresponds to stacked graphene layers (Figure 3a). On the contrary, CNT-PMMA or CNT-PS hybrids exhibit amorphous layers corresponding to the grafted polymer chains the thickness of which is  $\sim 1$  and  $2$  nm (Figs. 3b and 3c).

### References:

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### Figures:

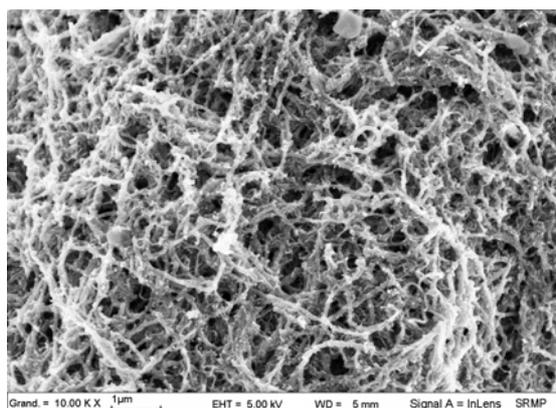


Figure 1. SEM image of CNTs grafted with BUMA

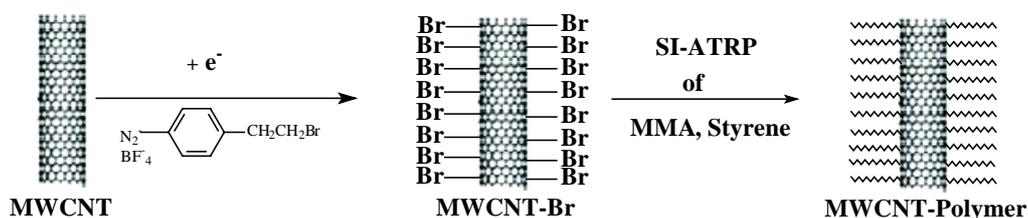


Figure 2. Brominated initiators are attached to CNTs via electrochemical reduction of the diazonium salt precursor. PS and PMMA chains are grafted by SI-ATRP from the CNT-Br platform.

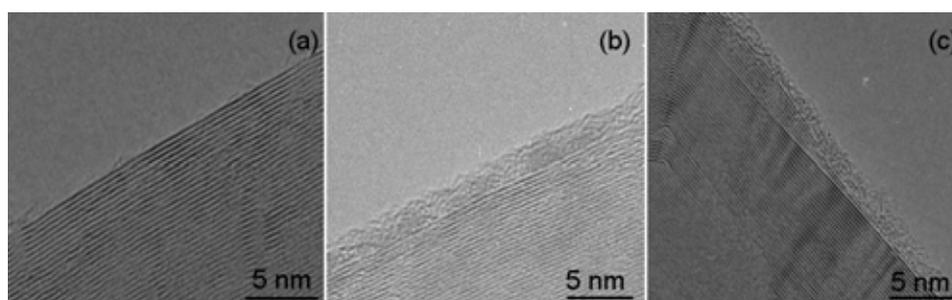


Figure 3. HRTEM images of untreated CNT (a), CNT-PMMA (b), CNT-PS (c).