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A new approach to functionalize multi-walled carbon nanotubes by the use of functional polymers

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Abstract

A new method to graft a large number of long polymer chains or small functional molecules onto multi-walled carbon nanotubes (MWNTs) indirectly is reported. First, MWNTs were slightly functionalized by reversible addition–fragmentation chain transfer (RAFT) copolymerization of styrene and maleic anhydride using the dithioester groups attached to MWNTs as RAFT agents. The highly reactive maleic anhydride groups could further react with a large number of long polymer chains or small functional molecules with hydroxyl or amino group easily. The resulted MWNTs have good solubility in organic solvents and water; the perfect structure of MWNTs is altered very little from the information of Raman spectra.

Keywords: Multi-walled carbon nanotubes (MWNTs); Reversible addition–fragmentation chain transfer (RAFT) polymerization; Functional polymer

1. Introduction

Carbon nanotubes (single-walled carbon nanotubes and multi-walled carbon nanotubes) have raised great expectations in a number of different applications, including field emission [1], energy storage [2], molecular electronics [3], atomic force microscopy [4], delivery of gene and drug [5,6], and so on.

A tremendous amount of work is being done on different aspects of carbon nanotubes such as synthesis, functionalization, and applications ranging from nanoscale electronic and memory devices to molecular sensors [7–13]. However, the inherent insolubility in most organic and aqueous solvents, poor chemical and biological compatibility of carbon nanotubes are the major limitations to the solution-phase manipulation and processability of these structures, greatly hindering the wide application of carbon nanotubes in real work [14]. Therefore, extensive research is focused on surface modification of carbon nanotubes mainly to enhance their compatibility and dissolution properties [15–27]. Noncovalent or covalent functionalization of carbon nanotubes can improve their solubility or chemical and biological compatibility. The noncovalent functionalization of carbon nanotubes include noncovalent surface coating with surfactants [28–30], surface wrapping with long polymer chains such as polystyrene sulfonate and hydrolyzed poly(styrene-*alt*-maleic anhydride) [31,32], noncovalent adsorption of hydrophilic noncharged polymer chains such as poly(vinylpyrrolidone) [33,34], poly(vinyl alcohol) [35], amylose [36], and poly(ethylene oxide) [37], on carbon nanotubes, and some electric acceptor systems stabilizing carbon nanotubes [38]. The advantage of noncovalent functionalization is that the structure and original properties of carbon nanotubes are not altered after modification. However, the surfactants, polymer chains and electric acceptors that can be used for this method are very limited, and high concentrations are usually necessary to obtain dispersions of carbon nanotubes, which is inconvenient for further processing carbon nanotubes into composite materials; the dispersions are not very stable, and most important, it is difficult to further modify carbon nanotubes with different functionalities [14].

Direct covalent functionalization can improve carbon nanotubes' solubility and compatibility greatly. Generally, long alkyl chains, polymer chains, and biomolecules can be grafted onto carbon nanotubes by esterification or amidation reactions [39–41]. The species grafted onto the surface of carbon nanotubes include fluorine [42], aryl radicals [43],

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aryl cations [44], hydrogen [45], nitrenes [46], carbenes [47], radicals [48], 1,3-dipoles [49], polystyrene [50–52], poly(methyl methacrylate) [53], poly(ethylene oxide) [54], polyetherimides [24], poly(aminobenzene sulfonic acid) [55], poly(*N*-isopropylacrylamide) [56,57], and hyperbranched polymers [25]. The covalent functionalization of carbon nanotubes reported often have some limitations, which includes the necessity of a high functionalization density for good solubility and compatibility; altering the structure and the corresponding properties of carbon nanotubes; as well as difficulty for further functionalization. Generally, the more modifications on the surface, the more outstanding properties of carbon nanotubes will be altered. High modification density of carbon nanotubes is often needed even use long polymer chains in order to get good solubility in organic or aqueous solvents. How to modify carbon nanotubes with altering the perfect structure and the original special properties very little has become a major challenge at present time.

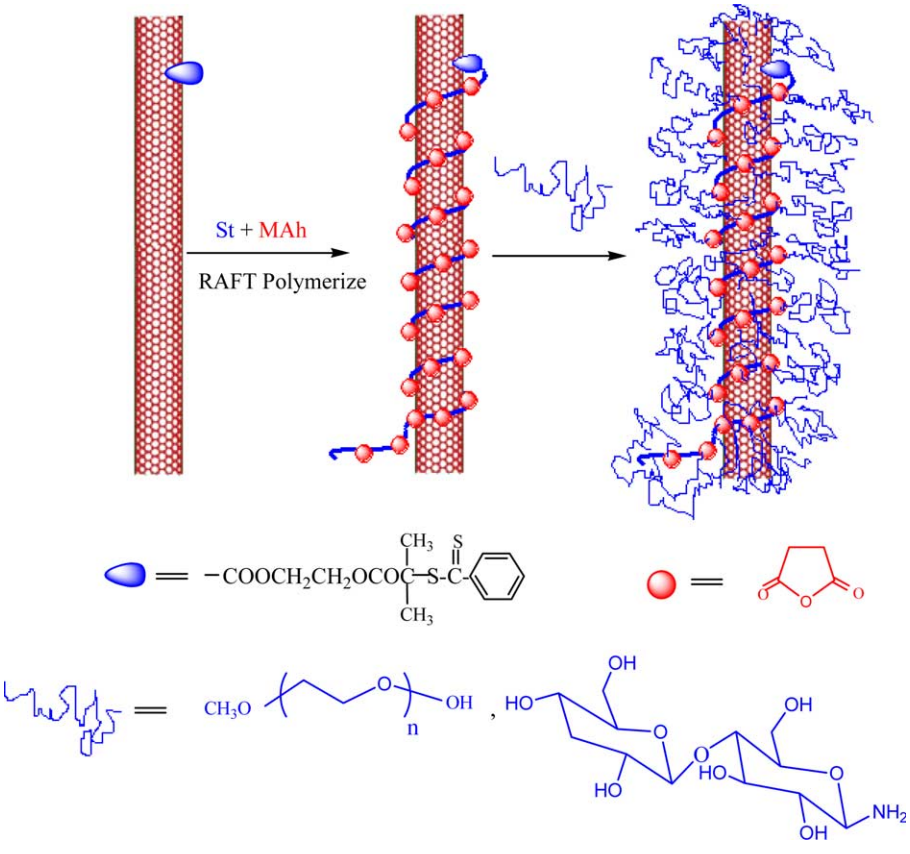
Among the various functional groups used in coupling chemistry, maleic anhydride has high reactivity and versatility in conjugation with long polymer chains, sugar, peptide, protein, lysine, biotin, dye and fluorinated probes, etc. [58–62]. Poly(styrene-*alt*-maleic anhydride), P(St-*alt*-MAh), is a special synthetic copolymer, having lots of highly reactive maleic anhydride groups in the main chain, which can be used for conjugation with long polymer chain, peptide, protein, etc. P(St-*alt*-MAh) conjugates have many potential applications, for example, conjugation of neocarzinostatin (a potent but very toxic antitumor protein) with P(St-*alt*-MAh) causes an increase of the neocarzinostatin plasma half-life and a decrease of its toxicity [60]; immobilization of Laminin peptide with P(St-*alt*-MAh) resulted in an increase of antimetastatic effect [62].

In this paper, instead of grafting a large number of long polymer chains or biomolecules onto carbon nanotubes directly and altering their structure and properties, we graft lots of long polymer chains or small functional molecules onto carbon nanotubes indirectly. The detailed procedure is outlined in Scheme 1: first, we used long polymer chains which contain lots of highly reactive maleic anhydride groups in the main chain to slightly functionalize MWNTs. Second, by reacting with these groups, it is very easy to graft many long chains, such as PEO-OH, proteins, peptides, etc. or small functional molecules such as amino sugars, onto the surface of MWNTs indirectly, which not only improves MWNTs' solubility in organic or aqueous solvents greatly, but also provide an easy way to make MWNTs biocompatible by further modification with amino sugars, biotins, proteins and peptides, etc. at maleic anhydride sites, the perfect structure of MWNTs altered very little.

2. Experimental sections

2.1. Materials

The MWNTs were purchased from Tsinghua-Nafine Nano-Powder Commercialization Engineering Centre in Beijing.



Scheme 1.