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Polystyrene grafted multi-walled carbon nanotubes

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Oxidised, multi-walled, carbon nanotubes can be grafted with polystyrene molecules using an *in situ* radical polymerisation reaction, thereby dramatically modifying their solubility and their suitability for nanocomposite applications.

There is intense interest in modifying the surfaces of carbon nanotubes[1] in order to improve both their processability in a range of solvents and the performance of nanocomposite materials. Nanotubes generally have very low solubilities in all solvents although they can be enhanced by surface treatment; for example, strong acids introduce oxygen-containing surface groups which lead to electrostatic stabilisation in polar solvents.[2] However, attachment of surface polymer chains is expected to provide much more effective, steric stabilisation in a wide range of solvents, as dictated by the nature of the polymer. Such controlled dispersions are desired in order to assemble nanotubes into a variety of structures, potentially *via* a lyotropic liquid crystalline phase. Due to the remarkable intrinsic mechanical properties of nanotubes there has been considerable focus on producing composite materials.[3] Despite promising results, further development requires, amongst other steps, the compatibilisation of nanotubes with the required matrix, and the formation of a strong nanotube–matrix interface.

There have been a number of reports describing the attachment of short chains to single walled nanotubes, mainly by esterification/amidation of surface acid groups,[4–8] However, very little attention has been paid to grafting onto multi-walled nanotubes despite their much wider availability and use in nanocomposites. Exceptions include the attachment of prepolymerised poly(propionylethylimine-co-ethylenimine) by esterification[8] and the formation of a polyaniline nanotube composite.[9] Here, we report the synthesis of individual, polystyrene-grafted nanotubes by an *in situ* radical polymerisation technique.

In our experiments, we have used multi-walled carbon nanotubes (MWNT) synthesized in-house by a chemical vapour deposition technique, which allows production of aligned nanotubes of controlled length and diameter.[10] These nanotubes were first treated with a 3 : 1 concentrated sulfuric–nitric acid mixture at 45 °C, and then washed to produce a dispersion in water, following a modified version of a previously reported method.[2] These dispersions were combined with purified styrene monomer and a radical initiator (benzoyl peroxide or potassium persulfate). The imisicible layers were stirred rapidly to produce an emulsion and the polymerisation conducted under argon at 80 °C for 2 h. After the reaction, the black colouration due to the nanotubes was transferred from the aqueous to the organic layer. The reaction mixture was diluted with toluene and the organic layer centrifuged at 4500 rpm to sediment the grafted nanotube product. Repeated centrifugation and resuspension in toluene was used to remove all of the non-grafted polystyrene. The relative masses of the initial nanotube content, non-grafted polymer and grafted product were used to calculate the grafting efficiency (fraction of total polymer grafted) and grafting ratio (ratio of grafted polymer to nanotube product). The aqueous layer was evaporated to dryness to confirm that no unreacted nanotubes remained.

The grafted nanotubes readily redisperse in solvents such as toluene, chloroform and THF, but are no longer compatible with water or acetone (see Fig. 1). Fig. 2 shows an SEM micrograph of the partially purified product containing both the grafted nanotubes and aggregates of ungrafted polystyrene. Most of the nanotubes are separated but there are examples of two or more

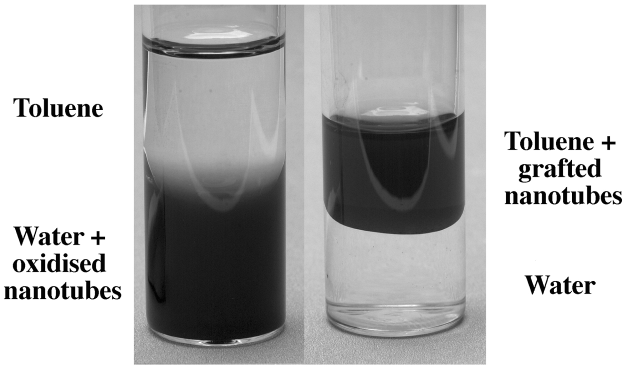

Fig. 1 Photograph showing the reversal of nanotube solubility produced by the reaction.

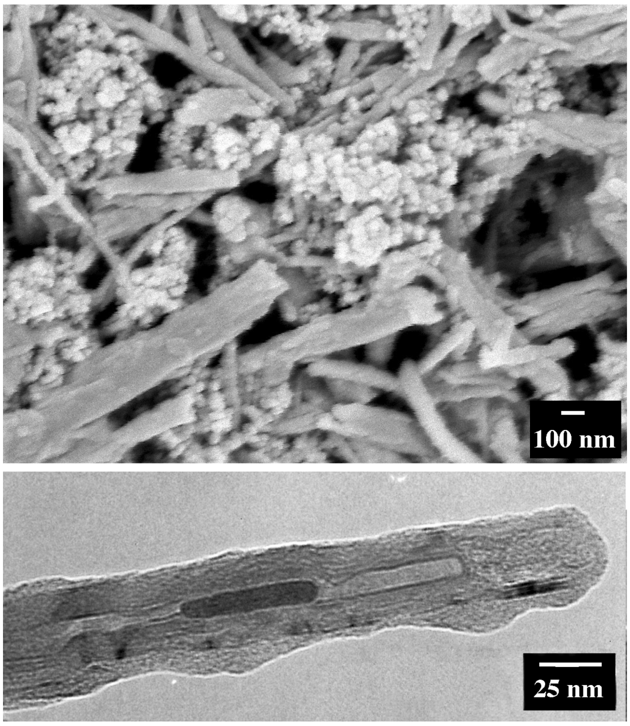

Fig. 2 SEM (top) of partially purified grafted nanotubes (the polymer aggregates disappeared after further purification) and TEM (bottom) of a single grafted nanotube.

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parallel nanotubes fused together by their polymeric jacket. Fig. 2 also shows a TEM micrograph of a typical grafted nanotube where a thin polymer coating (5–10 nm) can be seen. Thicker coatings have also been observed. The image shows an iron CVD catalyst particle trapped within the tube where it was protected from the aggressive acid mixture. Grafting ratios of 50–90% were observed depending on initial nanotube concentration. The grafting efficiency was around 0.5% for the benzoyl peroxide system, but reached 18% in the case of the potassium persulfate initiator.

In order to confirm that the results were not simply due to adsorption of the polymer onto the nanotube surface, an aqueous nanotube dispersion was stirred vigorously into a toluene–polystyrene solution. After centrifugal separation, the nanotubes were found to remain soluble in water and insoluble in toluene, whist TEM analysis confirmed that no polymer layer could be observed on the nanotube surface. Indeed, it seems unlikely that polystyrene would adsorb onto the hydrophilic surface of the oxidised nanotubes.

The grafting mechanism is likely to involve growing polymer radicals attaching themselves to the defective, oxidised, carbon surface of the nanotubes,[2] although the small molecule initiators may also attack the nanotubes directly. Both effects have been suggested for radical reactions on other carbonaceous materials such as fullerenes[11] and carbon blacks.[12] The different grafting efficiencies observed for the two initiators can be understood in terms of their solubilities in the organic phase. The benzoyl peroxide is present in the monomer styrene and can readily initiate polymerisation of the homopolymer; on the other hand, the persulfate resides in the aqueous phase where it is more likely to attack the nanotubes. In both cases, we believe that a fraction of the nanotubes originally present themselves at the water–styrene interface, but as the reaction proceeds they are drawn into the organic phase where they can continue to attract additional polymer chains. It is interesting to note that emulsions of water and styrene are much more stable (sometimes for many hours) in the presence of oxidised nanotubes, which strongly suggests that the nanotubes act as a surfactant, sitting in the interface between the two phases.

Thus, we have developed a straightforward procedure for grafting polystyrene onto multi-walled nanotubes that promises to enable the next generation of nanotube composites, and which may readily be extended to a wide range of other vinyl polymers. The reaction parameters may be adjusted to control the grafting ratio and efficiency.

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