

## Multiwalled Carbon Nanotubes Functionalized with PS via Emulsion Polymerization

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**Abstract:** This study demonstrated the in-situ functionalization with polymers of multi-walled carbon nanotubes (MWNTs) via emulsion polymerization. Polystyrene-functionalized MWNTs were prepared in an aqueous solution containing styrene monomer, non-ionic surfactant and a cationic coupling agent ([2-(methacryloyloxy)ethyl]trimethylammonium chloride (MATMAC)). This process produced an interesting morphology in which the MWNTs, consisting of bead-string shapes or MWNTs embedded in the beads, when polymer beads were sufficiently large, produced nanohybrid material. This morphology was attributed to the interaction between the cationic coupling agent and the nanotube surface which induced polymerization within the hemimicellar or hemicylindrical structures of surfactant micelles on the surface of the nanotubes. In a solution containing MATMAC alone without surfactant, carbon nanotubes (CNTs) were not well-dispersed, and in a solution containing only surfactant without MATMAC, polymeric beads were synthesized in isolation from CNTs and continued to exist separately. The incorporation of MATMAC and surfactant together enabled large amounts of CNTs (> 0.05 wt%) to be well-dispersed in water and very effectively encapsulated by polymer chains. This method could be applied to other well-dispersed CNT solutions containing amphiphilic molecules, regardless of the type (i.e., anionic, cationic or nonionic). In this way, the solubility and dispersion of nanotubes could be increased in a solvent or polymer matrix. By enhancing the interfacial adhesion, this method might also contribute to the improved dispersion of nanotubes in a polymer matrix and thus the creation of superior polymer nanocomposites.

**Keywords:** carbon nanotubes, emulsion polymerization, polymer functionalization, [2-(methacryloyloxy)ethyl]trimethylammonium chloride.

### Introduction

Since their discovery, carbon nanotubes (CNTs) have attracted considerable attention because of the wide range of their potential applications. The dispersion of nanotubes in a matrix and the interface adhesion between nanotubes and the matrix determine the processibility and performance of nanocomposite materials, and are thus vital issues in the development of appropriate applications. Clearly, the unique mechanical, electronic, thermal and optical properties of polymer/nanotubes composites must be carefully considered. One approach is the modification or functionalization of nanotube surfaces by introducing oxygen-containing functional groups such as -OH, -COOH, -C=O by surface treatment (e.g., strong acid treatment, plasma-oxidation process, etc.).<sup>1-10</sup> This leads to the electrostatic stabilization of

nanotubes in polar solvents. Other functional groups such as fluorine or thiol or amide groups can also be introduced to increase solubility in organic solvents.<sup>11-15</sup> In some reports, grafting polymer chains from or to these functional groups has been done through living anionic polymerization or radical polymerization such as atom transfer radical polymerization (ATRP) or reversible addition fragmentation chain transfer (RAFT) polymerization to provide steric stabilization and improve nanotube/polymer matrix interface adhesion.<sup>16-27</sup> These reports usually describe the attachment of short polymer chains to nanotubes by esterification or amidation of surface acid groups.

Such chemical modifications of carbon nanotubes can result in unfavorable changes to their wall structure, including loss of unique advantageous properties. However, the encapsulation of nanotubes with polymer chains via non-covalent bonding has been found to be especially desirable because this approach does not alter the wall structure of

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nanotubes.<sup>28-39</sup> Jerome *et al.* carried out the non-covalent functionalization of MWNTs by mixing polymers containing pyrene. This method was found to be a very efficient way to enable a good dispersion of CNT in organic solvent and prepare homogeneous CNT/polymer composites.<sup>35</sup> However, it required ATRP as an additional step to synthesize the special-targeted polymer containing pyrene.

Recently, inorganic carbonaceous fillers such as carbon nanotubes have been encapsulated using surfactant-aided mini-emulsion or emulsion polymerization. D.E. Resasco *et al.* prepared SWNT-polystyrene (PS) and SWNT-styrene-isoprene (SI) hybrid materials in situ under mini-emulsion polymerization utilizing a cationic surfactant solution. Their approach, however, was not applicable to MWNTs<sup>29</sup> because in mini-emulsion polymerization, nanotubes have to first be dispersed in a monomer droplet with a diameter of a few tens of nm to produce nanohybrid materials. Although SWNT has a diameter narrow enough to be incorporated within the monomer droplet, MWNT is too thick to be contained within the droplet. Meanwhile, emulsion polymerization has been used effectively for various size ranges of polymer beads up to several micrometers, and thus seemed to be applicable to MWNTs. In fact, the creation of polymer-grafted MWNTs via emulsion polymerization had been performed earlier.<sup>36,37</sup> It is important to note, however, that only cationic surfactants were utilized in emulsion polymerization in previous studies. These studies applied a similar procedure using anionic surfactant (sodium dodecyl sulfate (SDS)) but did not succeed in incorporating the nanotubes inside the polymeric matrix. This study suggests a way to overcome this surfactant limitation by incorporating a novel cationic coupling agent in aqueous micellar solution. As far as could be determined, no studies have yet reported using *non-cationic* surfactants for modifying nanotube surfaces with polymer. Nonetheless, this procedure can be applied to any surfactant-containing CNT solution provided that it shows a well-dispersed status.

The purpose of this study was to develop an effective and simple method for the side-wall functionalization of full-length MWNTs via emulsion polymerization using non-ionic surfactant and a coupling agent. This coupling agent, [2-(methacryloyloxy)ethyl]trimethylammonium chloride (MATMAC) not only has a cationic affinity with nanotube surfaces, but also has a double bond consisting of a polymerizable moiety with styrene monomers. These characteristics can induce polymerization on nanotube surfaces within the micellar structure of surfactants. The MWNT nanohybrid materials obtained in this study were embossed via encapsulation of PS beads or entirely embedded in polymer beads, depending on the size of the beads. Even though MWNTs have very attractive and unique properties in nanocomposites, not many studies have looked at their functionalization. The simple and novel approach for polymer functionalization developed in this study is expected to be

effective in dispersing MWNTs in solvents or polymer matrices and preparing nanotube-polymer nanocomposite materials.

This method offers several advantages. First, the use of a cationic coupling agent broadens the choice of the surfactant used for improving the dispersion of carbon nanotubes. Given the various types of surfactants reported in previous studies (cationic, anionic or nonionic), the method presented in this study could be easily applied to the polymer functionalization of nanotubes via mini-emulsion or emulsion polymerization, even in large amounts. Second, the method involves in-situ polymerization of nanotubes and monomers together. No preliminary steps are needed to synthesize a special-aimed polymer or surfactant. Furthermore, emulsion polymerization is a well-established method which can easily be applied to a variety of in-situ polymerization processes. An additional advantage is that by controlling the size of beads in emulsion polymerization, a different morphology of polymer-functionalized nanotubes can be achieved.

## Experimental

The MWNTs employed in this study were supplied by Hanyang University (Korea, CVD) and had diameters ranging from several nm to 30 nm with lengths between 10-50  $\mu\text{m}$ . Their aspect ratios as fibers were very large. Styrene (Aldrich, 99% purity), [2-(methacryloyloxy)ethyl]trimethylammonium chloride (MATMAC), Triton<sup>®</sup> X-405 (Aldrich, 70% aqueous solution) and potassium persulfate (KPS) (Aldrich, 99% purity) were used as received. Toluene (Aldrich) was used without further purification. Acid treatment was performed by treating the MWNTs (0.6 g) with an excess of concentrated nitric acid (120 mL of 70 wt% aqueous solution) for 2 h under refluxing at 130°C. Acid treated MWNTs were collected by filtration (ALBET<sup>®</sup>, 0.2  $\mu\text{m}$ , cellulose acetate) and washed several times with distilled water until pH of the filtrate was neutral. After washing, the acid treated MWNTs were freeze-dried for 5 days. To make the MWNTs disperse well in water, nonionic surfactant (Triton X-405) was applied. 4.5 g of Triton X-405 was added to 300 mL of deionized water in the absence of MWNTs. After 30 min of moderate sonication, the acid treated nanotubes were added and sonication was continued for 1 h under N<sub>2</sub> atmosphere. Then the coupling agent, [2-(methacryloyloxy)ethyl]trimethylammonium chloride (MATMAC) was mixed with this dark solution (surfactant/MWNTs). After 60 min of additional sonication, the solution was filtered via a microfiltration cell (ALBET<sup>®</sup>, 0.2  $\mu\text{m}$ , Cellulose acetate) and washed with deionized water several times to remove excess surfactant and modifier. The treated MWNTs were then freeze-dried for 5 days.

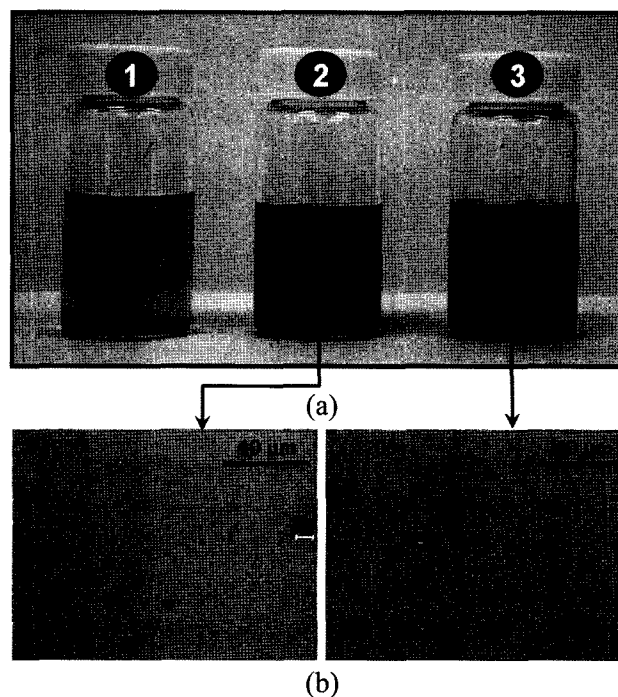
PS-functionalized MWNTs were prepared via the emulsion polymerization method. In a typical experiment, 0.15 g of nonionic surfactant (Triton X-405) was added to 100 mL

deionized water in the absence of MWNTs. After 20 min of sonication, pre-treated nanotube powders (0.05 g) were added to the aqueous solution and sonication was continued for 1 h. After sonication, 10 g of purified styrene monomer was added to the surfactant/nanotube solution and continuously stirred under  $N_2$  gas at  $70^\circ C$ . Then 0.05 g of radical initiator, potassium persulfate ( $K_2S_2O_8$ ), was added and polymerization was continued for 6 h. The grayish slurry was washed several times with methanol to remove the surfactant and then freeze-dried.

TEM images were taken using a Hitachi-7600 at an accelerating voltage of 80 kV and HR-TEM using Tecnai G2 (FEI Hong Kong Co., Ltd.) at 100 kV. One drop of PS grafted MWNT toluene suspension was placed on a carbon coated formvar grid. Samples were selected after drying at room temperature overnight. Atomic force microscopy (AFM) imaging was observed using a Nanoscope IV (Digital Instrument/Veeco Metrology Group, USA). This was operated in tapping mode with RTESP model Si/N tips.  $1\text{ cm} \times 1\text{ cm}$  silicon wafers were used as the substrate for spin coating the solution and soaked in a boiling solution of 3 : 1 by volume sulfuric acid and hydrogen peroxide (Piranha solution) for 1 h, then rinsed thoroughly with distilled water and dried with nitrogen gas. A small drop of a PS functionalized MWNT toluene suspension was placed on the prepared substrate and spin-coated at 2,000 rpm for 30 s, followed by AFM imaging. FE-SEM observations were performed with a Hitachi S-4200 scanning electron microscope operating at 10 kV. The specimens were gold-coated prior to examination.

## Results and Discussions

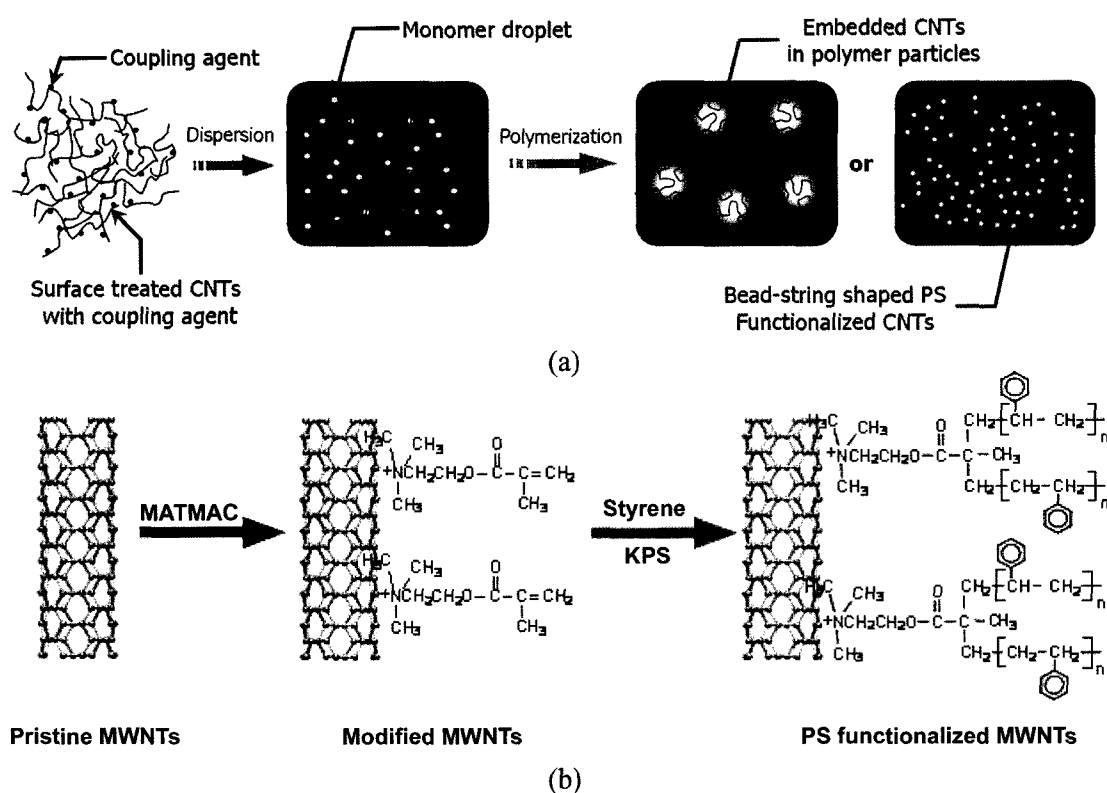
Figure 1 shows the MWNT/water suspensions containing equal concentrations of nanotubes at 0.05 wt%. In the left vial in Figure 1(a), MWNTs form the aggregation at the bottom of the vial and are not stabilized in the aqueous medium. Without surfactants, the MWNT suspension of 0.05 wt% is too concentrated to be well-dispersed in water. The addition of surfactant rendered good dispersion in the MWNT suspension which remained a homogeneous solution even after several weeks (middle and right vials in Figure 1(a)). Transmitted light microscopic pictures in Figure 1(b) reveal that MATMAC has an additional dispersing effect. The MWNT/Triton-X 405/MATMAC suspension shows even more homogeneous dispersion than the MWNT/Triton-X 405 suspension. Even though MATMAC alone didn't show sufficient dispersion, MATMAC played a key role as a coupling agent in preparing polymer-functionalized MWNTs with well-dispersed suspensions. Both functional groups at each end of MATMAC in Figure 2 further emphasize this point. The positive ammonium ion at one end interacted with the electron-rich nanotubes or some COOH groups on their surfaces which increased the chance



**Figure 1.** (a) Dispersed MWNT in distilled water (1) neat MWNT, (2) MWNT/Triton X-405, (3) MWNT/Triton X-405/MATMAC; (b) Transmitted light microscopic pictures of sample 2 (left) and 3 (right).

that its double bond at the other end joined the polymerization of PS within the micelle structure of TritonX-405 near the nanotubes. These moieties of MATMAC bring to the PS-functionalized nanotubes without destroying the chemical structure of the nanotubes whose morphology depends on the size of polymer particles as schematically shown in Figure 2(a). Figure 2 summarizes the schematic diagram of the entire procedure described above.

Figures 3(a) and (b) show field emission-scanning electron microscopy (FE-SEM) images of (a) bead-string shaped PS-functionalized MWNTs and (b) MWNTs-embedded in polymer particles obtained via emulsion polymerization in the aqueous medium containing Triton-X 405 and MATMAC. While neat nanotubes show aggregation, Figure 3(a) clearly indicates that all nanotubes are isolated from neat PS particles, and small or comparable size PS beads are located along its length. In Figure 3(b), whole nanotubes are embedded within one PS particle which maintains its spherical shape, which were prepared by similar procedures except the sonication process. Here the omission of sonication after mixing the monomer and nanotubes led to the broad size distribution of the polymer beads. Most nanotubes were enveloped by large beads over  $2\ \mu m$ . No isolated MWNTs were observed. These results show that the size of monomer droplets in emulsion polymerization may influence the morphology of polymer-functionalized nanotubes. In order to



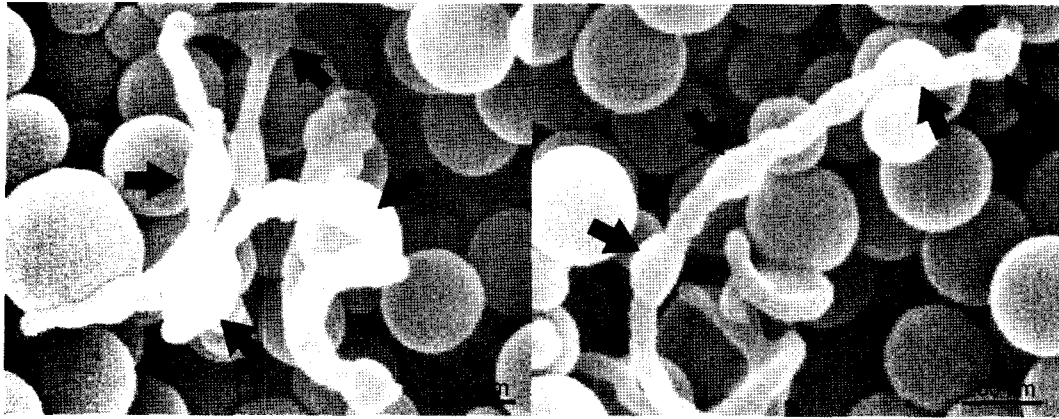
**Figure 2.** (a) Schematic diagrams of in-situ polymerization on MWNTs in the presence of surfactant and coupling agent (b) PS-functionalized MWNTs (MATMAC and KPS mean [2-(methacryloyloxy)ethyl]trimethylammonium chloride and potassium persulfate, respectively).

confirm the role of the coupling agent, the same emulsion polymerization was tried excluding only MATMAC, and eventually no PS-functionalized nanotubes remained (a very thin PS layer indicated that PS functionalization had occurred). PS particles and nanotubes existed separately, as presented in Figure 4. This figure mirrors previous results showing that polymer-grafted nanotubes prepared through emulsion or mini-emulsion polymerization were not successfully functionalized in the absence of cationic affinity.<sup>29</sup> The exact mechanism for this process will be discussed later. The PS-rich and PS-deficient parts on a single nanotube were found in an AFM image (Figure 5) as indicated with arrows. Section profiles revealed that the difference between their heights was about 19.5 nm or larger which corresponded to the amount of PS around a nanotube.

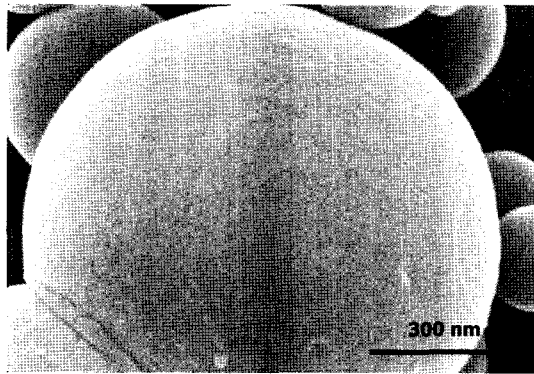
To experimentally confirm the existence of PS on the nanotubes, TEM analysis was done after eliminating the surrounding bulky PS particles which were too thick to be penetrated by the transmitted beam. The final products were thoroughly dissolved in toluene over 72 h, filtered via microfiltration and washed with toluene a few times. Isolated PS beads or some PS chains far from the nanotubes might have been washed away because they interacted weakly with the nanotubes via physical bonding. Only PS-

functionalized nanotubes were obtained as black powder. Figure 6 shows the transmission electron microscopy (TEM) images of PS-functionalized nanotubes. By dissolving the bead-string shaped nanotubes in toluene, the bead shaped morphology disappeared and the aromatic nature of the styrene and nanotubes enabled PS polymer chains to be redistributed flatly along the nanotubes with a thickness of several nm, which is energetically favorable for increasing the binding energy and surface coverage of PS molecules onto nanotubes. The flat layer of functionalized PS on the MWNTs is indicated clearly in the TEM images in Figure 6. While the wall of neat nanotubes shows a homogeneous dark color, the PS-functionalized nanotubes have an irregular coated layer of PS and all nanotubes are isolated.

We now return to the mechanism of the bead-string shaped nanotubes, as illustrated in Figure 7. It appears that TritonX-405, the surfactant used in this study, had a significant effect on forming a bead-string shape. In our view, surfactant molecules may be absorbed with a hemimicellar or hemicylindrical shape onto the nanotubes regardless of surfactant type (cationic, anionic or nonionic).<sup>40,41</sup> Because of the long alkyl chain, the benzene ring and bulky headgroup of the adjoining surfactant molecules (Triton-X 405) were able to lie flat on the CNT surface along the length of the

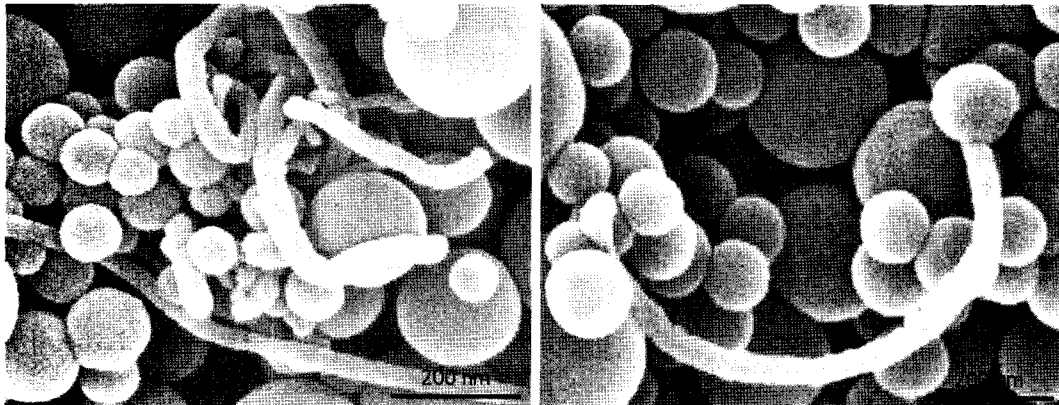


(a)



(b)

**Figure 3.** FE-SEM images of (a) bead-string shaped PS-functionalized MWNTs. MWNTs penetrate into PS particles indicated by arrows. (b) nanotube-embedded PS particles prepared with sonication.



**Figure 4.** FE-SEM images of separate MWNTs and polymer particles prepared without coupling agent (MATMAC). No PS-functionalized nanotubes exist and only neat PS particles are synthesized separately from nanotubes.

nanotubes as shown in Figure 7(a). Due to the small curvature radius of the nanotubes, surfactant molecules are probably unable to wrap around the nanotube. Hansma *et al.* and Ducker *et al.* have already visualized hemicylindrical or hemispherical micelles on a graphite plate by AFM.<sup>41</sup> The

cationic coupling agent, MATMAC, interacted with the electro-rich graphite surface or COOH functional groups of the nanotubes. The styrene monomers diffused into hemimicelles on the nanotube surface as well as the micellar structure of surfactants in aqueous media from the monomer

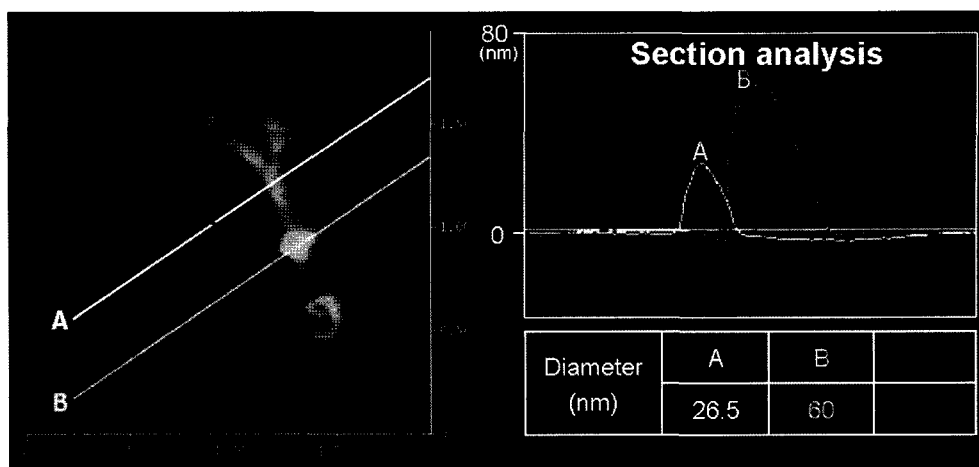


Figure 5. AFM image and section analysis of PS functionalized MWNTs.

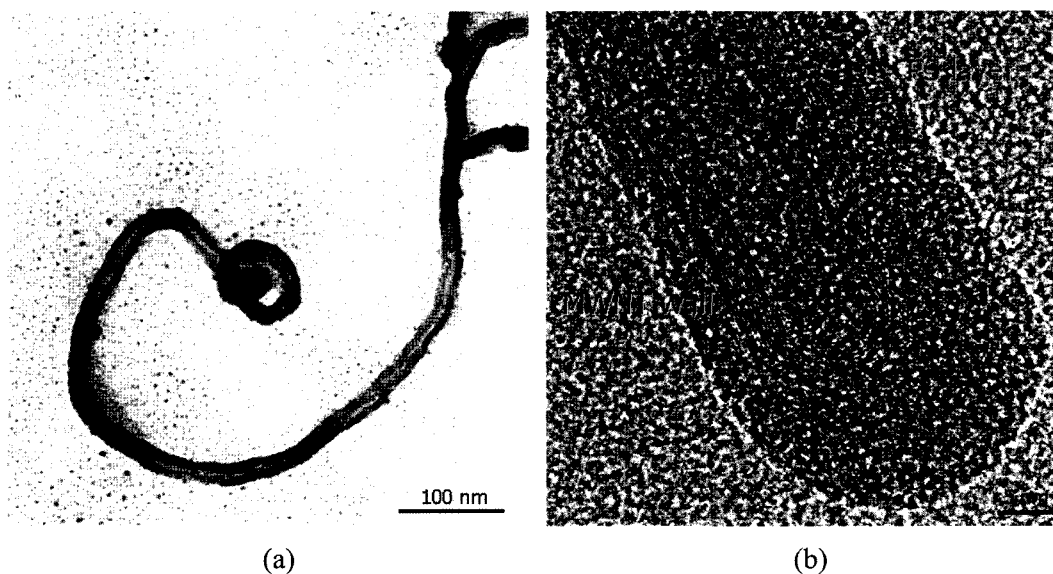


Figure 6. (a) TEM of PS functionalized MWNTs and (b) high resolution-TEM image of enlarged morphology.

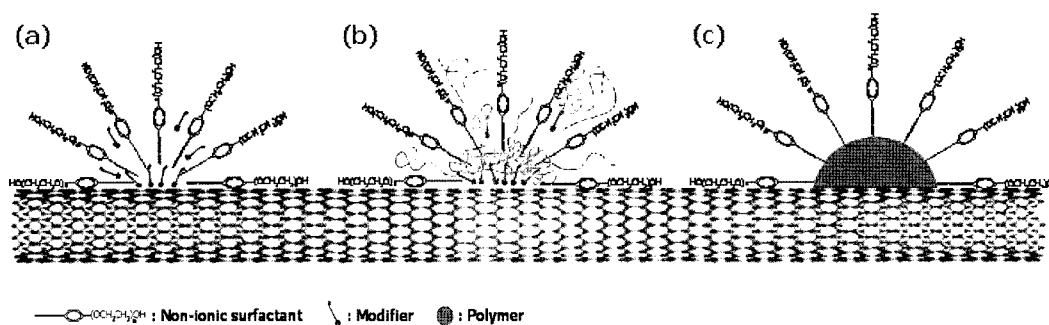


Figure 7. Mechanism of PS-functionalized nanotubes prepared with surfactant and coupling agent (MATMAC).

droplets. When the PS was polymerized within the hemimicelles on the nanotube surfaces, the double bond of MATMAC may have joined that reaction. Furthermore, the

synthesized PS chains may have stayed near the nanotubes due to the hydrophobic interaction between PS and the nanotubes as well as the cationic affinity of MATMAC in the

aqueous medium which kept the hemispherical shapes. As polymerization proceeded, the micelle size grew large enough to incorporate neighboring micelles and cylinders into one large shape. This resulted in a series of PS beads penetrated by nanotubes. If the micelles were large enough, the entire structure of the nanotubes became imbedded within them.

We think that polymer functionalization likely involves partial grafting of polymer radical chains which attach themselves to oxidized and defective CNT surfaces through radical polymerization.<sup>21</sup> The existence of a PS layer after thorough washing with toluene suggests chemical functionalization of polymer chains or a strong physical interaction between MWNTs and PS. However, it is clear that the incorporation of cationic coupling agent and surfactant during emulsion polymerization enabled large amounts of CNTs to be well-dispersed in water, then effectively encapsulated them via non-covalent interaction into polymer chains with a bead shape. In the case where MATMAC was not present in the emulsion polymerization process, it was observed that nanotubes didn't participate in emulsion polymerization, but rather, existed separately while forming some aggregates. As discussed previously, Resasco *et al.* observed that SWNT-filled PS composites could be prepared by mini-emulsion polymerization in the presence of cationic surfactants; however, a similar procedure using anionic surfactant consistently produced only neat polymer and a dispersed nanotube solution.<sup>29</sup> The same phenomenon was also observed in a study by Liu *et al.*<sup>36</sup> The cationic affinity of the coupling agent in this study performed the role of mediating between nanotubes and polymer just as cationic surfactants have done in previous research. Therefore, the procedures used in this study could be expected to succeed in initiating cooperation between polymer and nanotubes in the presence of any type of amphiphilic molecules which have previously been reported to make nanotubes soluble. The construction of high performance nanocomposites within a polymer matrix using these types of PS-functionalized nanotubes will soon be reported.<sup>42</sup>

## Conclusions

This study demonstrated the fabrication of polymer-functionalized MWNTs prepared with a nonionic surfactant and cationic coupling agent. The micelle structure of the nonionic surfactant (TritonX-405) produced an interesting morphology of PS on nanotubes consisting of bead-string shaped PS-functionalized MWNTs or MWNT-embedded polymeric particles. The morphology of the polymer-functionalized nanotubes depended on the size of the polymer beads. It was also found that the presence of cationic affinity in polymerization is very important as a coupling agent, though not as a stabilizing agent. This affinity causes the polymer chain to remain near the nanotubes via non-covalent

interaction and induces polymer functionalization on the nanotubes. This process could be applied to most well-dispersed MWNT solutions regardless of the type of surfactant. The process could also be useful in effectively stabilizing and dispersing nanotubes in solvent or polymer matrix to develop high performance nanocomposites with MWNTs.

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