Synthesis of PEGylated Single Wall Carbon Nanotubes by a Photoinitiated Graft From Polymerization

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A considerable amount of research has been devoted to carbon nanotubes because of their unique electrical, mechanical, optical, and chemical properties. Here, in this report, we introduce a novel, simple ultraviolet initiated "graft from" polymerization method to synthesize PEGylated carbon nanotubes. This grafting procedure significantly enhanced nanotube aqueous dispersibility and long term stability in solution. Mass of grafted polymer chains was easily modulated by adjusting polymerization reaction time, and nanomaterials containing up to 80% polymer by weight were synthesized. Nanotube morphology was characterized by SEM, TEM before and after the functionalization. In addition, the covalent bonding of polymer chains to the nanotubes structure was elucidated by Raman, ATR-FTIR, and XPS spectroscopy. © 2009 American Institute of Chemical Engineers *AIChE J,* 56: 1610–1615, 2010

Keywords: PEGylation, carbon nanotubes, functionalization, "graft from" polymerization

Introduction

Single wall carbon nanotubes (SWNTs) are regarded as great substrate materials for diverse future applications because of the unique and interesting mechanical, electrical, optical, and thermal properties.[1–4] However, to maximize their versatility, the poor dispersibility of carbon nanotubes in aqueous solutions needs to be addressed.[5,6] Functionalization of SWNTs with polymer molecules, done either by non-covalent or covalent methods, is one of the most common methods for enhancing nanotube dispersibility.[7–9] In one of the simplest examples, Bandyopadhyaya et al.[5] mixed as-grown carbon nanotubes with a solution of gum arabic, a polysaccharide derived from the Acacia senegal tree. Adsorbed chains radiate outwards from the SWNT surface and prevent agglomeration through steric hindrance. A second example of non-covalent SWNT functionalization uses single stranded DNA (ssDNA) to provide for aqueous dispersion. Zheng et al.[10] reported that through π-π interactions, the DNA molecule was helically wrapped around the carbon nanotube surface. Similarly, equilibrium is created between the intertube force and the binding force, which prevent the nanotubes from aggregation. Although dispersion enhancement through noncovalent means is relatively simple, covalent functionalization is more popular and gives better results. Fernando et al.[11] reported using poly (propionylethylenimin-co-ethylenimine, PPEI-EI) and poly (vinyl alcohol, PVA) to increase carbon nanotubes dispersibility. The PPEI-EI/PVA SWNT conjugates were formed through an arylation-amidation reaction. After the functionalization, the carbon nanotube dispersibility in water and organic solvents increased dramatically to more than 1 mg/ml.

The addition of polymer chains to the surface of carbon nanotubes is an appealing technology as these macromolecules not only help to disperse the carbon nanotubes in solvent, but also provide functional groups for further functionalization, e.g., sites for bonding between the polymer matrix and nanomaterial in polymer nanocomposites.[12–15] In the traditional "graft to" method, sonochemical treatment is used to introduce reactive sites on the SWNTs surface.

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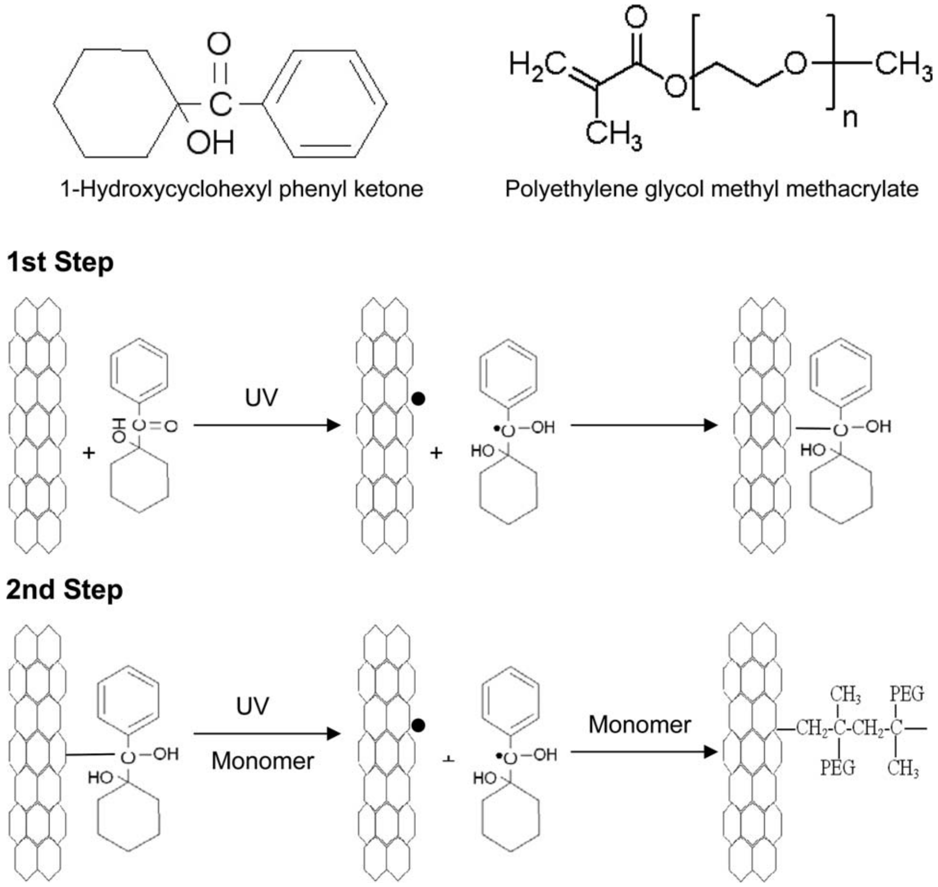

Scheme 1. Illustration of the process of ultraviolet initiated "graft from" polymerization method to synthesize polymer functionalized carbon nanotube.

Polymer molecules are then synthesized and grafted to the SWNTs surface through various chemical reactions. Steric hindrance from previously attached chains slows further macromolecular addition, a disadvantage of this method. Additionally, the pristine carbon nanotube's surface must be first functionalized to accept polymer grafts, a process which can partially destroy the electrical or mechanical properties.[16]

Alternatively, Mylvaganam and Zhang[17] noted that conducting a free radical polymerization in the presence of carbon nanotubes led to termination of the propagating species at the nanotube surface. A separation step may then be conducted to remove polymer functionalized nanotube from the unbound chains.

Here, we report a ''graft from'' method where polymer molecules are synthesized from initiation sites directly on the nanotube surface. We have adopted the method proposed by Ma et al.[18] for the modification of poly (propylene) surfaces and tailored it for use with carbon nanotubes. Immobilization of initiator on the nanotube surface provides sites for polymer growth. Irradiation of dissolved photoinitiator leads to dissociation into radical fragments which subsequently attack the nanotube surface. Unbound photoinitiator is then removed by centrifugation or dialysis. Further irradiation leads to cleavage of this newly formed bond and, in the presence of monomer, the creation of a site for polymerization (Scheme 1).

Grafted structure rich in the polymer poly(ethylene glycol) (PEG) were created on the nanotube surface by polymerizing the macromonomer poly(ethylene glycol) monomethacrylate (PEGMA).[19]

Experimental Section

Materials

The HiPCO™ SWNTs (outer diameter 1–2 nm, length 5–30 μm, purity >90 wt %, ash <1.5 wt %) were purchased from Carbon Nanotechnogies Inc. and were used as received without any further treatment. Polyethylene glycol methyl methacrylate (PEGMA) macromonomer ($M_n \sim 1100$, Sigma Aldrich, St. Louis, MO), 1-hydroxycyclohexyl phenyl ketone (HCPK, purity $\geq$ 99%, Sigma Aldrich, St. Louis, MO) were used as received. Water used in all experiment was purified in aquaMax ultra purification system (labwater.com, van Nuys, CA) and had a resistivity of 18.2 MΩ/cm.

Functionalization of SWNTs

SWNTs (30 mg) were dispersed in 75 ml of a 50:50 (v/v) water:ethanol solution and sonicated (Fisher Scientific, 130 W

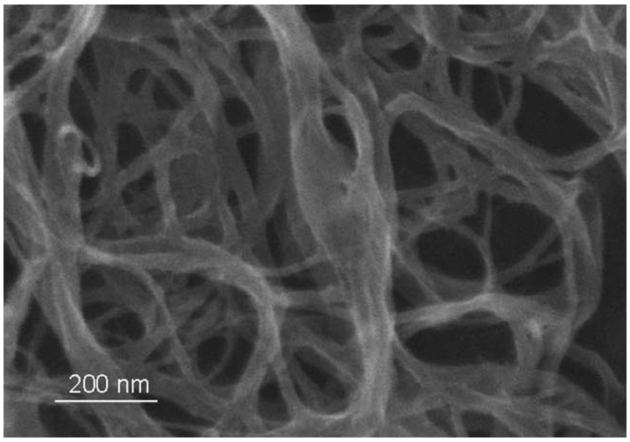

Figure 1. SEM image of pristine SWNTs. Scale bar, 500 nm.

and 40 kHz, Pittsburgh, PA) for 1 h at room temperature. The free radical photoinitiator HCPK was introduced at 1% of the total weight of the solution and the solution was mildly shaken by a vortex mixer (Vortex Gene 2, Fisher Scientific, Pittsburgh, PA) for another 10 min. The entire 75 ml well-dispersed SWNTs solution was evenly poured into three petri dish and was stirred at 80 rpm, when under UV irradiation. Irradiation of the mixture with ultraviolet light (365 nm, 150 mW/cm^2, IntelliRay 600, UViTron International, West Springfield, MA) was then carried out with direct irradiation into the mixture in a nitrogen atmosphere at room temperature. After 30 min of UV exposure, the reaction was stopped. Excess unbound HCPK molecules were removed by centrifugation at 4000*g* for three times (Eppendorf, 5810R, Westbury, NY).

PEGMA monomer was then introduced and polymerization was done with a further 30 min of UV irradiation in a nitrogen atmosphere at room temperature. After the polymerization reaction, the suspension was diluted with water to dissolve unreacted monomer, and then removed by repeated centrifugation at 10,000*g* and the functionalized carbon nanotubes were collected on 0.45 μm nylon membrane filters (Whatman, Maidstone, England) by filtration. Washing with water was repeated several times to remove any physically adsorbed species. Finally, the resultant PEGylated SWNTs were rinsed thoroughly with water and dried at 70°C in a vacuum oven (10 kPa) overnight for further characterization.

Characterization

The morphology of pristine SWNTs were studied by a transmission electron microscope (TEM) (EM 430, Philips, Eind- hoven, The Netherlands) operating at 250 kV. A small drop of the carbon nanotubes suspension was put on a 400-mesh carbon-coated copper TEM grid (Electron Microcopy Sciences, Hatfield, PA) and allowed to dry in the atmosphere. Field emission scanning electron microscopy (FE-SEM) was conducted on a Hitachi S-4700 SEM (Hitachi, Osaka, Japan) to investigate the morphology of the PEGylated SWNTs. Attenuated total reflection Fourier transform infrared (ATR-FTIR, Nicolet 6700, Thermo Electron Corporation, Madison, WI) was used to characterize the functional groups covalently bound to the carbon nanotubes. X-ray photoelectron spectroscopy (XPS) (Kratos Axis 165, Kratos Analytical, Chestnut Ridge, NY) analysis was used to investigate the surface of polymer chemistry PEGylated SWNTs. Raman spectroscopy (633 nm, Horiba Jobin YVON, Edison, NJ) was utilized to observe both pristine and PEGylated SWNTs. Thermogravimetric analysis (TGA, Netzsch, Exton, PA) experiments were carried out under nitrogen at 10°C/min to 600°C.

Results and Discussion

Pristine SWNTs in powder and dispersed in aqueous solution were characterized by SEM and TEM, respectively (Figures 1 and 2). It can be observed that the diameter of the pristine SWNTs was between 10 and 15 nm, which indicating the nanotubes were not individually dispersed, and that small nanotube bundles may exist.

Raman spectroscopy was utilized to investigate grafted chain bonding after carbon nanotube functionalization (Figure 3). The Raman spectra of pristine SWNTs show typical breathing modes at 190–250 cm^{-1} and tangential modes at 1590 cm^{-1} (G-band). Covalent functionalization will convert sp^2 carbon atoms to sp^3 hybridization and disrupt the π-conjugation system, which leads to the signal intensity increasing in the D-band.[2,20] The increasing intensity at 1301 cm^{-1} (D-band) after functionalization indicates the formation of sp^3 carbon atom, additional evidence that the polymer chains were covalently grafted to the SWNT surface.

Figure 4 shows the ATR-FTIR spectra of pristine and PEGylated SWNTs after different polymerization times. The pristine SWNTs spectrum is featureless, while the spectrum of nanotubes subject to 1 min of polymerization time did not show any noticeable feature, either. However, the peak at ~2890 cm^{-1} corresponding to the stretch mode of C—H bond vibration associated with —CH$_2$— can be observed in

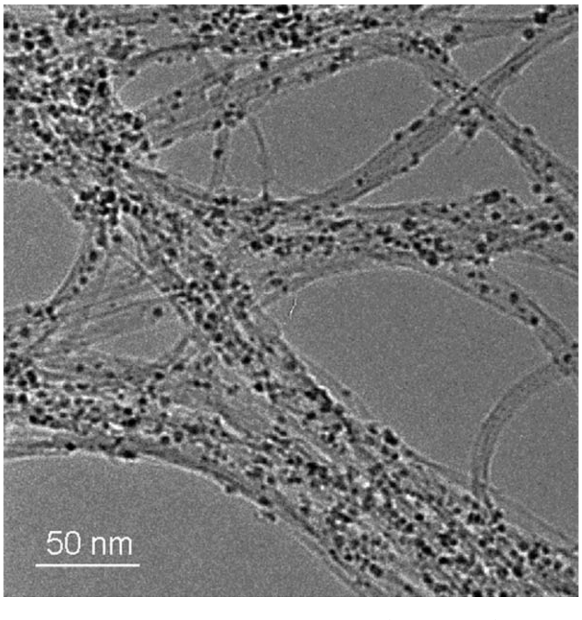

Figure 2. TEM image of pristine SNWTs. Scale bar, 500 nm.

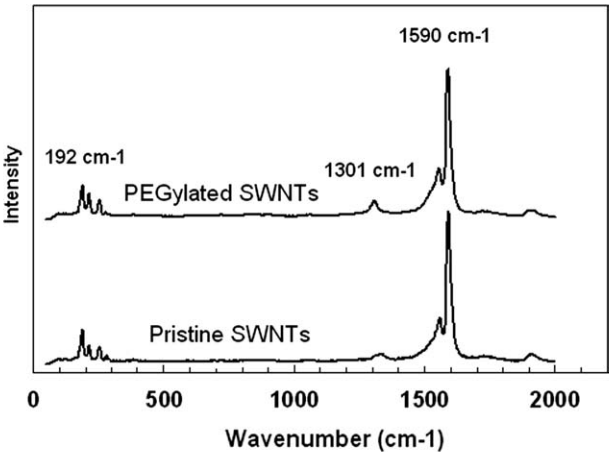

Figure 3. Raman spectra of pristine SWNTs and PEGylated SWNTs.

samples polymerized for 5, 15, and 30 min. As the polymerization time increased, the intensity of this peak also increased. The peaks at $\sim$1110 cm^{-1} were attributed to the C—O symmetric stretch of the PEG sidechain. It is also can be observed that as the polymerization time increased, the intensity of this peak also increased.

To confirm the importance of the polymerization reaction, a control experiment was conducted where nanotubes were mixed with PEGMA monomer but no reaction was conducted. After conducting the washing and filtration protocol outlined previously, complete removal of the free macromonomer from the nanotubes surface was indicated by the absence of relevant ATR-FTIR peaks. The ATR-FTIR spectra illustrated the effectiveness of the photoinitiated polymerization reaction and also further reinforced that hypothesis that the PEG-rich chains were covalently bonded on the CNT surface. In addition, another control experiment was conducted by decreasing the initiator concentration to zero. After conducting the same UV polymerization, washing and filtration procedure, no polymer on the nanotubes surface was observed as indicated from FTIR spectra in Figure 5. This convincing evidence proved and importance of the initiator and it also can be deduced that the polymer was covalently attached on the nanotubes surface, which is consistent with the Raman analysis.

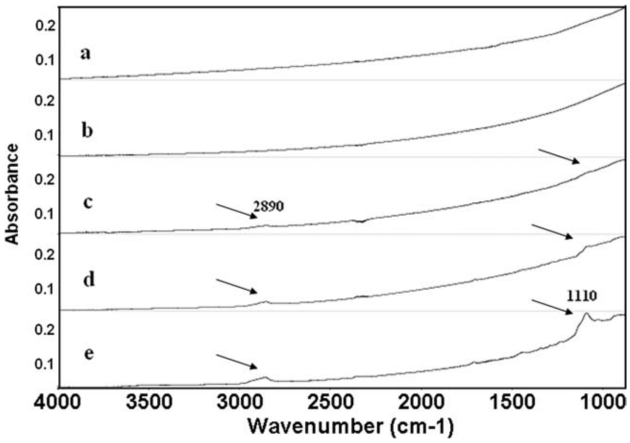

Figure 4. ATR-FTIR spectra of PEGylated carbon nanotubes with different polymerization times (a) pristine SWNTs, (b) 1, (c) 5, (d) 15, (e) 30 min, (f) control experiment.

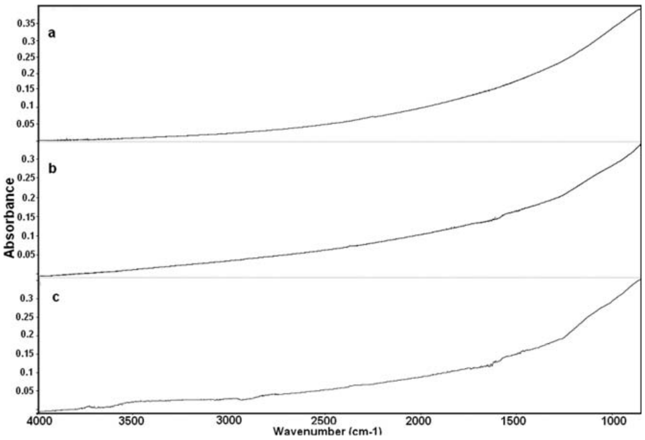

Figure 5. ATR-FTIR spectra of (a) pristine SWNTs and (b) the second control experiment without initiator.

XPS analysis was used to investigate the surface chemistry of the PEGylated SWNTs, and the results are shown in Figure 6. The major peak component at a binding energy of about 285.5 eV is assigned to C1s. The minor peak component (binding energy of 534.0 eV) is attributed to O1s of the PEG chain in the attached polymer. The narrow scan spectra of the O1s region for both pristine and PEGylated SWNTs are shown in Figure 7. Only trace amounts of oxygen were detected in pristine carbon nanotube samples, likely from the metal oxide catalysts used in carbon nanotubes manufacture. Compared with pristine SWNTs (atomic oxygen percentage of only 4.06%), the atomic oxygen percentage rose significantly in the functionalized SWNTs to 24.18% after 30 min of polymerization, confirming the presence of polymer. This atomic oxygen percentage was higher than reported by researchers using a graft to method,[21] which illustrates the utility of the graft from method. The sample from the

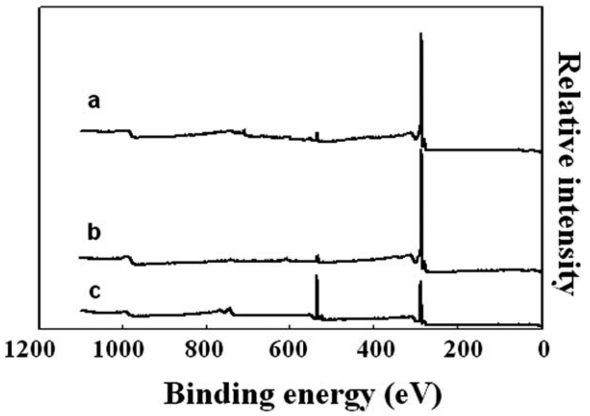

Figure 6. Survey X-ray photoelectron spectra of (a) pristine SWNTs, (b) PEGylated SWNTs after 30 min polymerization.

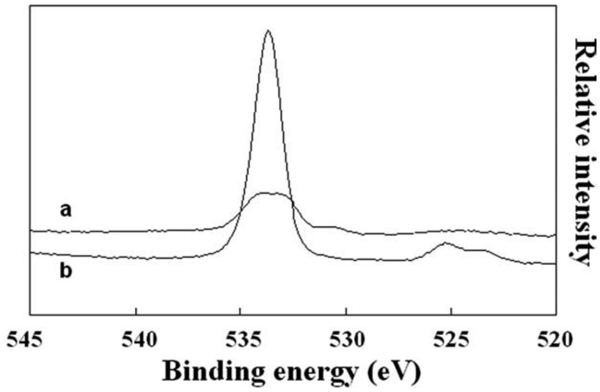

Figure 7. O1s narrow scan X-ray photoelectron spectra of (a) pristine SWNTs, (b) PEGylated SWNTs after 30 min polymerization.

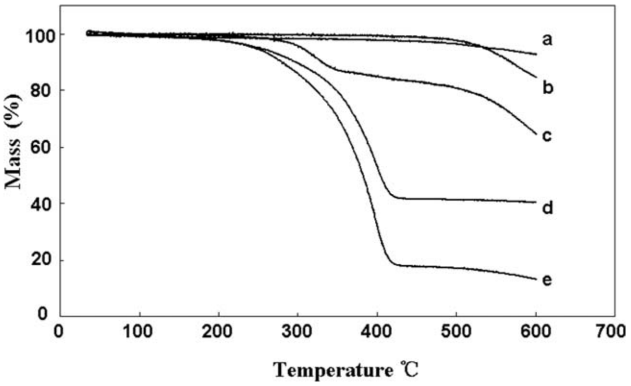

Figure 8. TGA curves of PEGylated carbon nanotubes with different polymerization times (a) pristine SWNTs, (b) 1, (c) 5, (d) 15, (e) 30 min.

control experiment, where PEGMA monomers were mixed with the SWNTs but no reaction was conducted, was also analyzed by XPS. As it can be seen from Figure 5, the atomic oxygen percentage almost did not change, which also prove the previous FTIR analysis that the polymer molecules were covalently adsorbed on the SWNTs surface. We summarize the binding energy and the element composition of pristine, PEGylated SWNTs and control sample on Table 1.

TGA analysis was used to further evaluate the extent of polymer functionalization. Figure 8 shows mass loss data for pristine carbon nanotubes and four samples with different polymerization times as a function of temperature. All TGA scans were conducted in a nitrogen environment. The percentage weight loss curves indicate that the overall weight loss during the process was 15.4%, 34.7%, 60.5%, and 87.8% for polymerization times of 1, 5, 15, and 30 minutes, respectively. The pristine carbon nanotubes have good thermal stability as no obvious weight loss was observed below temperatures of 500°C. The polymer attached on the surface of the carbon nanotubes started to decompose when the temperature reached 200°C, and the weight of PEGylated SWNTs decreased drastically between 300°C and 400°C. As the pristine SWNTs showed little decomposition below 500°C, the PEGylated SWNTs weight loss at 500°C was used to estimate the relative weight of grafted polymer on the surface of carbon nanotubes. The differences of weight loss at 500°C, between the pristine and the four PEGylated SWNTs samples were 3.4%, 22.4%, 48.5%, and 79.8%, respectively. Such high weight loss further confirms the previous XPS results and demonstrates this ‘‘graft from’’ polymerization route was effective, efficient and yielded nanomaterials with high levels of polymer grafting.

Table 1. Binding Energy and Atomic Composition of Pristine, PEGylated Nanotubes and Control Sample as Measured by XPS

	Pristine CNT		PEGylated CNT		Control Sample	
Element	BE	At%	BE	At%	BE	At%
C1s	285.5	94.65	287.5	75.82	285.5	95.01
O1s	534	4.06	533.5	24.18	533	4.99
Fe	708.0	1.29				

The dispersion of carbon nanotubes in water without any modification is difficult, even with the help of sonication. The dispersibility of carbon nanotubes was significantly enhanced after surface polymerization. As can been seen in Figure 9, pristine carbon nanotubes bear almost no dispersibility at all. The 15 min polymerization samples show moderate dispersibility with a concentration of 0.8 mg/ml, while the samples after 30 min of polymerization were highly dispersible in aqueous solution, which has a concentration of 1.3 mg/ml. No precipitation or flocculation was observed even after a month. Resuspension of dried PEGylated SWNTs was easily accomplished.

Conclusions

This ‘‘graft from’’ technique allows for the production of polymer modified carbon nanotubes without harsh sonochemical treatment. In addition, the proposed technique features grafted structures secured by stable C—C bonds, a significant advantage over physical adsorption techniques or the potentially hydrolysable linkages introduced in sonochemical treatment. Furthermore, photoinitiated polymerization conducted

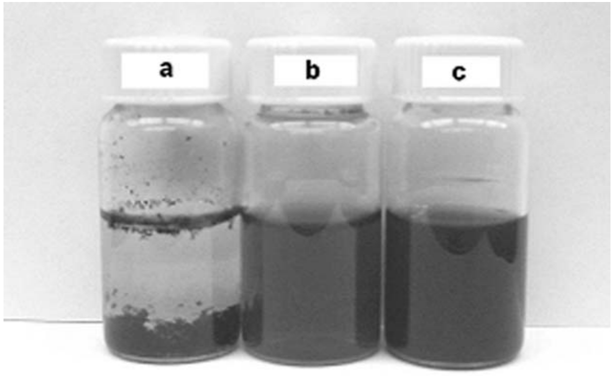

Figure 9. Photographs of nanotubes after three days in water (a) pristine SWNTs and (b) PEGylated SWNTs with 15 min polymerization time, (c) with 30 min polymerization time.

in a large amount of solvent allows for lower reaction temperatures when compared to traditional thermal of sonically initiated polymerization,[22,23] a tremendous benefit, which may be used in the study of attachment of biomolecules such as enzymes and antibodies. The obtained functionalized carbon nanotube aqueous solution was homogeneous and well dispersed. In conclusion, the ultraviolet initiated "graft from" polymerization method was used to synthesize polymer functionalized carbon nanotube in a simple and effective method.

Acknowledgments

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