

Functionalization of Multi-Walled Carbon Nanotubes with Poly(ϵ -caprolactone) Using Click Chemistry

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ABSTRACT: Multi-walled carbon nanotubes (MWNTs) were covalently functionalized with poly(ϵ -caprolactone) (PCL) using click chemistry. First, chlorine moiety-containing PCL was synthesized by the copolymerization of α -chloro- ϵ -caprolactone with ϵ -caprolactone monomer using ring opening polymerization, and further converted to azide moiety-containing PCL. The alkyne-functionalized MWNTs were prepared with the treatment of *p*-amino propargyl ether using a solvent free diazotization procedure. The covalent functionalization of alkyne-derived MWNTs with azide

moiety-containing PCL was accomplished using Cu(I)-catalyzed [3+2] Huisgen dipolar cycloaddition click chemistry. The PCL-functionalization of MWNTs was confirmed by the measurements of Fourier transform infra-red, NMR, Raman spectroscopy, scanning electron microscopy, and transmission electron microscopy. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 31–37, 2011

Key words: carbon nanotubes; poly(ϵ -caprolactone); ring opening polymerization; click chemistry

INTRODUCTION

Since the discovery in 1991 by Iijima,¹ carbon nanotubes (CNTs) have attracted a great attention of researchers due to their unmatched electronic, mechanical, thermal, and chemical properties.^{2,3} CNT-based materials show extremely promising applications from material science to medicinal chemistry.^{4,5} However, the dispersibility and poor solubility in aqueous and nonaqueous solutions impose a considerable challenge for their separation and assembly, which limits their importance in various application areas. Several approaches for functionalization of CNTs,⁶ including covalent sidewall coupling reactions,^{7,8} and noncovalent exohedral interactions,⁹ have been developed to overcome the solubility limitations. Solubilization of CNTs in organic solvents has been described mainly on the

basis of the attachment of building blocks to the carboxylic acid functionality, which is formed by oxidation of CNTs in strong acids.^{10,11} However, due to acid treatment, the CNTs get damage and it disturbs the structural integrity of CNTs.¹² The covalent functionalization of CNTs with polymeric structures has shown the enhancement of dispersion in polymeric matrix,^{13–15} and thus has played an important role for load transfer between polymer and CNT in composites.

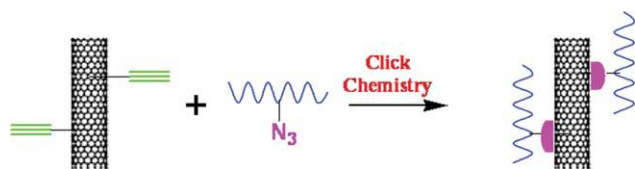
Functionalization of carbon nanotubes with biocompatible polymers and their dispersion in polymer matrix showed enormous potential as a structural support material in tissue engineering.¹⁶ Poly(ϵ -caprolactone) (PCL)^{17,18} which has a fully biodegradable and biocompatible nature, may lead to significantly advanced materials by an incorporation of CNTs. Zeng et al. prepared the functionalized CNTs with PCL and measured their biodegradability,^{19,20} and found that the presence of CNTs did not affect the biodegradability of PCL. Buffa et al.²¹ also reported the functionalized CNTs with PCL by using 'grafting from' approach which promises the highly functionalized CNTs though it is difficult to control the molecular weight of grafted polymer.

In this work, the covalent functionalization of multi-walled carbon nanotubes (MWNTs) with PCL is carried out in the 'grafting to' approach by employing the click chemistry reaction (Scheme 1). Click chemistry is a powerful, modular, tolerant,

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Scheme 1 General functionalization of CNTs via click chemistry. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and reliable synthetic approach toward new molecules by joining the small units together by heteroatom links. The Cu(I)-catalyzed [3+2] Huisgen dipolar cycloaddition between azides and alkynes provides 1,2,3 triazole ring with 1,4 regioselectivity and quantitative transformation under mild reaction conditions.²² This reaction has been used for small-molecule organic synthesis, dendrimers, dendronized polymers, and biologically-derived macromolecular structures.^{23,24} Click chemistry has emerged as a strategy for the rapid and efficient assembly of molecules with diverse functionality, which guarantees reliable synthesis of the desired products in high yield and purity. Apart from the synthetic promise, triazole moieties are also interesting conjugation entities as they are proven to be relatively stable to metabolic degradation and the triazole ring also can participate in the hydrogen bonding, which can be excellent in the context of biomolecular targets and solubility.²⁵ The similar approach has been used for functionalization of CNTs with metal particles,²⁶ polystyrene,²⁷ β -cyclodextrin,²⁸ and amino acids²⁹ which shows remarkable solubility in several solvents.

Here, we report the functionalization of MWNTs with PCL using click chemistry and the effects of polymer molecular weight and functionalization on MWNT dispersion are also investigated.

EXPERIMENTAL

Materials

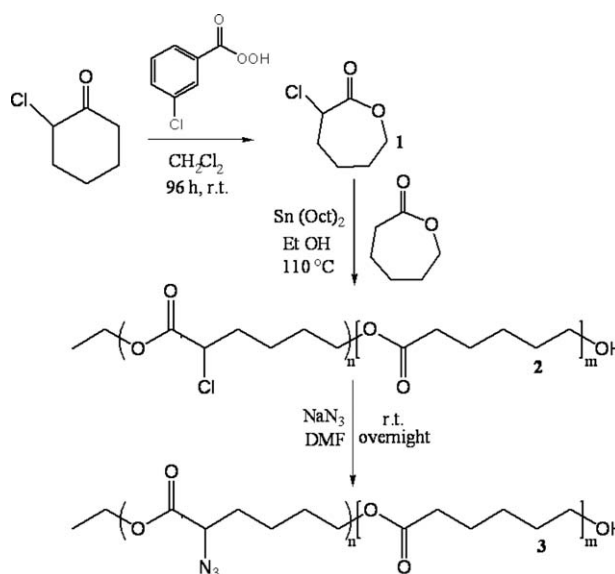
2-Chlorocyclohexane, *p*-nitrophenol, and isoamyl nitrite were purchased from (Tokyo Chemical Industry Co. Ltd., Tokyo, Japan), *m*-chloroperoxybenzoic acid (*m*CPBA), sodium azide, copper iodide, 1,8 diazobicyclo (5,4,0) undec-7-ene, ϵ -caprolactone, and stannous octate were received from Aldrich Co. (St. Louis, MO). All other reagents and solvents were purchased from commercial suppliers (SK Chemicals, Ulsan, Korea) and purified by distillation before using. MWNTs were purchased from Iljin Nanotech (Seoul, Korea), having a diameter of 10–20 nm and an average length of 20 μ m and were purified using sonication.

Synthesis of α -chloro- ϵ -caprolactone monomer (1)

The monomer was synthesized by using the same procedure as mentioned in Ref.³⁰ *m*CPBA of 10 g (41 mmol) (70%) was added to a solution of 5 g (38 mmol) of 2-chlorocyclohexanone in 60 mL of dichloromethane at room temperature. After 96 h, the reaction flask was cooled to -20°C to precipitate *m*-chlorobenzoic acid, using the refrigerating bath circulator (Jeio Tech, RW-1025G) for 30 min. After filtration, the solution was washed with a saturated aqueous solution of NaHSO_3 with an aqueous solution of NaHCO_3 and finally with water. After drying over MgSO_4 , the organic phase was filtered, and the solvent was removed under reduced pressure. The residue was distilled under reduced pressure, and 4 g of α -chloro- ϵ -caprolactone was collected.

Synthesis of poly(α -chloro- ϵ -caprolactone-*co*- ϵ -caprolactone) using ring opening polymerization (2)

Poly(α -chloro- ϵ -caprolactone-*co*- ϵ -caprolactone) (poly(α Cl- ϵ CL-*co*- ϵ CL)) was synthesized using ring opening polymerization (ROP) (Scheme 2) by the copolymerization of α -chloro- ϵ -caprolactone with ϵ -caprolactone at 110°C temperature for 24 h using ethanol as an initiator and $\text{Sn}(\text{Oct})_2$ as a catalyst in dry tetrahydrofuran containing 35 mol % of α -chloro- ϵ -caprolactone. The molecular weight of poly(α Cl- ϵ CL-*co*- ϵ CL) was monitored from 3000 g/mol.



Scheme 2 Synthesis of azide functionality containing poly(ϵ -caprolactone).

Synthesis of poly(α -azide- ϵ -caprolactone-co- ϵ -caprolactone) (3)

Poly(α Cl- ϵ -CL-co- ϵ CL) was dissolved in tetrahydrofuran (THF) in a glass reactor, followed by the addition of NaN₃. The reaction mixture was kept overnight at room temperature under middle stirring speed. After elimination of THF in vacuo, excess of toluene was added, and the insoluble salt was removed by centrifugation. The copolymer was recovered by solvent evaporation under vacuum and further characterized.

Preparation of alkyne-functionalized MWNTs (4)

First, *p*-aminophenyl propargyl ether was synthesized by following the procedure as mentioned in Ref. ³¹. MWNTs (162 mg, 13.33 mmol of carbon) and *p*-aminophenyl propargyl ether compound (7.85 g, 53.32 mmol, 4 equiv/mol of carbon) were added to a flask equipped with a reflux condenser and a magnetic stir bar. The flask was evacuated and back-filled with nitrogen three times and then left under nitrogen till the reaction was accomplished. Subsequently, isoamyl nitrite (7.81 g, 66.65 mmol, 5 equiv/mol of carbon) was added slowly via syringe. The mixture was then placed in an oil bath and stirred vigorously at 60°C for 5 h. The resulting paste was diluted with dimethylformamide (DMF) (250 mL) and filtered through a PTFE (450 nm pore size) membrane. The collected solid was washed with DMF until the filtrate became colorless. Dispersing the solid in DMF by sonication followed by filtration afforded purified functionalized MWNTs. DMF was removed by washing with diethyl ether, and the final compound was obtained after drying in a vacuum oven at 55°C for 72 h.

Coupling of PCL with MWNTs using click chemistry (5)

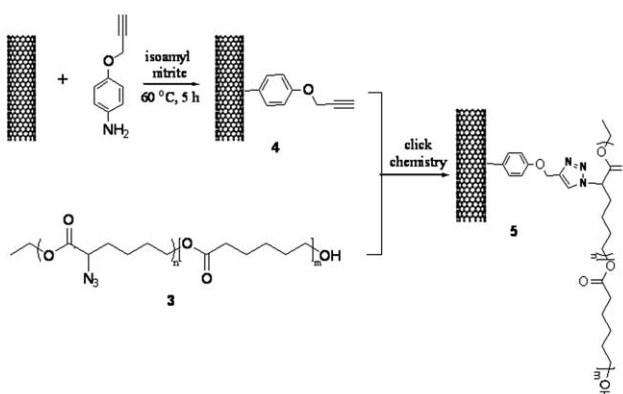
Cu(I)-catalyzed click chemistry was applied for coupling of azide moiety-containing PCL with alkyne-functionalized MWNTs. A 100 mL round-bottomed flask was charged with 30 mg MWNTs, and 50 mL DMF, after sonicating for 10 min at room temperature a DMF solution of azide moiety-containing PCL (2.0 g) and equal mole of CuI and 1,8-diazabicyclo [5.4.0] undec-7-ene was added. The reaction mixture was kept at 60°C for 24 h. After cooling to room temperature, the mixture was diluted with DMF, and further purified. For removing the copper salt, the final material was washed using aqueous ammonium hydroxide solution (28%), water, and DCM (1 × 100 mL of each), and then dried under vacuum overnight.

Measurements

¹H-NMR spectra were recorded on Bruker 400 MHz (California). Fourier transform infra-red (FT-IR) spectroscopic measurements were recorded by using Jasco FT-IR 300E device (Tokyo, Japan). Raman study was completed by using SPEX 1403 Spectrometer (Edison, NJ). Molecular weight and its distribution were determined by gel permeation chromatography (GPC), Model 515 (Texas). CNT dispersion in composites was analyzed by scanning electron microscopy (SEM, JSM-6380, JEOL, Tokyo, Japan), and transmission electron microscopy (TEM, JEM 2100F, JEOL, Tokyo, Japan) at room temperature. A thermogravimetric analysis (TGA) was carried out in a TA Q50 system TGA (New Castle, DE) by scanning the samples from 50 to 550°C at a heating rate of 10°C/min in presence of nitrogen.

RESULTS AND DISCUSSION

The PCL-functionalized MWNTs were synthesized using Cu(I)-catalyzed Huisgen [3+2] cycloaddition click chemistry between alkyne-functionalized MWNTs and azide moiety-containing poly(α N₃- ϵ CL-co- ϵ CL) (Scheme 3). The alkyne-functionalized MWNTs were prepared by the treatment of *p*-amino propargyl ether with MWNTs using a solvent free diazotization and coupling procedure.³² This chemistry allows a high degree of functionalization of MWNTs. α -Chloro- ϵ -caprolactone was synthesized successfully by the oxidation of α -chlorocyclohexane in presence of *m*-chloroperoxybenzoic acid. It was further copolymerized with ϵ -caprolactone (35 : 65) using ROP,³³ in presence of ethanol as an initiator and Sn(Oct)₂ as a catalyst, to get poly(α Cl- ϵ CL-co- ϵ CL). The poly(α Cl- ϵ CL-co- ϵ CL) was further treated with sodium azide to get the poly(α N₃- ϵ CL-co- ϵ CL). The reaction can be confirmed by ¹H-NMR, which indicates the presence of -CHN₃ group at 3.8 ppm as shown in Figure 1. The quantitative analysis of



Scheme 3 Synthesis of PCL-functionalized MWNTs.

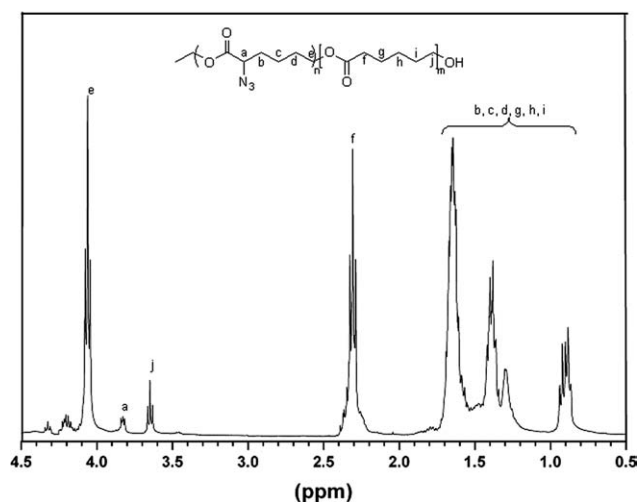


Figure 1 $^1\text{H-NMR}$ spectra of poly($\alpha\text{N}_3\text{-}\epsilon\text{CL-co-}\epsilon\text{CL}$).

copolymer components was done using the molar fraction method from $^1\text{H-NMR}$ analysis.³⁴ The molar fraction of $\alpha\text{N}_3\text{-}\epsilon\text{CL}$ ($F_{\alpha\text{N}_3\text{-}\epsilon\text{CL}}$) was calculated by integrating the peak at 2.3 ppm (I_F) (Fig. 1, peak f) ($\text{CH}_2\text{C=O}$ proton of the ϵCL unit) and at 3.8 ppm (I_A) (Fig. 1, peak a) (CH-N_3) proton of the $\alpha\text{N}_3\text{-}\epsilon\text{CL}$ unit), respectively [eq. (1)].

$$F_{\alpha\text{N}_3\text{-}\epsilon\text{CL}} = I_A/I_A + I_F/2 \quad (1)$$

Using the eq. (1), it could be confirmed that all the compositions had the molar fraction of 34 mol % of $\alpha\text{N}_3\text{-}\epsilon\text{CL}$.

Figure 2 shows FT-IR spectra of poly($\alpha\text{N}_3\text{-}\epsilon\text{CL-co-}\epsilon\text{CL}$) synthesized in this study, where the peaks at 2937 and 2867 cm^{-1} are due to asymmetric and symmetric CH_2 stretching, respectively. The peak at 1730 cm^{-1} is due to carbonyl stretching, 1240 cm^{-1} due to asymmetric COC stretching, and 1170 cm^{-1} due to

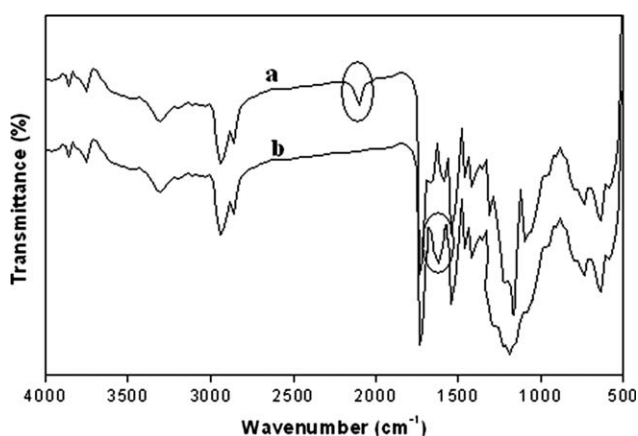


Figure 2 FT-IR spectra of (a) poly(α -azide- ϵ -caprolactone), and (b) poly(α -azide- ϵ -caprolactone) after click coupling.

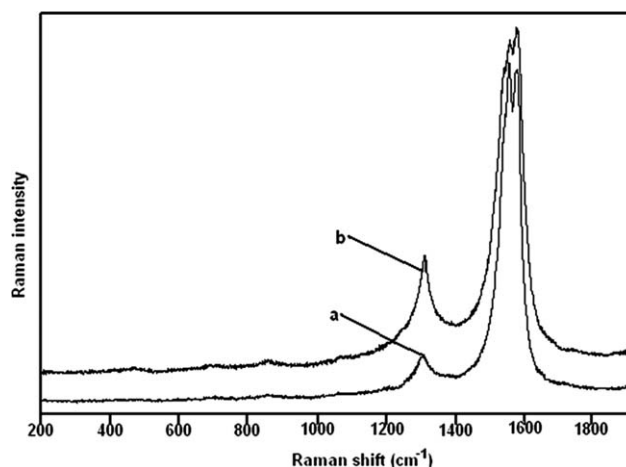


Figure 3 Raman spectra of (a) pristine MWNTs, and (b) PCL-functionalized MWNTs.

symmetric COC stretching, respectively.³⁵ The peak at 2106 cm^{-1} confirms the azide functionality on poly($\alpha\text{N}_3\text{-}\epsilon\text{CL-co-}\epsilon\text{CL}$). The click reaction between MWNTs and poly($\alpha\text{N}_3\text{-}\epsilon\text{CL-co-}\epsilon\text{CL}$) is also confirmed by IR measurements. After the reaction, a new characteristic peak appeared around 1650 cm^{-1} due to the triazole ring formation with disappearance of the IR peak at 2100 cm^{-1} . From these IR data, it can be well supported that the PCL-functionalized MWNTs were synthesized successfully. Raman spectra measurements were utilized to confirm the functionalization of MWNTs. Figure 3 shows that pristine MWNTs have two bands around 1292 and 1580 cm^{-1} which are assigned to disorder mode (D-band) and tangential mode (G-band) for sp^3 and sp^2 hybridized carbons, respectively.³⁶ The relative D-band intensity in functionalized MWNTs increased compared with pristine MWNTs, showing the increased D/G band ratio after the functionalization of

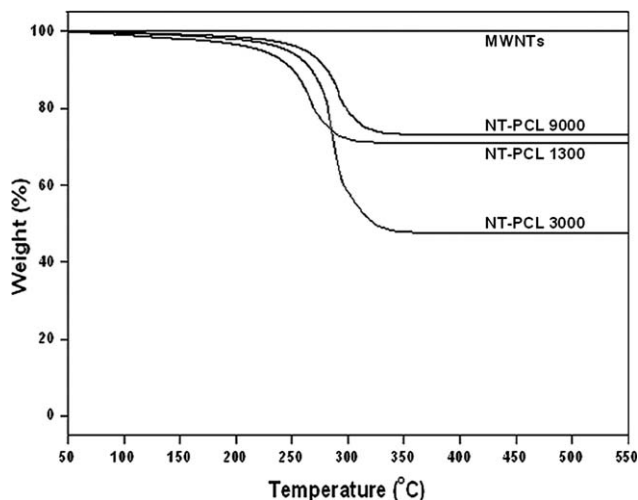


Figure 4 TGA curves of pristine and functionalized MWNTs with different PCL molecular weights.

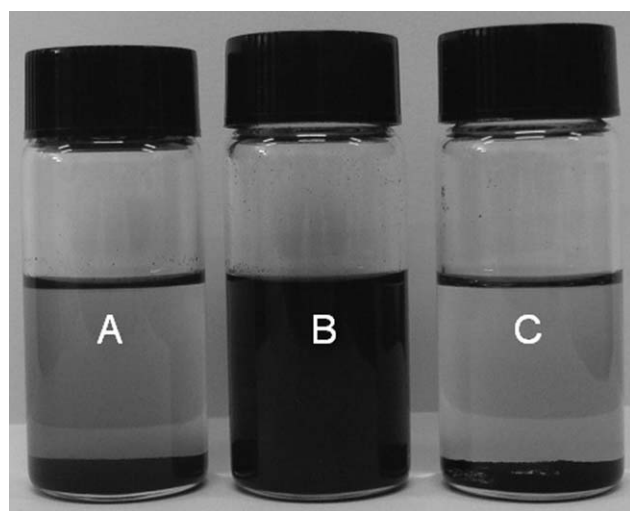


Figure 5 Solubility tests of PCL-functionalized MWNTs in THF: (A) NT-PCL 1300, (B) NT-PCL 3000, and (C) NT-PCL 9000.

MWNTs. It reflects the functionalization on MWNTs as described in the FT-IR results.

The thermogravimetric analysis was carried out for the PCL-functionalized MWNTs as shown in Figure 4. The TGA curves of PCL-functionalized-MWNTs showed a major weight loss in the temperature range of 200–350°C, which are due to thermal degradation of PCL.²¹ For understanding the effect of PCL molecular weight on MWNTs functionalization, the azide moiety-containing PCL with molecular weight 1300 and 9000 g/mol was also synthesized using the same procedure as discussed earlier. The molecular weight of poly(ϵ -caprolactone) was monitored by GPC in THF (relative to polystyrene standard). For samples containing the molecular weight of 1300, 3000, and 9000 g/mol, the PDI value was observed as 1.30, 1.42, and 1.23, respectively. The molecular weight for each composition is in agreement with the value expected for a living polymerization at complete monomer conversion. The functionalized MWNTs samples with PCL molecular weight of 1300, 3000, and 9000 g/mol were coded as NT-PCL 1300, NT-PCL 3000, and NT-PCL 9000, respectively. From comparison of these samples, it can be seen that the TGA spectrum shows different behavior in weight loss with different molecular weight functionalized MWNTs. The weight loss increased from 27 to 52 wt % with increasing of the molecular weight of PCL from 1300 to 3000 g/mol, and further decreases to 24 wt %, when the molecular weight increases to 9000 g/mol. It indicates that the highest amount of PCL was attached on MWNTs with molecular weight 3000 g/mol.

The solubility test of functionalized materials was evaluated in different organic solvents such as chloroform and THF, as it is well known that the

solubility of functionalized CNTs depends upon the interaction between grafted polymer and solvent. As PCL is well dissolved in low boiling solvents, THF was chosen as the solvent, and the results are shown in Figure 5. The results show that the molecular weight of PCL plays an important role for the solubility of MWNTs. There are three vials (A, B, C) in Figure 5, containing same amount of functionalized MWNTs material in THF with different molecular weight of PCL. The results show that the

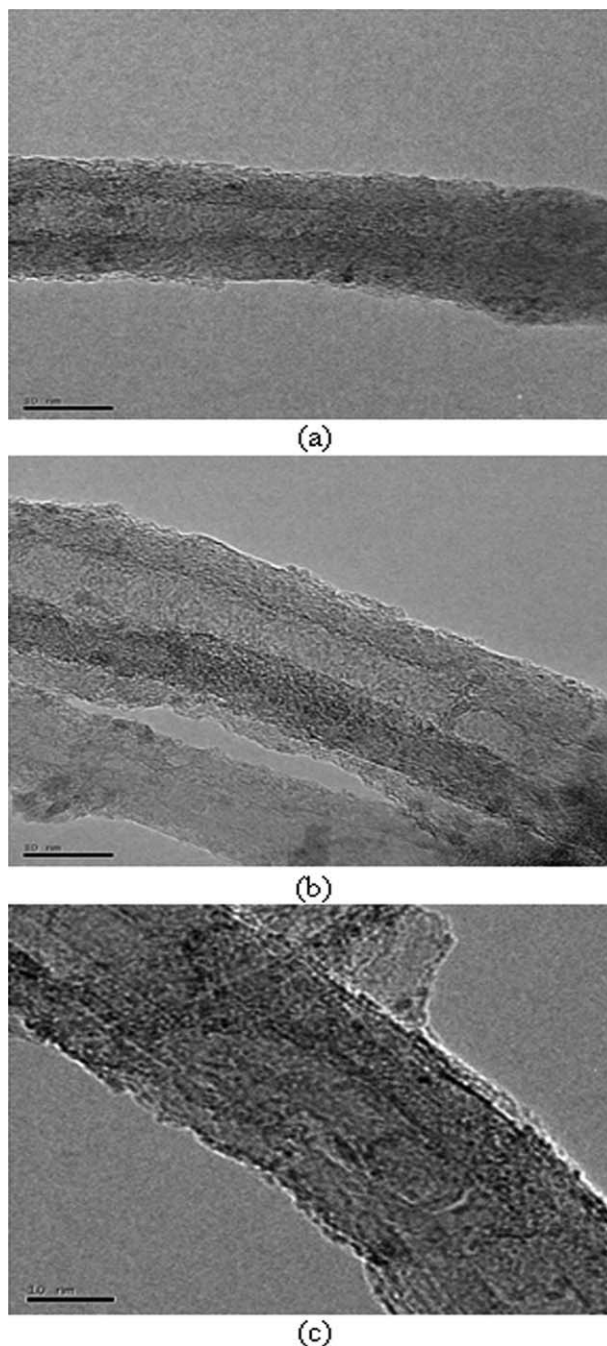
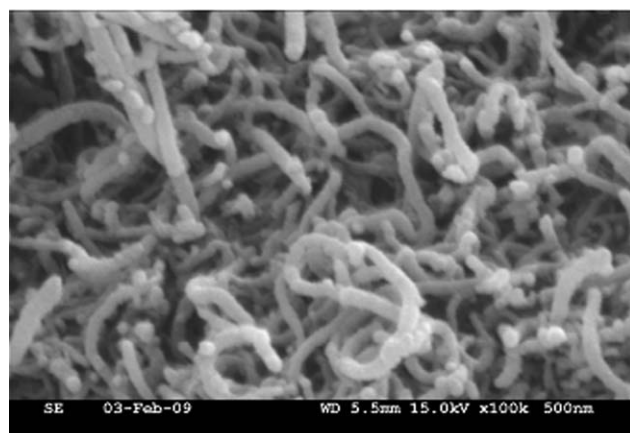
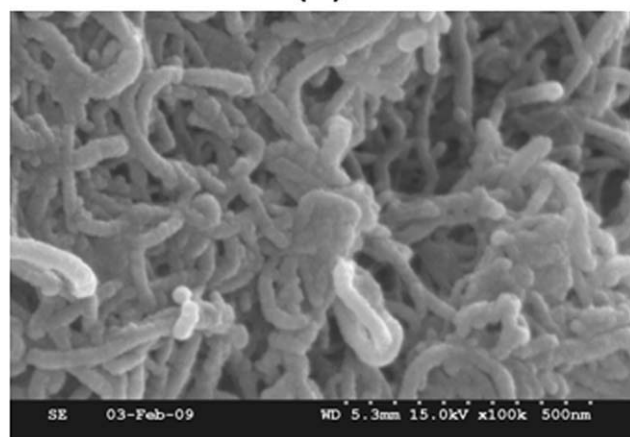


Figure 6 TEM images of (a) NT-PCL 1300, (b) NT-PCL 3000, and (c) NT-PCL 9000.



(a)



(b)

Figure 7 SEM images of (a) NT-PCL 1300, and (b) NT-PCL 3000.

functionalized MWNTs with PCL molecular weight of 3000 g/mol show better solubility compared with MWNTs attached with less and high molecular weight PCL. This may be because if molecular weight is very low, an interaction between polymer and solvent is still low, to easily allow aggregation of MWNTs. Inversely if the polymer molecular weight of PCL is too high, then grafting percentage of polymer may be less, because of bulky molecules, and some alkyne moiety may be unreacted which may further affect the solubility. As a result, it is regarded that PCL molecular weight of 3000 g/mol has better solubility as well as higher weight loss in TGA measurements compared with different molecular weight PCL.

The nanostructures of PCL-functionalized MWNTs can easily be observed by high-resolution transmission electron microscopy. As shown in Figure 6(a–c), as PCL molecular weight increased from 1300 to 3000 g/mol, the PCL coating on MWNTs increased. For sample NT-PCL 3000, a uniform PCL coating was observed [Fig. 6(b)], where polymer layer between MWNTs supports the effect of polymer coating to

reduce the force interaction among the MWNTs,³⁷ which could be useful for tube solvent interaction and applicable to achieve the good solubility. When the polymer molecular weight is very high (NT-PCL 9000), the PCL grafting is limited, which is expected due to bulky molecules. Figure 7 compares the SEM images of functionalized CNTs. From Figure 7(a–b), it can be found that the amount of grafted PCL increased with increasing the PCL molecular weight. The average diameter of MWNTs increases due to higher chain length of the polymer. The TEM and SEM images further support the functionalization of MWNTs as well as the effect of polymer molecular weight on functionalization of MWNTs.

CONCLUSIONS

PCL-functionalized MWNTs were synthesized successfully using ROP and click chemistry. In case of PCL with molecular weight of 3000 g/mol, better solubility in solvents and higher weight loss in TGA measurements were obtained compared with low and high molecular weight PCL-functionalized MWNTs. The resulting MWNTs may be available to biomedical systems and bionanomaterials for multifunctional applications due to the biocompatible nature of PCL.

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