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

Chun-Yan Hong [a,*], Ye-Zi You [b], Cai-Yuan Pan [a]

[a] *Department of Polymer Science and Engineering, University of Science and Technology of China, No. 96 Jinzhai Road, Hefei, Anhui 230026, People's Republic of China*
[b] *Department of Polymer Science and Engineering, Hefei University of Technology, Hefei, Anhui 230009, People's Republic of China*

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.
© 2006 Published by Elsevier Ltd.

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],

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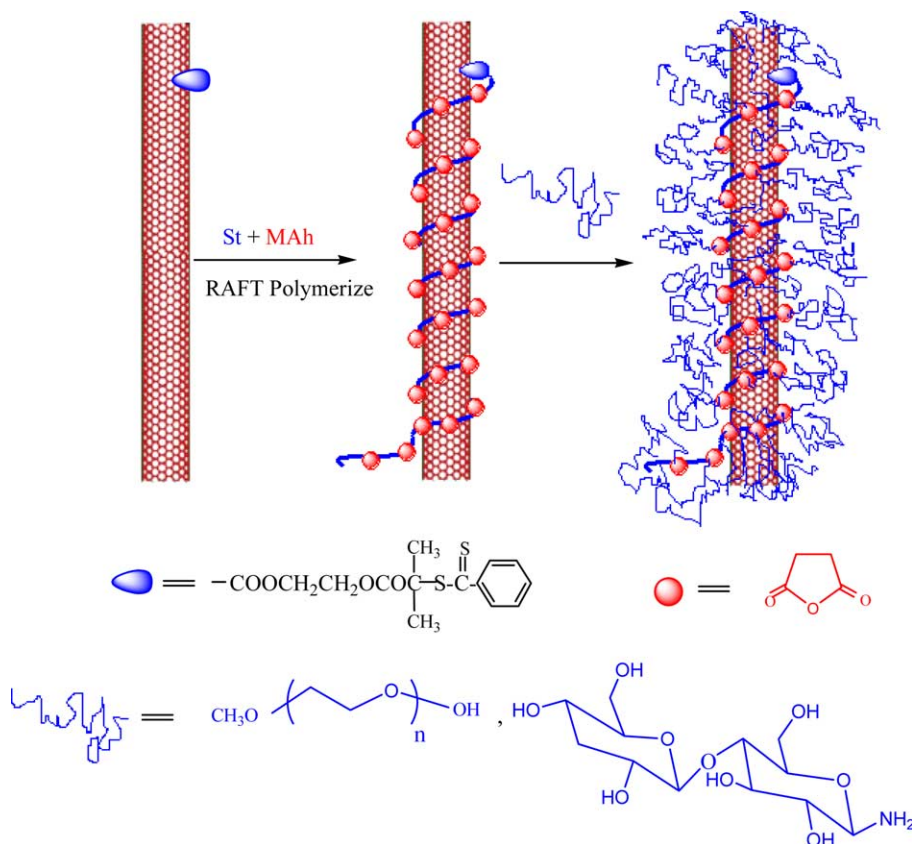 of neocarzinostatin (a potent but very toxic antitumor protein) with P(St-*alt*-MAh) causes an increase of the neocarzinostatin plasma half-life and a decrease of its toxicity [60]; immobilization of Laminin peptide with P(St-*alt*-MAh) resulted in an increase of antimetastatic effect [62].

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.

1-Amino-1-deoxy-β-D-lactose was obtained from Sigma. Thionyl chloride (SOCl₂), tetrahydrofuran (THF), ethylene glycol (HOCH₂CH₂OH), 2-bromoisobutyric acid, and other organic reagents were obtained from Shanghai Reagent Co. Styrene was distilled under reduced pressure, and maleic anhydride was sublimed at 50 °C/2.5 kPa.

2.2. Synthesis of 2-hydroxyethyl-2′-bromoisobutyrate

2-Hydroxyethyl-2′-bromoisobutyrate (HOCH₂CH₂-OCOC(CH₃)₂Br, HEBrIB), was prepared as follows: 31.0 g (0.50 mol) of ethylene glycol, 6.68 g (0.04 mol) of 2-bromoisobutyric acid and 0.3 g of *p*-toluenesulfonic acid in 150 mL of anhydrous benzene were added into a 250 mL round bottom flask equipped with a magnetic stirrer. The mixture was refluxed for 36 h, and the water generated by the esterification reaction was removed by Dean Stark trap. The reaction mixture was then poured into 200 mL of distilled water, and the organic phase was separated. After the water phase was saturated with sodium chloride, another small portion of organic phase was separated. The two organic portions were combined, dissolved in methylene chloride, and dried over anhydrous magnesium sulfate overnight. After filtration from the magnesium salt, and removal of solvent, the 2-hydroxyethyl-2′-bromoisobutyrate was obtained as a colorless liquid (5.0 g, yield: 59.2%). ¹H NMR (300 MHz, CDCl₃): δ 1.0 (s, 6H, –CH₃), 3.7 (t, 2H, OCH₂CH₂OH), 4.30 (t, 2H, –COOCH₂–CH₂–).

2.3. Slightly functionalize carbon nanotubes with carboxyl groups

Crude MWNTs (3.02 g) were added to 60% HNO₃ aqueous solution (40.0 mL). The mixture was treated with an ultrasonic bath (40 kHz) for 10 min and stirred for 2 h at reflux, then filtered through 0.2 μm poly(tetrafluoroethylene) membrane and washed with distilled water until the pH of the filtrate was 7.0. The filtered solid was dried under vacuum for 28 h at 40 °C, obtaining MWNT-COOH (2.71 g).

2.4. Preparation of bromoisobutyrate groups functionalized carbon nanotubes

A 100 mL flask was charged with 2.01 g of MWNT-COOH, 30 mL of SOCl₂, and 20 mL of anhydrous benzene, then the mixture was stirred at 60 °C for 8 h. The solvent was removed under vacuum. The remaining solid (MWNT-COCl) was washed three times with anhydrous THF, and dried at 40 °C for 2 h. 2-Hydroxyethyl-2′-bromoisobutyrate (3.1 mL) in 100 mL of anhydrous toluene was added into the flask containing MWNT-COCl (1.82 g), and refluxed for 15 h. The solid was separated by filtration through a 0.2 μm poly(tetrafluoroethylene) membrane, thoroughly washed with methanol and diethyl ether, and dried for 10 h to yield 1.56 g of MWNT-Br.

2.5. Synthesis of dithioester groups slightly functionalized MWNTs

Phenylmagnesium bromide was prepared from bromobenzene (6.5 g) and magnesium turnings (0.9 g) in dry THF (90 mL). The solution was heated to 40 °C and carbon disulfide (5.0 mL) was added over 10 min, then the reaction mixture was kept at 40 °C for another 2 h to form a brown mixture. To the resultant mixture was added MWNT-Br (1.18 g), and the reaction was kept refluxed for 60 h. Ice hydrochloric acid (1.0 M, 50 mL) was added, the product was washed with distilled water 5 times, then washed with acetone 5 times. The RAFT agent slightly functionalized MWNTs (MWNT-SC(S)Ph) obtained were dried under vacuum at room temperature.

2.6. Synthesis of MWNTs enwrapped with long polymer chains containing highly reactive maleic anhydride groups
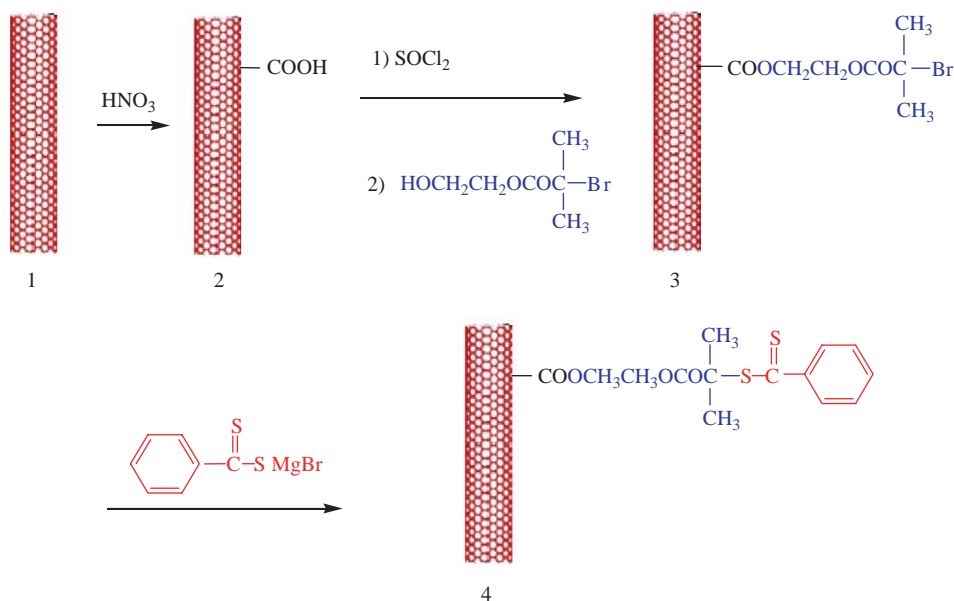
MWNT-SC(S)Ph (100 mg), St (250 mg, 2.4 mmol) and MAh (240 mg, 2.4 mmol) in THF (2.0 mL) were added into a polymerization tube. The polymerization tube was sealed under vacuum and placed in a thermostated oil bath at 80 °C. After a prescribed time, the polymerization was stopped by opening the polymerization tube to air; the mixture was diluted with 50 mL of THF, sonicated for 10 min, and filtered through a 0.2 μm poly(tetrafluoroethylene) membrane. The solid was washed with THF to remove the free polymer. ¹H NMR (300 MHz, d₆-acetone): δ 6.2–7.6 (aromatic protons), 3.0–3.6 (–CH–CH–), 1.3–2.9 (–CH₂–CH–).

2.7. Grafting PEO chains on MWNTs through reaction of PEO with highly reactive maleic anhydride groups

MWNTs enwrapped with P(St-*alt*-MAh) (0.1 g) and PEO-OH ($M_n = 5000$, 3.8 g) dissolved in 20 mL DMF were put into a 50 mL polymerization tube. The tube was sealed under vacuum and placed in a thermostated oil bath at 80 °C for 48 h. The tube was opened, and the mixture was diluted by 50 mL of DMF, sonicated for 20 min, filtered through a 0.2 μm poly(tetrafluoroethylene) membrane, and washed with THF to remove the unreacted polymer. ¹H NMR (300 MHz, d₆-acetone): δ 6.2–7.5 (aromatic protons), 3.66 (OCH₂CH₂O), 3.0–3.5 (–CH–CH–), 1.3–2.9 (–CH₂–CH–).

2.8. Further functionalization of carbon nanotubes through reaction of amino sugars with maleic anhydride groups on the surface of MWNTs

Ten percent solution of MWNT-P(St-*alt*-MAh) in DMSO (0.5 mL) was mixed with a 0.5 M NaHCO₃ buffer solution (20 mL, pH=9). 1-Amino-1-deoxy-β-D-lactose was added to the solution up to the final molar ratio 5:1 of amino sugar to polymer repeating unit. The mixture was stirred at room temperature for 10 h, then filtered, washed with distilled water, and dried under vacuum.

Scheme 2.

2.9. Measurements

Fourier transform infrared spectra were recorded on a Bruker VECTOR-22 IR spectrometer. ^{1}H nuclear magnetic resonance (NMR) spectra were analyzed on a Bruker DMX-300 instrument. Thermal gravimetric analyses (TGA) were carried out on a PE TGA-7 instrument with a heating rate of 20 °C/min under nitrogen. Conventional transmission electron microscopy (TEM) analyses were conducted on a JEOL JEL2010 electron microscope at 200 kV, and the sample for TEM measurements was prepared by placing one drop of sample suspension on copper grid coated with carbon. Raman spectroscopic analysis was carried out on a LABRAM-HR confocal laser micro-Raman spectrometer at room temperature.

3. Results and discussions

Schemes 1 and 2 outline the strategy used for growing long polymer chains containing highly reactive groups from the surface of MWNTs, then using these highly reactive groups as reacting sites for further modification with different kinds of molecules to make MWNTs soluble in organic or aqueous solvents, and compatible with bio-system.

3.1. RAFT agents slightly functionalized MWNTs

Dithiobenzoate is an excellent RAFT agent for living radical polymerization of styrene and MAh, so we should fix dithiobenzoate onto MWNTs in order to synthesize MWNTs grafted with P(St-*alt*-MAh). After treatment with nitric acid, MWNTs are slightly functionalized with carboxylic groups. The MWNT-COOHs were treated with thionyl chloride, and then reacted with excess 2-hydroxyethyl-2′-bromoisobutyrate. Thus, MWNTs with bromoisobutyrate groups on the surface

(MWNT-Br, **3**) were obtained. Adding MWNT-Br into PhC(S)SMgBr solution, substitute reaction occurred, forming dithioester groups slightly functionalized MWNTs (MWNT-SC(S)Ph, **4**). The pristine MWNTs will decompose around 800 °C under nitrogen. RAFT agents immobilized on the surface of MWNTs were determined from the thermogravimetric analysis (TGA) of **4**, which showed about 4.0% weight loss before 450 °C corresponding to the decomposition of the RAFT agents as shown in Fig. 1. The molar percent of the RAFT agents on MWNTs was calculated by using the weight percent and the molecular weight of RAFT agent fragment (311 g mol^{-1}), shows approximately 1.5 RAFT agent functions per 1000 carbon atoms, which means that the density of RAFT agents on the surface of MWNTs is very low.

X-ray photoelectron spectroscopy (XPS) analysis was employed to determine the composition of the MWNT-SC(S)Ph, and the result is shown in Fig. 2. The major peak component at the binding energy (BE) of about 285.60 eV is assigned to the C1s, the minor peak component at the BE of
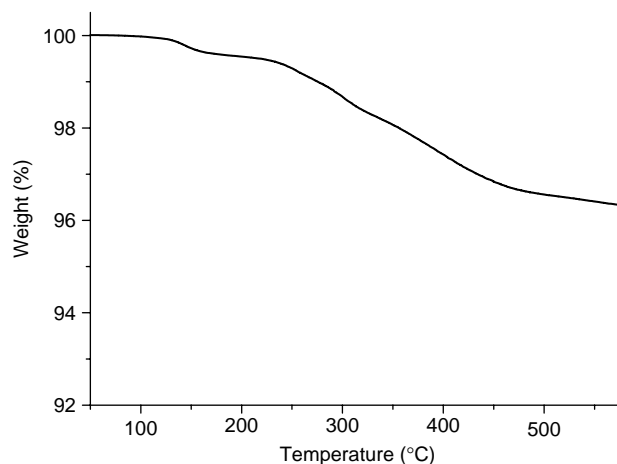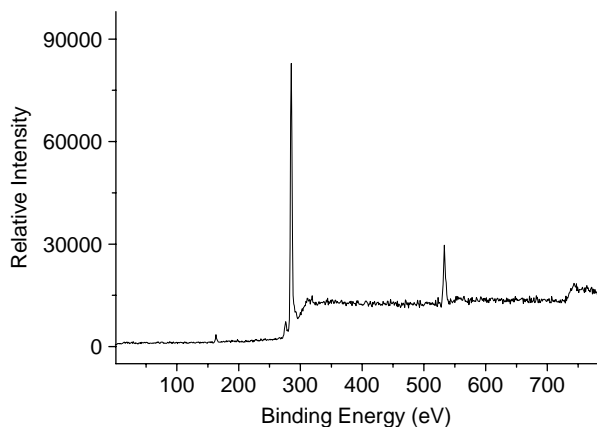

Fig. 1. TGA curve of MWNT-SC(S)Ph.

Fig. 2. XPS spectrum of MWNT-SC(S)Ph.

Fig. 3. TGA curves of MWNT-P(St-*alt*-MAh) (A), MWNT-P(St-*alt*-MAh)-*g*-PEO (B) and the glycoconjugates of poly(styrene-*alt*-maleic acid) enwrapped MWNTs (C).

532.80 eV is attributable to O1s of the ester groups on the surface of MWNTs, and the very weak peak at the BE of 163.50 eV corresponds to S2p of the RAFT agent functions on MWNTs. The mole content of the RAFT agents on the surface of MWNTs is about 0.11% with respect to carbon, which is close to the result obtained from TGA.

3.2. Growing long polymer chains with lots of highly reactive anhydride groups in the main chain onto the surface of MWNTs

Compared with anionic polymerization, cationic polymerization, ring-opening polymerization and ATRP method, RAFT polymerization is more versatile to control the polymerization of water-soluble and functional monomers such as amine monomer and MAh monomer [63–67]. Previous research showed that polymer chains could be easily grafted from the surface of solid or microsphere in a controlled manner via RAFT polymerization in the presence of RAFT agents immobilized on the surface [68–72].

The surface RAFT polymerization of St and MAh was performed in THF solution. After the polymerization, the weight of functionalized MWNTs was greater than that of MWNT-SC(S)Ph, which indicates the presence of surface-grown functional polymer. The TGA analysis of functionalized MWNTs under nitrogen showed one major decomposition in the temperature range at 200–450 °C corresponding to the surface grown P(St-*alt*-MAh). The amount of P(St-*alt*-MAh) covalently attached to MWNTs determined by TGA is 42.0 wt% as shown in Fig. 3(A). It was found that samples exist as lumpy aggregates, and after broken into powder, they are soluble in some organic solvents such as acetone and THF, however, the solutions are not very stable and some carbon nanotubes settled down after 10 days, which may result from that the number of long polymer chains is not enough to stabilize the carbon nanotubes in organic solvents. On the other hand, dispersion of these MWNTs enwrapped with P(St-*alt*-MAh) in methylene chloride and chloroform is very difficult. The FT-IR spectrum of MWNT-P(St-*alt*-MAh) showed characteristic vibration bands for PSt, and the characteristic carbonyl stretching bands of the maleic anhydride at 1780 and
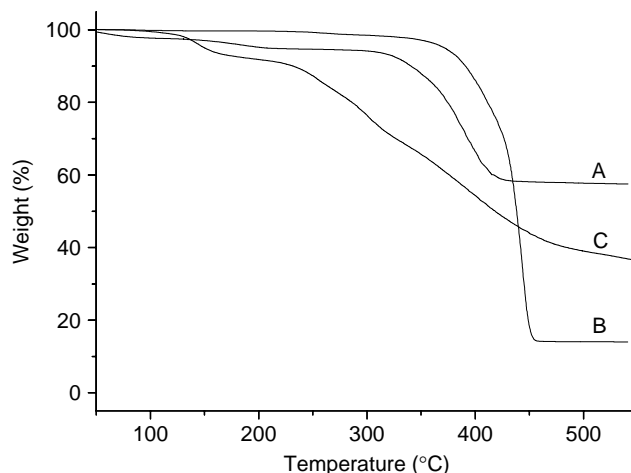
1860 cm^{-1} are also found in Fig. 4(A), which confirms the existence of anhydride groups in the polymer chain.

The number of highly reactive maleic anhydride groups in the long polymer chain is very important to further functionalize MWNTs. Therefore, the ^{1}H NMR spectrum of MWNT-P(St-*alt*-MAh) is measured and shown in Fig. 5. The characteristic peaks of surface grown P(St-*alt*-MAh) with highly reactive groups in the main chain, such as the peak at $\delta = 6.2–7.6$ ppm ascribed to the aromatic protons of the St unit, the peak at $\delta = 3.0–3.6$ ppm corresponding to the methine protons in MAh unit, 1.3–2.9 ppm ascribed to the methine and methylene protons of the St unit, were clearly found in this ^{1}H NMR spectrum, and the observed proton signals are entirely due to the polymer chains grown from MWNTs. The integral value ratio for the peaks at 6.2–7.6 to 3.0–3.6 ppm is near to 5:2, which indicates that the molar ratio of St and MAh units in main chain is almost equal to 1, that is to say, the long chains have lots of highly reactive maleic anhydride groups in main chain with St-*alt*-MAh structure.
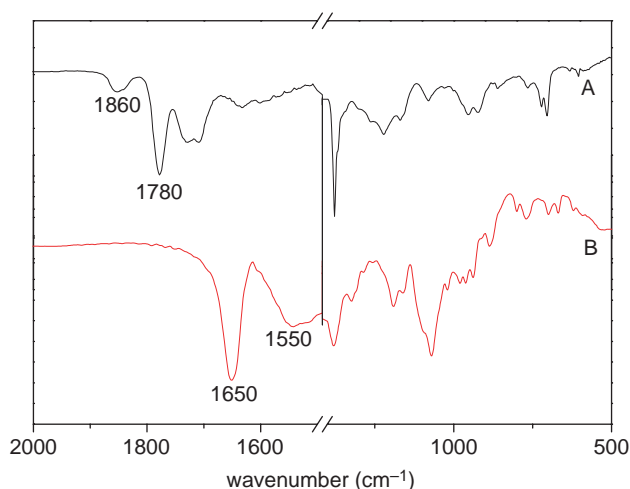

Fig. 4. FT-IR spectra of poly(St-*alt*-MAh) enwrapped MWNTs (A) and the glycoconjugates of poly(styrene-*alt*-maleic acid) enwrapped MWNTs (B).
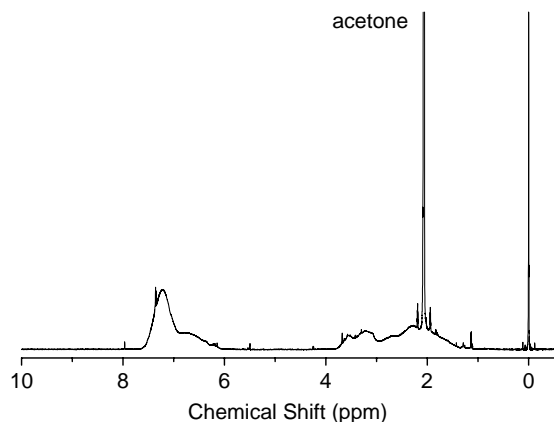
Fig. 5. ^{1}H NMR spectrum of MWNT-P(St-*alt*-MAh) in d_6-acetone.

A control experiment was also carried out under identical conditions with St, MAh and pristine MWNTs that contained no RAFT agent. After polymerization, the product was washed with THF thoroughly until no polymer was found in the filtrate. The obtained MWNTs with black color had almost no major polymer decomposition in TGA curve before 500 °C under nitrogen, as well as no characteristic carbonyl stretching bands of the maleic anhydride at 1780 and 1860 cm^{-1} in its FT-IR spectrum, confirming that for MWNT-P(St-*alt*-MAh), the long chains containing maleic anhydride groups are only covalently anchored on the surface of MWNTs from RAFT agent sites, and not by physical adsorption.

3.3. Raman spectra analysis

Although most directly covalent modifications of MWNTs improve their solubility and compatibility greatly, the structure and the outstanding electronic, mechanical, spectroscopic properties of MWNTs are often altered. Here, the density of RAFT agents on surface of MWNTs is very low, so the alteration on the structure of MWNTs should be very little. Raman spectrum can provide qualitative information on the status of sidewall functionalization, which corresponds to the change of properties for MWNTs [14]. The Raman spectra for the pristine MWNTs and RAFT agents functionalized MWNTs are shown in Fig. 6(A) and (B). Two peaks around 1350 cm^{-1} (D-band) and 1580 cm^{-1} (G-band) were detected. The peak at 1580 cm^{-1} (G-band) is related to the vibration of sp^2-bonded carbon atoms in a two-dimensional hexagonal lattice, such as in a graphitic layer. The D-band around 1350 cm^{-1} is associated with the presence of defects in the hexagonal graphitic layers. The intensity of the D-band is known to be high for badly graphitized materials, the higher the intensity of D-band, the more perfect structure and corresponding properties of MWNTs are altered. The value of intensity ratio between the G- and D-bands (I_G/I_D) serves as a measure of the graphitic ordering and indicates the approximate crystalline size in the hexagonal plane. In Raman spectra Fig. 6(A) and (B), the I_G/I_D of pristine MWNTs is about 1.25, while I_G/I_D is around 1.18 after functionalization, which shows that the functionalization of MWNTs caused a very small decrease in
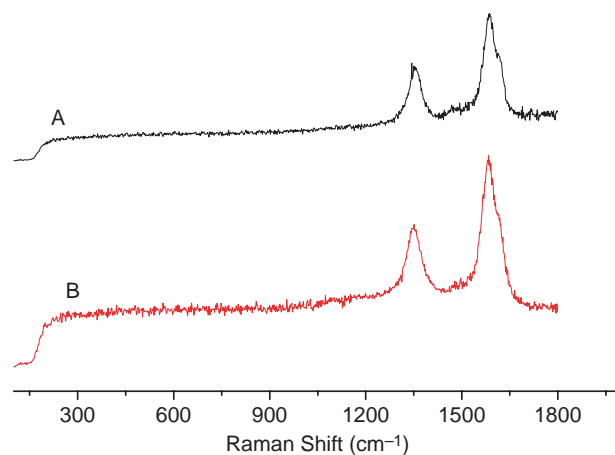

Fig. 6. Raman spectra of pristine MWNTs (A) and RAFT agents slightly functionalized MWNTs (B).

the I_G/I_D compared with that of the pristine MWNTs, indicating very little alteration in the structure of MWNTs after functionalization.

3.4. Further functionalization of MWNTs using the reaction of PEO-OH with maleic anhydride groups

Maleic anhydride can react with amino groups or hydroxyl groups easily [58,73], therefore, it will be easy to further functionalize MWNT-P(St-*alt*-MAh) with different functions. In our experiment, we chose PEO-OH as long water-soluble and biocompatible chain to further functionalize MWNTs. The reaction was performed in DMF solution, and the product obtained was washed with THF. The ^{1}H NMR spectrum of the product is shown in Fig. 7, it is very clear that the characteristic peak at 3.6 ppm corresponding to ethylene protons of PEO appeared besides those peaks ascribed for St and maleic anhydride units at 6.3–7.6, 3.0–3.5 and 1.3–2.8 ppm. The TGA curve of MWNT-P(St-*alt*-MAh)-*g*-PEO is shown in Fig. 3(B); it is clear the weight loss before 500 °C corresponding to surface grown P(St-*alt*-MAh)-*g*-PEO is up to 85%, which is
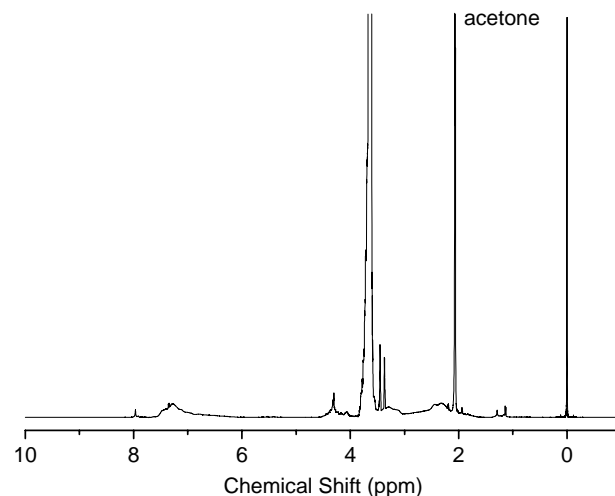

Fig. 7. The ^{1}H NMR spectrum of MWNT-P(St-*alt*-MAh)-*g*-PEO in d_6-acetone.
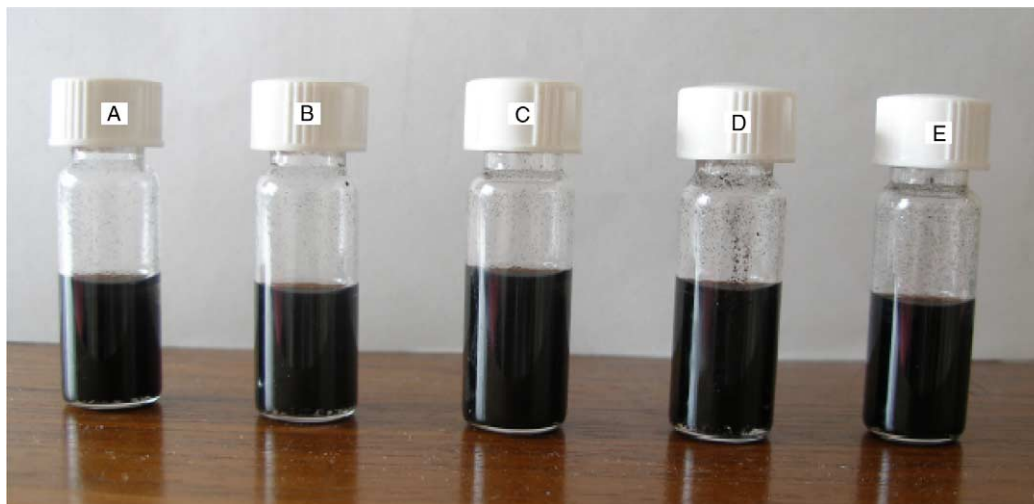
Fig. 8. The images of MWNT-P(St-*alt*-MAh)-*g*-PEO in pure water (A), methanol (B), THF (C), chloroform (D) and acetone (E).
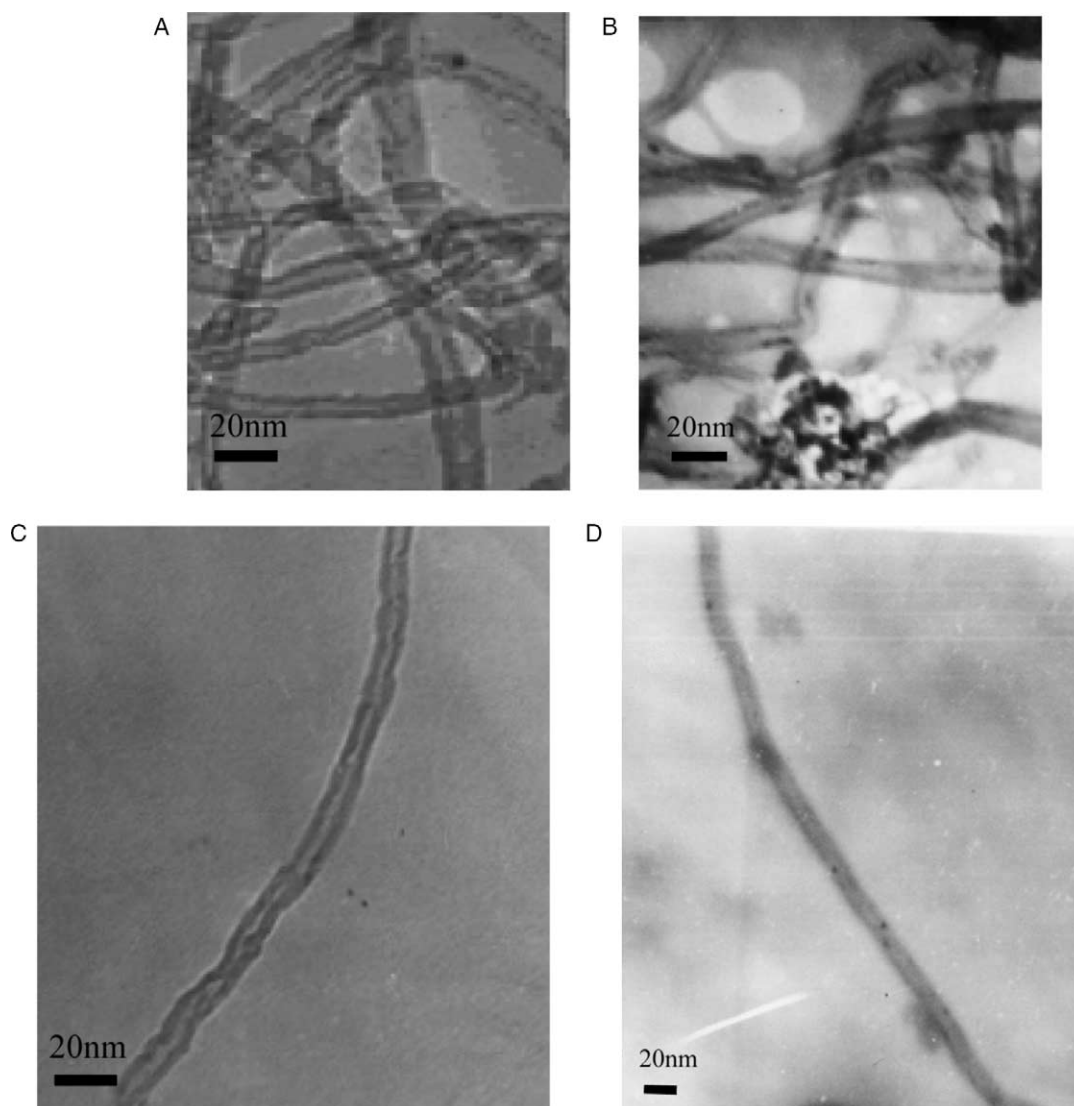

Fig. 9. TEM images of MWNT-SC(S)Ph (A), MWNTs-poly(St-*alt*-MAh) (B), MWNTs-poly(St-*alt*-MAh)-*g*-PEO (C) and glycoconjugates of poly(styrene-*alt*-maleic acid) enwrapped MWNTs (D).

Fig. 10. The glycoconjugates of poly(styrene-*alt*-maleic acid) enwrapped MWNTs in distilled water (A), PBS buffer with pH of 7.4 (B) and DMF (C).

much higher than that of precursor, indicating that long PEO chains have been grafted onto the surface of MWNTs indirectly.

A control experiment was also carried out under similar condition, P(St-*alt*-MAh), PEO–OH and pristine MWNTs in DMF were sonicated, heated, then washed with THF thoroughly until no polymer was found in the filtrate. The obtained MWNTs with black color had no peak in the ^{1}H NMR spectrum, confirming that the PEO chains on MWNT-P(St-*alt*-MAh)-*g*-PEO are bounded on MWNTs from maleic anhydride sites indirectly, not physically adsorbed on MWNTs.

MWNTs functionalized with PEO chains indirectly have very good solubility in organic and aqueous solvents. Fig. 8 shows the good solubility of MWNT-P(St-*alt*-MAh)-*g*-PEO in pure water (Fig. 8(A)), methanol (Fig. 8(B)), THF (Fig. 8(C)), chloroform (Fig. 8(D)) and acetone (Fig. 8(E)). TEM images of MWNT-SC(S)Ph showed that the MWNTs were piled up (Fig. 9(A)), on the other hand, it is very clear that PEO enwrapped MWNTs were dispersed individually from TEM image as shown in Fig. 9(C), indicating that original MWNTs can be separated into individual tube after functionalization.

3.5. Amino sugars further functionalized MWNTs from reactive maleic anhydride sites

Although carbon nanotubes have unique structural, mechanical, and electrical properties, and consequently numerous potential applications in biology, including sensing, imaging, scaffolding for cell growth and transporter for drug and gene delivery, few of these applications have yet been realized due to that the carbon nanotube's surface is hydrophobic, incompatible with biological components such as cells, blood and proteins, and prone to nonspecific bioadsorption without functionalities on the surface. From maleic anhydride sites, we can further functionalize MWNTs with different kinds of biomolecules such as amino acid,

amino sugar or biotin to improve their biocompatibility. Here, we use amino sugar to further functionalize MWNTs, the formation of glycoconjugate of poly(styrene-*alt*-maleic acid) enwrapped MWNTs can be confirmed by FT-IR. In the FT-IR spectrum for glycoconjugate of poly(styrene-*alt*-maleic acid) enwrapped MWNTs shown in Fig. 4(B), the characteristic C=O stretching absorption band (1780 cm^{-1}) and (1860 cm^{-1}) of the anhydride units disappeared, and the signals corresponding to the C=O stretching vibrations of amide group (1650 cm^{-1}) developed instead. The vibrational band corresponding to the N–H bending of the amide group located at 1550 cm^{-1} also appeared. The amount of glycoconjugates of poly(styrene-*alt*-maleic acid) attached to MWNTs was determined by TGA. There are about 61% weight loss for glycoconjugates of poly(styrene-*alt*-maleic acid) enwrapped MWNTs before 500 °C as shown in Fig. 3(C). After further modification by grafting amino sugar onto MWNTs indirectly, the MWNTs not only have very good solubility in aqueous solvents such as distilled water, PBS buffer with pH of 7.4, but also in organic solvents such as DMF as shown in Fig. 10, there is no MWNTs settle down to the bottom after 10 days. The TEM image is shown in Fig. 9(D), it is very clear that modified MWNTs are individually separated.

4. Conclusion

The dithioester groups were successfully immobilized on the surface of MWNTs by covalent chemical bonds. Using these dithioester groups on the surface of MWNTs as RAFT agents, long polymer chains containing lots of highly reactive groups can be grafted onto MWNTs by RAFT copolymerization of St and MAh. The highly reactive maleic anhydride groups can react with long PEO-OH chains or bio-molecules to make the MWNTs soluble in different kinds of organic solvents, distilled water and PBS buffer. Compared with MWNTs functionalized with long

polymer chains or small molecules directly, this method needs not to graft large number of reactive groups on the surface of MWNT directly (only slightly functionalize MWNTs with reactive groups), but lots of long polymer chains or bio-molecules can be grafted onto the surface of MWNTs indirectly. The perfect structure of MWNTs are altered very little, the solubility in organic and aqueous solvents can be improved very much, afford MWNTs with different functionalities based on need. Therefore, it solves the conflict of retaining perfect structure with improving the solubility and compatibility of carbon nanotubes, which should be very useful to investigate the potential applications of carbon nanotubes in biology.

Acknowledgements

References

[1] Dresselhaus MS, Dresselhaus G, Eklund PC, editors. Science of fullerenes and carbon nanotubes; 1996.
[2] Ajayan PM. Chem Rev 1999;99:1787–99.
[3] Dai H. Acc Chem Res 2002;35:1035–44.
[4] Hirsch A. Angew Chem Int Ed 2002;41:1853–9.
[5] Kostarelos K. Adv Colloid Interface Sci 2003;106:147–68.
[6] Pantarotto D, Singh R, McCarthy D, Erhardt M, Briand J, Prato M, et al. Angew Chem Int Ed 2004;43:5242–6.
[7] Baughman RH, Zakhidov AA, de Heer WA. Science 2002;297:787–92.
[8] Chen J, Hamon MA, Hu H, Chen Y, Rao AM, Eklund PC, et al. Science 1998;282:95–8.
[9] Liu J, Rinzler AG, Dai HJ, Hafner JH, Bradley RK, Boul PJ, et al. Science 1998;280:1253–6.
[10] Keren K, Berman RS, Buchstab E, Sivan U, Braun E. Science 2003;302:1380–2.
[11] Balavoine F, Schultz P, Richard C, Mallouh V, Ebbesen TW, Moiskowski C. Angew Chem Int Ed 1999;38:1912–5.
[12] Williams KA, Veenhuizen PTM, de la Torre BG, Eritja R, Dekker C. Nature 2002;420:761.
[13] Dieckmann GR, Dalton AB, Johnson PA, Razal J, Chen J, Giordano GM, et al. J Am Chem Soc 2003;125:1770–7.
[14] Qin SH, Qin DQ, Ford WT, Resasco DE, Herrera JE. J Am Chem Soc 2004;126:170–6.
[15] Lou XD, Detrembleur C, Sciannamea V, Pagnoulle C, Jérôme R. Polymer 2004;45:6097–102.
[16] (a) Star A, Stoddart JF, Steuerman D, Diehl M, Boukai A, Wong EW, et al. Angew Chem 2001;113:1771–5.
(b) Star A, Stoddart JF, Steuerman D, Diehl M, Boukai A, Wong EW, et al. Angew Chem Int Ed 2001;40:1721–5.
[17] Dyke CA, Tour JM. Nano Lett 2003;3:1215–8.
[18] Wang W, Lin Y, Sun YP. Polymer 2005;46:8634–40.
[19] Viswanathan G, Chakrapani N, Yang H, Wei B, Chung H, Cho K, et al. J Am Chem Soc 2003;125:9258–9.
[20] Banerjee S, Kahn MGC, Wong SS. Chem Eur J 2003;9:1898–908.
[21] Lou XD, Detremleur C, Pagnoulle C, Jérôme R, Bocharovar V, Kiriy A, et al. Adv Mater 2004;16:2123–7.
[22] Baskaran D, Mays JW, Bratcher MS. Polymer 2005;46:5050–7.
[23] Kong H, Luo P, Gao C, Yan DY. Polymer 2005;46:2472–85.
[24] Ge JJ, Zhang D, Li Q, Hou H, Graham MJ, Dai L, et al. J Am Chem Soc 2005;127:9984–5.
[25] Hong CY, You YZ, Wu DC, Liu Y, Pan CY. Macromolecules 2005;38:2606–11.
[26] Liu YQ, Yao ZL, Adronov A. Macromolecules 2005;38:1172–9.
[27] Lee KM, Li LC, Dai L. J Am Chem Soc 2005;127:4122–3.
[28] Chen Y, Haddon RC, Fang S, Rao AM, Eklund PC, Lee WH, et al. J Mater Res 1998;13:2423–31.
[29] Ying Y, Saini RK, Liang F, Sadana AK, Billups WE. Org Lett 2003;5:1471–3.
[30] Georgakilas V, Kordatos K, Prato M, Guldi DM, Holzinger M, Hirsch A. J Am Chem Soc 2002;124:760–1.
[31] Stevens JL, Huang AY, Peng H, Chiang IW, Khabashesku VN, Margrave JL. Nano Lett 2003;3:331–6.
[32] Milner ST. Science 1991;251:905–14.
[33] Zhao B, Brittain WJ. Prog Polym Sci 2000;25:677–710.
[34] Huang W, Skanth G, Baker GL, Bruening ML. Langmuir 2001;17:1731–6.
[35] Matyjaszewski K, Miller PJ, Shukla N, Immaraporn B, Gelman A, Luokala BB, et al. Macromolecules 1999;32:8716–24.
[36] Husseman M, Malmstroem EE, McNamara M, Mate M, Mecerreyes D, Benoit DG, et al. Macromolecules 1999;32:1424–31.
[37] Ejaz M, Yamamoto S, Ohno K, Tsujii Y, Fukuda T. Macromolecules 1998;31:5934–6.
[38] Guldi DM, Rahman GMA, Jux N, Tagmatarchis N, Prato M. Angew Chem Int Ed 2004;43:5526–30.
[39] Sano M, Kamino A, Okamura J, Shinkai S. Langmuir 2001;17:5125–8.
[40] Niyogi S, Hamon MA, Hu H, Zhao B, Bhowmik P, Sen R, et al. Acc Chem Res 2002;35:1105–13.
[41] Pompeo F, Resasco DE. Nano Lett 2002;2:369–73.
[42] Viswanathan G, Chakrapani N, Yang H, Wei B, Chung H, Cho K, et al. J Am Chem Soc 2003;125:9258–9.
[43] Mickelson ET, Huffman CB, Rinzler AG, Smalley RE, Hauge RH, Margrave JL. Chem Phys Lett 1998;296:188–94.
[44] Bahr JL, Yang J, Kosynkin DV, Bronikowski MJ, Smalley RE, Tour JM. J Am Chem Soc 2001;123:6536–42.
[45] Dyke CA, Tour JM. J Am Chem Soc 2003;125:1156–7.
[46] Pekker S, Salvetat JP, Jakab E, Bonard JM, Forro L. J Phys Chem B 2001;105:7938–43.
[47] Holzinger M, Vostrowsky O, Hirsch A, Hennrich F, Kappes M, Weiss R, et al. Angew Chem. Int Ed 2001;40:4002–5.
[48] Chen Y, Haddon RC, Fang S, Rao AM, Eklund PC, Lee WH, et al. J Mater Res 1998;13:2423–31.
[49] Ying Y, Saini RK, Liang F, Sadana AK, Billups WE. Org Lett 2003;5:1471–3.
[50] Cui J, Wang WP, You YZ, Liu CH, Wang PH. Polymer 2004;45:8717–21.
[51] Kong H, Gao C, Yan D. Macromolecules 2004;37:4022–30.
[52] Qin SH, Qin DQ, Ford WT, Resasco DE, Herrera JE. Macromolecules 2004;37:752–7.
[53] Baskaran D, Dunlap JR, Mays JW, Bratcher MS. Macromol Rapid Commun 2005;26:481–6.
[54] Zhao B, Hu H, Yu AP, Perea D, Haddon RC. J Am Chem Soc 2005;127:8197–203.
[55] Zhao B, Hu H, Haddon RC. Adv Funct Mater 2004;14:71–6.
[56] Hong CY, You YZ, Pan CY. Chem Mater 2005;17:2247–54.
[57] Sun TL, Liu H, Song WL, Wang X, Jiang L, Li L, et al. Angew Chem Int Ed 2004;43:4663–6.
[58] Wirsen A, Sun H, Emilsson L, Albertsson AC. Biomacromolecules 2005;6:2281–9.
[59] Ladaviere C, Lorenzo C, Elaissari A, Mandrand B, Delair T. Bioconjugate Chem 2000;11(2):146–52.
[60] Mu Y, Kamada H, Kaneda Y, Yamamoto Y, Kodaira H, Tsunoda S, et al. Biochem Biophys Res Commun 1999;255:75–9.
[61] Donati I, Gamini A, Vetere A, Campa C, Paoletti S. Biomacromolecules 2002;3:805–12.
[62] Maeda H, Ueda M, Morinaga T, Matsumoto T. J Med Chem 1985;28:455.
[63] de Lambert B, Charreyre MT, Chaix C, Pichot C. Polymer 2005;46:623–37.
[64] Zhou GC, Harruna II, Ingram CW. Polymer 2005;46:10672–7.

C.-Y. Hong et al. / Polymer 47 (2006) 4300–4309 4309

[65] Favier A, Charreyre MT, Pichot C. Polymer 2004;45:8661–74.
[66] You YZ, Hong CY, Pan CY. Eur Polym J 2002;38:1289–95.
[67] Thomas DB, Convertine AJ, Myrick LJ, Scales CW, Smith AE, Lowe AB, et al. Macromolecules 2004;37:8941–50.
[68] Joso R, Stenzel MH, Davis TP, Baraner-Kowollik C, Barner L. Aust J Chem 2005;58:468–71.
[69] Hu TJ, You YZ, Pan CY, Wu C. J Phys Chem B 2002;106:6659–62.
[70] Ganachaud F, Monteiro MJ, Gilbert RG, Dourges MA, Thang SH, Rizzardo E. Macromolecules 2000;33:6738–45.
[71] Tsujii Y, Ejaz M, Sato K, Goto A, Fukuda T. Macromolecules 2001;34: 8872–8.
[72] Salem N, Shipp DA. Polymer 2005;46:8573–81.
[73] You YZ, Hong CY, Wang WP, Wang PH, Lu WQ, Pan CY. Macromolecules 2004;37:7140–5.