Polym. Bull. (2013) 70:3563–3574
DOI 10.1007/s00289-013-1040-y

ORIGINAL PAPER

Modification of multiwall carbon nanotube by thiol-ene click chemistry

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Received: 17 August 2012 / Revised: 22 June 2013 / Accepted: 21 August 2013 /
Published online: 3 September 2013

Abstract Thiol-ene click chemistry was used for the preparation of polystyrene grafted multiwall carbon nanotubes (MWCNTs) via the thermal initiation method. The thiol end-functional PSt (PSt-SH) was prepared by the nucleophilic substitution reaction of the bromide end groups of PSt obtained by atom transfer radical polymerization. PSt-SH grafted to the surface of the MWCNTs by thiol-ene click chemistry via the thermal initiation method.

Keywords Carbon nanotube · Click chemistry · Functionalization · Thiol-ene

Introduction

In recent years, carbon nanotubes (CNTs) have attracted enormous attention in material science due to their extensive use in molecular electronics [1], photovoltaics [2], supercapacitors [3], field emission displays [4], sensors [5, 6], high-strength materials [7] and drug delivery agents [8, 9]. Since their first use as fillers in

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1994, numerous studies concerning design and fabrication of CNT-based nanocomposites have been reported.

Although CNTs exhibit powerful properties such as low mass density, electrical conductivity and nanocomposite component, they are hindered by several difficulties such as self aggregation, poor solubility in organic solvents and dispersion in polymeric matrices [10]. To overcome the latter drawback, several approaches involving non-covalent and covalent functionalization methods have been reported [11–18] and thus CNTs with improved solubility were obtained. Non-covalent functionalizations such as $\pi-\pi$ stacking interactions between the surface of CNTs and polynuclear groups of polymers are based on Van der Waals forces [11]. Covalent functionalization examples include grafting of macromolecules using both "grafting onto" [12–14] and "grafting from" [12–15] approaches. The "grafting onto" method is the most widely used functionalization approach to prepare modified CNTs with various types of polymers. Depending on the type of polymer used, the resultant composites may exhibit hydrophilic [16], hydrophobic [17] or amphiphilic [18] properties.

A variety of cross chemical reactions such as click chemistry [19–21], Diels–Alder [22, 23], and radical coupling [23–29], have been developed to obtain functional polymers in quantitative yield. Among them, 1, 3- Huisgen dipolar cycloaddition [30–33] which takes place at room temperature in the presence of a Cu (I) catalyst is the most widely used reaction for the synthesis of telechelic polymers [34, 35], functional dendrimers [36, 37], hyperbranched polymers [38], biopolymers [39], polymeric photoinitiators [40], water soluble macromolecules [41], thermoset materials [42–44] and so on. However, after the reaction, the requirement for the removal of the metal catalysts by various purification methods makes this approach impractical for some applications.

Recently, thiol-ene chemistry has been introduced as a new type of click chemistry which can be conducted photochemically or thermally in the absence of a metal catalyst [45]. Click efficiencies were recently evaluated for both initiator systems using well-defined linear polystyrene (PSt) possessing mercapto end groups [46]. Despite some problems associated with low efficiency in certain cases and the use of odorous thiol compounds, thiol-ene click chemistry has been successfully employed to synthesize biomaterials [47, 48], star polymers [49], macrocyclic polymers [50], polymeric photoinitiators [51], crosslinked materials [52], UV-curable coatings [53, 54] and organic and inorganic nano coatings [55].

In this study, we report the results of the synthesis of dispersible and stable PS attached MWCNTs by "thiol-ene click chemistry". As will be shown below, while the MWCNT acted as the "ene" component, the thiol functional PSt (PSt-SH) was prepared by the nucleophilic substitution reaction of bromide end groups of PSt obtained by atom transfer radical polymerization (ATRP). Subsequently, PSt-SH grafted to the surface of the MWCNTs by thiol-ene click chemistry via the thermal initiation method. The intermediate and final PSt-based MWCNTs were characterized by ^{1}H NMR, Raman Spectroscopy and Scanning Electron Microscopy (SEM).

Experimental section

Materials

Styrene (St, 99 %, Aldrich) was distilled under reduced pressure before use. 2, 2′-Azobis(isobutyronitrile) (AIBN, 98 %, Aldrich) was recrystallized from ethanol. Tetrahydrofuran (THF, 99.8 %, J.T. Baker) was dried and distilled over benzophenone-Na. *N*, *N*, *N*′, *N*″, *N*″-Pentamethyldiethylenetriamine (PMDETA, Aldrich) was distilled over NaOH before use. CuBr (99.9 %, Aldrich), Ethyl-2-bromopropionate (>99 %, Aldrich) and trimethylolpropane tris(2-mercaptoacetate) (technical grade, Aldrich) were used as received. Multiwall carbon nanotube (MWCNT) Baytubes® C 150 P (Bayer) was used as received. All other reagents were purchased from Aldrich and used as received.

General procedure for atom transfer radical polymerization

To a Schlenk tube equipped with a magnetic stirring bar, the degassed monomer (St, 44 mmol), ligand (PMDETA, 0.44 mmol), catalyst (CuBr, 0.44 mmol) and initiator (ethyl-2-bromopropionate, 0.44 mmol) were added, respectively. The tube was degassed by three freeze–pump–thaw cycles, left under vacuum, and placed in a thermostated oil bath. After the polymerization, the reaction mixture was diluted with THF and then passed through a column of neutral alumina to remove the metal salt. The excess of THF and unreacted monomer were evaporated under reduced pressure. The polymer was dissolved in THF and precipitated in 10-fold excess methanol. The final polymer was dried in vacuum at room temperature. Molecular weights and molecular weight distributions of the polymers (M_n = 3,000 g mol^{-1}, PDI = 1.18 and M_n = 9,000 g mol^{-1}, PDI = 1.19) were determined by GPC.

Synthesis of thiol end-functional polystyrene (PSt-SH)

The thiol end-functional polystyrenes were synthesized from the above obtained PSt-Br by organic substitution reaction following the literature procedure [56]. Thus, a mixture of 1.0 g of polystyrene (PSt-Br), of thiourea (0.08 g, 1.05 mmol, 10 equiv.) and 30 ml of DMF was heated at 100 °C under flow for 24 h. NaOH (0.042 g, 1.05 mmol, 10 equiv.) which was dissolved in 0.8 ml of water, was added and the mixture heated to 110 °C for 24 h. Two drops of 95 % sulfuric acid in 0.5 ml of water were added and the mixture was stirred at room temperature for an additional 5 h. The functionalized polymer was purified by successive precipitations in methanol.

Modification of MWCNT with PSt-SH by thiol-ene click chemistry

PSt-SH (150 mg) and a catalytic amount of AIBN (1–2 % w/w) were dissolved in 30 mL of DMF, and 50 mg MWCNT was added. The mixture was sonicated for 10 min in an ultrasonic bath and the resulting suspension was bubbled with argon for 15 min. Then the suspension was sonicated again for 10 min and allowed to stir

at 80 °C overnight. At the end of the period, the resulting mixture was centrifuged to remove solvent and unreacted polymer. Modified MWCNT was redispersed in fresh THF using mild sonication and then centrifuged again. The redispersion and recentrifugation process were then repeated three times to remove any free PSt. The final product was dried in vacuum.

Characterization

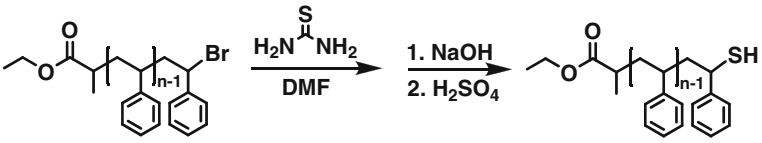
The ^{1}H NMR (250 MHz) spectra were recorded on a Bruker NMR Spectrometer in $CDCl_3$. Gel permeation chromatography (GPC) measurements were obtained from a Viscotek GPCmax Autosampler system consisting of a pump, three ViscoGEL GPC columns ($G2000H_{HR}$, $G3000H_{HR}$ and $G4000H_{HR}$), a Viscotek UV detector and a Viscotek differential refractive index (RI) detector with a THF flow rate of 1.0 mL min^{-1} at 30 °C. Both detectors were calibrated with PS standards having narrow molecular weight distribution. Data were analyzed using Viscotek Omni-SEC Omni-01 software. UV spectra were recorded on a Shimadzu UV-1601 spectrometer. Thermal gravimetric analysis (TGA) was performed on a Perkin–Elmer Diamond TA/TGA with a heating rate of 10 °C min^{-1} under nitrogen flow. Scanning electron microscopy (SEM) was performed with a Philips XL30S-FEG microscope. Samples were gold coated prior to SEM observation.

Results and discussion

As stated previously, modification of MWCNTs was achieved by thiol-ene click chemistry. As the polymeric click component, appropriate thiol-end functionalized linear polystyrenes were synthesized by ATRP according to the procedures reported by Hilborn and co-workers [56]. To obtain thiol-end functionalized polystyrene (PSt-SH), ethyl-2-bromopropionate was used as the initiator in the ATRP of styrene and the resulting halide end-functional polystyrene was then converted to a thiol group by organic substitution reaction (Scheme 1).

The polymers were also characterized by ^{1}H NMR analyses. As can be seen from Fig. 1, where the ^{1}H NMR spectra of PSt-Br and PSt-SH were recorded, the methine proton close to the halide chain end has a chemical shift at 4.30–4.42 ppm, which shifts quantitatively to 3.80 ppm as a result of efficient nucleophilic substitution of the halogen atom at the polymer chain end by a thiol.

Although the photochemical methods of radical generation processes are known to be more efficient for thiol-ene reactions [57], in the present work the thermal



Scheme 1 Overall process for the synthesis of thiol end-functional polystyrene

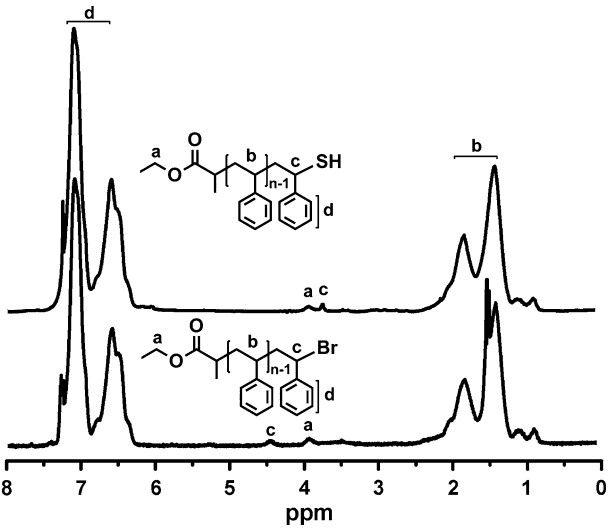


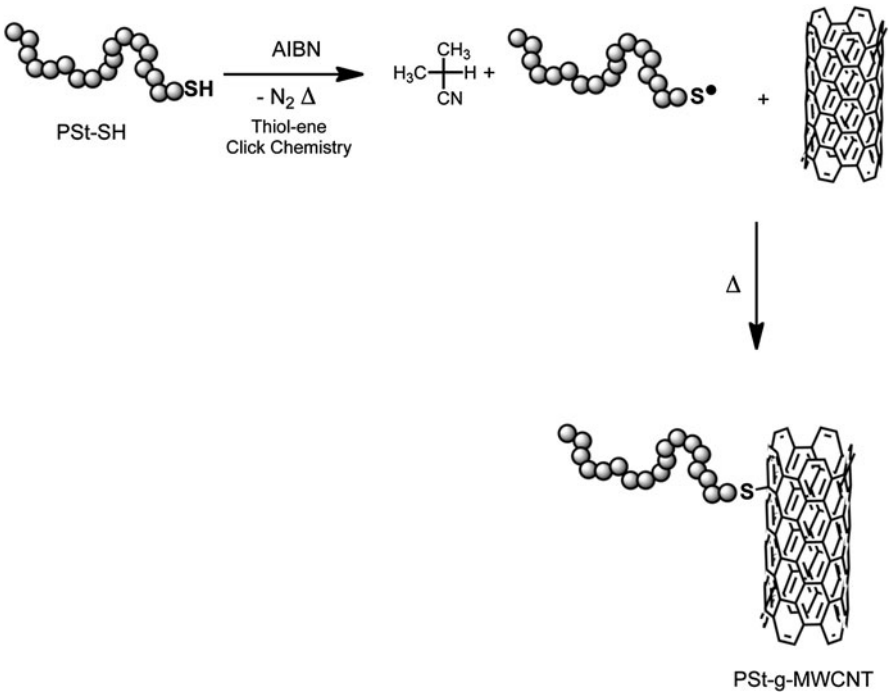
Fig. 1 ^{1}H NMR spectra of PSt-Br and PSt-SH in $CDCl_3$

mode was deliberately selected to form abstracting radicals. This is due to the fact that in this particular case sufficient absorption of light by the photoinitiator cannot be achieved through the mixtures containing CNTs. Thus, a thermally induced thiol-ene reaction was applied at 80 °C using 2, 2′-azobis (isobutyronitrile) (AIBN) to graft PSt onto the MWCNT through the reactions depicted in Scheme 2.

At the end of the reaction, the dark suspension was first centrifuged and then washed with fresh THF several times to remove the unreacted polystyrene. Successful grafting of PSt onto the MWCNT was confirmed by ^{1}H NMR analysis. As can be seen from Fig. 2, after the click reaction, the characteristic protons of PSt were noted.

The absorption characteristic of MWCNT-*g*-PSt was also investigated. As can be seen from Fig. 3, the $\pi-\pi^*$ transition of the phenyl groups of PSt chains present in MWCNT-*g*-PSt was observed at around 300 nm. This observation is more pronounced with PSt chains with relatively lower molecular weights. However, it should be pointed out that although the solubility of the CNT is significantly increased by the modification, there still exist some dispersion problems, which interfere with the light transmission particularly with MWCNTs having higher molecular weight PSt grafts.

According to Raman spectroscopy analysis, pristine MWCNT and PSt-*g*-MWCNT spectra were compared as shown in Fig. 4 and the Raman spectrum of PSt-*g*-MWCNT shows that the strong G band is associated with the vibration of sp^2-bonded carbon atoms in a nanotube layer accompanied by a D′ band at 1,608 cm^{-1} as a shoulder that may be attributed to the disorder in the nanotubes. This could be evidence for sidewall functionalization of MWCNT, when compared with the pristine MWCNT.



Scheme 2 Grafting PSt onto MWCNT via thermally induced thiol-ene reaction

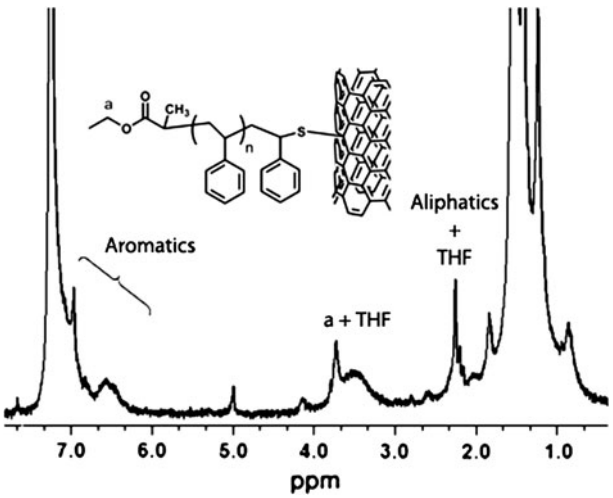


Fig. 2 ^{1}H NMR spectra of PSt grafted MWCNT in $CDCl_3$

Modification of MWCNTs was further verified by visual observation of the appearance of the solutions containing MWCNTs before and after thiol-ene modification. Figure 5 shows the digital photographs of modified and pristine CNT

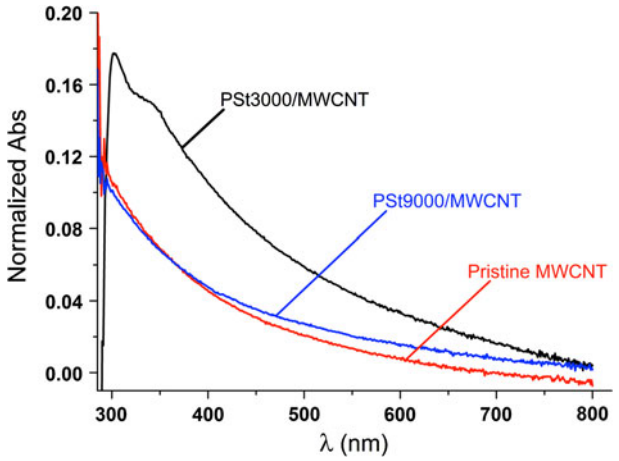


Fig. 3 UV absorption spectra of pristine MWCNT, PSt3000/MWCNT and PSt9000/MWCNT in THF

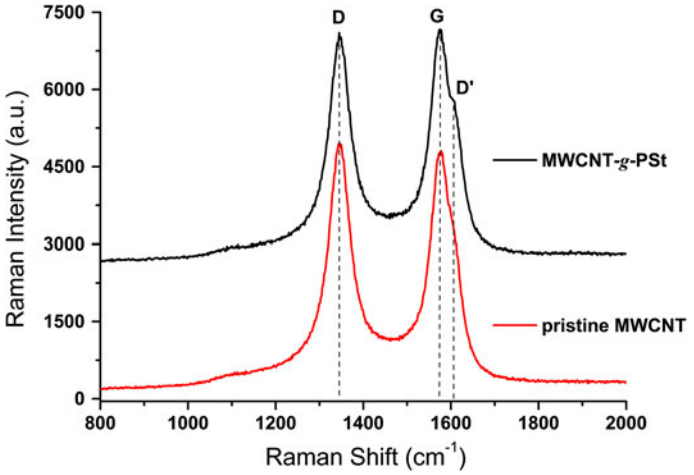


Fig. 4 Raman spectra of as-received and modified MWCNT

solutions. Notably, after sonication, CNT samples, especially those which were grafted with low molecular weight PSt chains exhibit very good dispersion in THF. In complete contrast, the dispersion of unreacted CNTs was extremely poor under the same conditions. The PSt9000/MWCNT sample started to precipitate at the bottom after several hours, whereas PSt3000/MWCNT did not exhibit obvious aggregation. As each polymer chain contains thiol-end group, the grafting is directly related to the molecular weights of polymers. Grafting of PSt9000 seems to be lower compared to PSt3000 due to the low thiol density.

To check further the influence of PSt grafts on the surface layer of the CNTs, we investigated the morphology of the MWCNT before and after the grafting process. Figure 6 shows the SEM pictures of pristine MWCNT and PSt3000/MWCNT

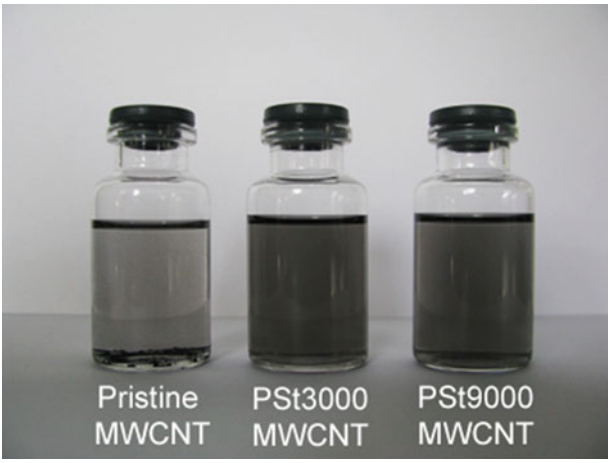


Fig. 5 Dispersions of pristine MWCNT, PSt3000/MWCNT and PSt9000/MWCNT in THF

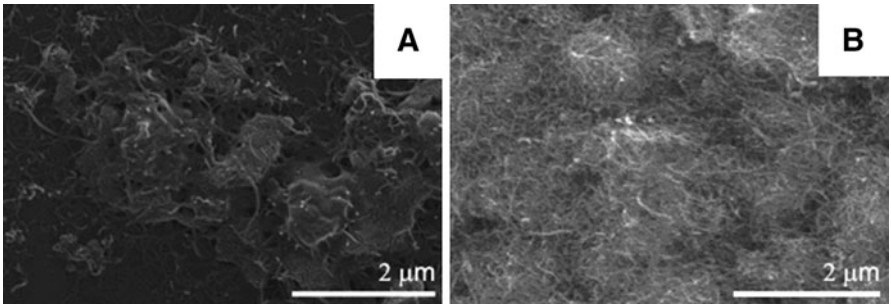


Fig. 6 Scanning electron microscope (SEM) images of (A) MWCNT-*g*-PSt3000 and (B) MWCNT

which clearly indicate a good dispersion of CNTs in the PSt matrix after the click reaction.

The thermal stability of PSt-*g*-MWCNT was investigated by thermal gravimetric analysis (TGA) and compared with that of the precursors MWCNT and PSt. TGA profiles of pristine MWCNT, PSt3000/MWCNT, PSt9000/MWCNT, neat PSt3000 and PSt9000 under nitrogen atmosphere are presented in Fig. 7. As expected, pristine MWCNT is exceptionally thermally stable and its 99 % mass remained even at 900 °C. PSt3000 is thermally unstable and decomposes almost completely before the temperature reaches 400 °C. However, regardless of the molecular weight, the thermal stability of PSt increased when grafted onto the MWCNTs. As clearly seen from Fig. 7, PSt9000/MWCNT starts to decompose at lower temperature compared to PSt3000/MWCNT due to the higher polymer content.

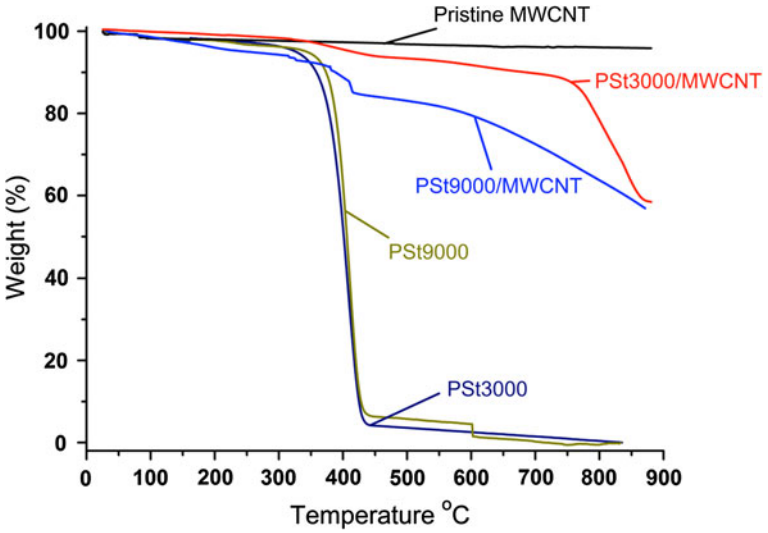


Fig. 7 Thermal gravimetric analysis (TGA) curves of MWCNT, PSt3000, PSt9000, PSt3000/MWCNT and PSt9000/MWCNT under nitrogen atmosphere

Conclusion

In summary, we have demonstrated the potential of thiol-ene click reactions as a versatile synthetic route to modify CNTs by polymer chains. In this work, thiol end-functional PSt, prepared by ATRP and subsequent nucleophilic substitution reaction, was grafted onto MWCNTs by a thermally induced click process. At least in principle, any polymer possessing thiol-end groups can be used as the click compound in conjunction with CNTs in the described method to give corresponding nanocomposites with the properties governed by both components. Further studies along this line are now in progress.

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