

Rapid Communication

IN SITU ETHYLENE COPOLYMERIZATION WITH AN OLEFIN-TYPE MONOMER FOR ONE-POT SYNTHESIS OF POLYETHYLENE TETHERED ON MULTI-WALLED CARBON NANOTUBES*

Ji-jun Tang, Shi-yun Li**

Department of Materials Science and Engineering, Jiangsu University of Science and Technology,
Zhenjiang 212003, China

Yan-hui Wang** and Tao Tang

State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry,
Chinese Academy of Sciences, Changchun 130022, China

Abstract A one-pot procedure for the synthesis of polyethylene tethered on multi-walled carbon nanotubes by *in situ* ethylene copolymerization with an olefin-type comonomer, α -alkene functionalized multi-walled carbon nanotubes (MW-CH=CH₂) is reported. The covalent linkage between polyethylene and multi-walled carbon nanotubes is demonstrated. The MWCNTs are chemically oxidized first by a strong oxidizing agent and then functionalized with chlorocarbonyl groups (MW-COCl) *via* reacting with thionyl chloride. The MW-CH=CH₂ are obtained by esterification of ω -undecylenyl alcohol with MW-COCl. The MW-CH=CH₂ may serve as olefin-type comonomers to further synthesize core-shell structured copolymers with a multi-walled carbon nanotubes core grafted with side chains of polyethylene *via* *rac*-(en)(THInd)₂ZrCl₂ copolymerization catalyst. The core-shell structured nanocomposites were characterized by means of ¹H-NMR, SEM, FTIR and TGA. The results confirmed the formation of polyethylene chains growing from the surface of multi-walled carbon nanotubes.

Keywords: Carbon nanotubes; Copolymerization; Polyethylene; Nanocomposite.

INTRODUCTION

Developing nanofillers functionalized polyolefins is an important and challenging theme in the research and development of polyolefins. The presence of nanofillers in the non-polar polyolefins may result in some enhanced materials properties, such as toughness and barrier properties. It is well known that carbon nanotubes (CNTs) show a great potential for many applications because of their unique structure and properties^[1]. Covalently attaching polymers onto the surface of CNTs has attracted considerable attention as it endows the surfaces with novel structures and properties and promotes the dispersion of CNTs in polymer matrix. Both “graft from” and “graft to” techniques are often used to accomplish covalent attachment of polymer to the surface of CNTs^[2–4]. And the established chemical linkage between polymer and the surface of modified CNTs, can greatly improve interfacial strength of CNTs-polymer mixture and the dispersion of CNTs in polymer matrices. However, the above methods have limited success on *in situ* formation of polyolefin chains, because of the highly oxophilic nature of the most metal catalyst systems for olefin coordination polymerization. For optimal performance in polyolefin/CNTs nanocomposites, CNTs should be separated into individual tubes or

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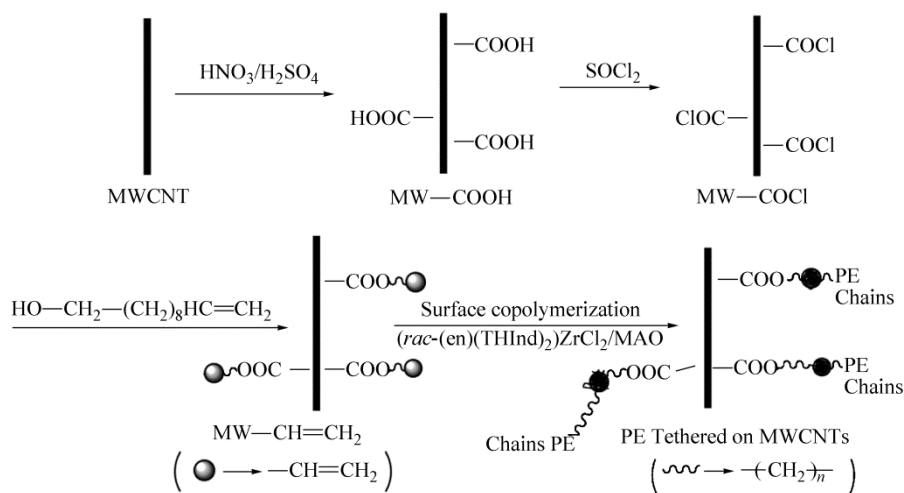
** Corresponding author: Shi-yun Li (李世云), E-mail: shiyunlee@hotmail.com

Yan-hui Wang (王艳辉), E-mail: wangyh@ciac.jl.cn

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bundles of a few tubes and compatible with the host polyolefin, which is not easily realized. The application of covalent method has been reported successfully in fabricating composites consisted of other polymers and CNTs, and only noncovalent methods have been applied in the fabrication of polyolefin/CNTs composites^[2]. Only a few papers have been reported on polyolefin covalent with CNTs, at present our group has reported successful preparing polyethylene-g-SWCNTs *via* copolymerization, using a 1, 3-dipolar cycloaddition reaction on the SWCNTs^[5].

In this paper, we demonstrated an *in situ* copolymerization method to grow polyethylene from the surface of multi-walled carbon nanotubes (MWCNTs). In comparison with other polymerization methods reported before, such as *in situ* coordination polymerization, the *in situ* copolymerization is expected to be a better way to obtain a strong interfacial linkage between polyethylene and MWCNTs, which would promote the dispersion of MWCNTs in PE matrix. In place of the present general “graft from” methods by immobilizing the initiators on the surface of CNTs first, here we attached α -alkene to the surface of MWCNTs ($\text{MW}-\text{CH}=\text{CH}_2$) by acyl chloride method, which can disperse well in the organic solvent. Then the $\text{MW}-\text{CH}=\text{CH}_2$ have been directly used as an olefin-type comonomer to synthesize functionalized MWCNTs with polyethylene arms tethered on the MWCNTs core by *in situ* ethylene copolymerization (Scheme1), which provides a novel route to fabricate core-shell polyolefin/MWCNTs nanocomposites with high-performance.



Scheme 1 Schematic synthetic procedure

EXPERIMENTAL

Syntheses of α -alkene Functionalized MWCNTs and MWCNTs-PE

MWCNTs (10–20 nm) with carboxylic groups on the surface ($\text{MW}-\text{COOH}$) were formed by a strong oxidizing agent (3/1 concentrated $\text{H}_2\text{SO}_4/\text{HNO}_3$ mixture)^[6]. α -Alkene groups were covalently attached to the surface of MWCNTs by esterification of ω -undecylenyl alcohol with chlorocarboxylic groups on MWCNTs ($\text{MW}-\text{COCl}$), forming α -alkene functionalized MWCNTs ($\text{MW}-\text{CH}=\text{CH}_2$). The content of α -alkene functional groups was $8.4 \text{ mmol} \cdot (\text{mol C})^{-1}$ measured by TGA. The propagation of PE chain takes place first *via* coordination of α -alkene on the surface of MWCNTs with $\text{rac}-(\text{en})(\text{THfnd})_2\text{ZrCl}_2/\text{MAO}$, followed by an insertion of ethylene monomer. The MWCNT-PE nanocomposites with different grafted PE quantities were prepared by controlling copolymerization time at about 10 min (MP-1) and 20 min (MP-2). The amount of PE attached to MWCNTs calculated by TGA varied from 36 wt% in MP-1 to 84 wt% in MP-2.

Characterization

^1H -NMR spectra of the samples were recorded on a Bruker 400 MHz FT-NMR spectrometer. Field emission scanning electron microscope (FESEM, XL303SEM) was used to observe the dispersion states of the MWCNTs. And the microstructure of the obtained nanocomposites were observed by means of transmission electron

microscope (TEM, JEOL2010, operating at 200 kV). All samples are sputtered with gold to endure high voltage within examination by FESEM. FTIR spectra were recorded on a Bio-Rad FTS 135 spectrophotometer. Thermogravimetric analyses (TGA) were carried out on a SDT Q600 TA instrument with a heating rate of $10\text{ K}\cdot\text{min}^{-1}$ under a nitrogen atmosphere ($100\text{--}700\text{ }^{\circ}\text{C}$).

RESULTS AND DISCUSSION

Scheme 1 shows the synthetic procedure of α -alkene fixed on the surface of MWCNTs and PE growing from MWCNTs surface. The propagation of PE chain takes place first *via* coordination of α -alkene on the surface of MWCNTs with *rac*-(en)(THInd)₂ZrCl₂/MAO, followed by an insertion of ethylene monomer. The chemical structures of MW-CH=CH₂ and MP-1 are characterized by ¹H-NMR (Fig. 1). For comparison, ¹H-NMR spectrum of ω -undecylenyl alcohol and pure PE are also included in Fig. 1. The α -alkene groups of MW-CH=CH₂ show two broad peaks at $\delta = 5.8$ and $\delta = 4.9$ (Fig. 1b). The presence of proton signals of -COOCH₂- ($\delta = 3.6$), -OCH₂CH₂- ($\delta = 1.9$), and =CH-CH₂- ($\delta = 2.0$) are clearly visible in Fig. 1(b). The corresponding aliphatic resonances are observed at $\delta = 0.9$ and $\delta = 1.2$. The signal of OH groups ($\delta = 3.0$ in Fig. 1a) disappears in Fig. 1(b), and the broadening of all the resonance peaks in comparison with those of

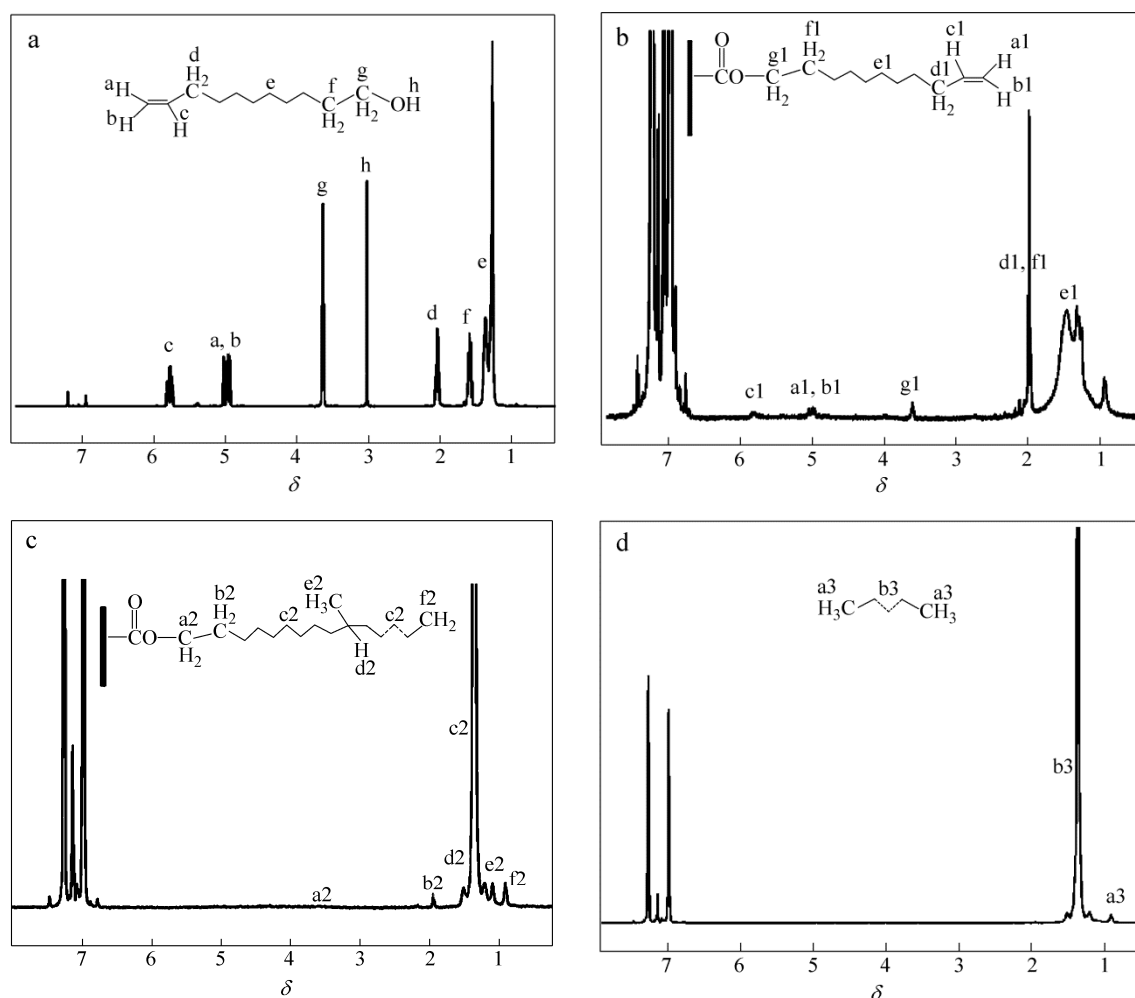


Fig. 1 (a) ω -Undecylenyl alcohol ($\text{C}_6\text{D}_4\text{Cl}_2$ solvent, $25\text{ }^{\circ}\text{C}$), (b) MW-CH=CH₂ ($\text{C}_6\text{D}_4\text{Cl}_2$ solvent, $25\text{ }^{\circ}\text{C}$), (c) MP-1 (51 wt%, $\text{C}_6\text{D}_4\text{Cl}_2$ solvent, $130\text{ }^{\circ}\text{C}$) and (d) PE ($\text{C}_6\text{D}_4\text{Cl}_2$ solvent, $130\text{ }^{\circ}\text{C}$)

ω -undecylenyl alcohol results from the effect of the partial orientation of the magnetically anisotropic carbon nanotubes in the magnetic field^[7], further suggesting that $\text{MW}-\text{CH}=\text{CH}_2$ was successfully obtained. In ^1H -NMR spectrum of MP-1 (Fig. 1c), olefinic resonances are absent, indicating that the polymer is free of residual comonomer ($\text{MW}-\text{CH}=\text{CH}_2$). The resonances of the $-\text{OCH}_2\text{CH}_2-$ ($\delta = 1.9$) is well-resolved. However, the signal of the $-\text{COOCH}_2-$ protons on the MWCNTs is very weak (Fig. 1c). All the evidence confirmed the growth of PE polymer chains on the surface of MWCNTs by ethylene copolymerization with $\text{MW}-\text{CH}=\text{CH}_2$.

The morphologies of the samples are observed by means of FESEM (Fig. 2). To compare the suspension stabilities of $\text{MW}-\text{COOH}$ and $\text{MW}-\text{CH}=\text{CH}_2$, 5 mg of both samples was added into the same amount of toluene followed by ultrasonication for 30 min and then deposition for 10 min (Inserts in Fig. 2b). The obvious improvement in the suspension stability of $\text{MW}-\text{CH}=\text{CH}_2$ further confirms that the α -alkene organic groups are covalently linked onto MWCNTs. This behavior provides a stable reaction system for synthesizing MWCNTs-PE nanocomposites. Generally, comparing with the $\text{MW}-\text{COOH}$ and $\text{MW}-\text{CH}=\text{CH}_2$ (Figs. 2a and 2b), MWCNTs are coated by PE phase in the resultant MWCNTs-PE nanocomposites (Figs. 2c and 2d), and the rod-like nanostructures can still be clearly observed. The TEM image (Fig. 2e) shows the core-shell structure of the MP-2 nanocomposite indicated by the black arrows. When the content of the grown PE increases, the PE phase becomes more continuous, and the rods become thicker and less distinct (Figs. 2c and 2d).

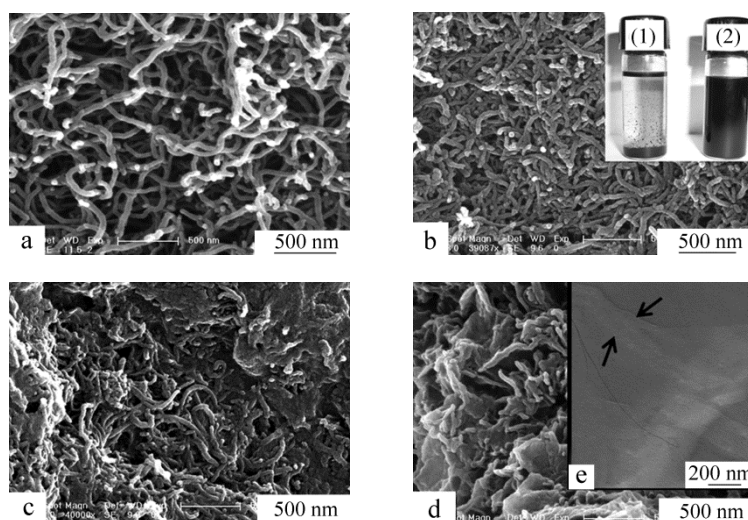


Fig. 2 FESEM images of (a) $\text{MWCNT}-\text{COOH}$, (b) $\text{MW}-\text{CH}=\text{CH}_2$, (c) MP-1, (d) MP-2 and (e) TEM image of core-shell structure for MP-2 (Insert: The stabilities of suspensions of (1) $\text{MW}-\text{COOH}$ and (2) $\text{MW}-\text{CH}=\text{CH}_2$ in toluene)

FTIR spectra of pristine MWCNTs, $\text{MW}-\text{COOH}$, $\text{MW}-\text{CH}=\text{CH}_2$, MWCNTs-PE nanocomposites and pristine PE are presented in Fig. 3. The peak around 1580 cm^{-1} in Fig. 3(a) corresponds to aromatic ring on MWCNTs^[8]. As compared with the FTIR spectra of MWCNTs (Fig. 3a) and $\text{MW}-\text{COOH}$ (Fig. 3b), the peaks appearing at around 1721 and 1180 cm^{-1} in Fig. 3(c) are from the stretching vibration of $\text{C}=\text{O}$ and $-\text{C}-\text{O}-\text{C}$ groups in carboxyl group ($-\text{COOCH}_2-$) of $\text{MW}-\text{CH}=\text{CH}_2$, respectively. The discernible peaks 1634 cm^{-1} results from the $\text{C}=\text{C}$ stretching vibrations of the appended terminal alkene groups. The vinyl $=\text{CH}_2$ bending vibration appears at 910 and 990 cm^{-1} , which further indicate the presence of the α -alkene groups on $\text{MW}-\text{CH}=\text{CH}_2$. Additionally, the peaks appear at 2920 and 2850 cm^{-1} , corresponding to stretching vibrations of $\text{C}-\text{C}$ and $\text{C}-\text{H}$ of the long chain ($-\text{CH}_2-$) served as linker between MWCNTs and the vinyl group, respectively.

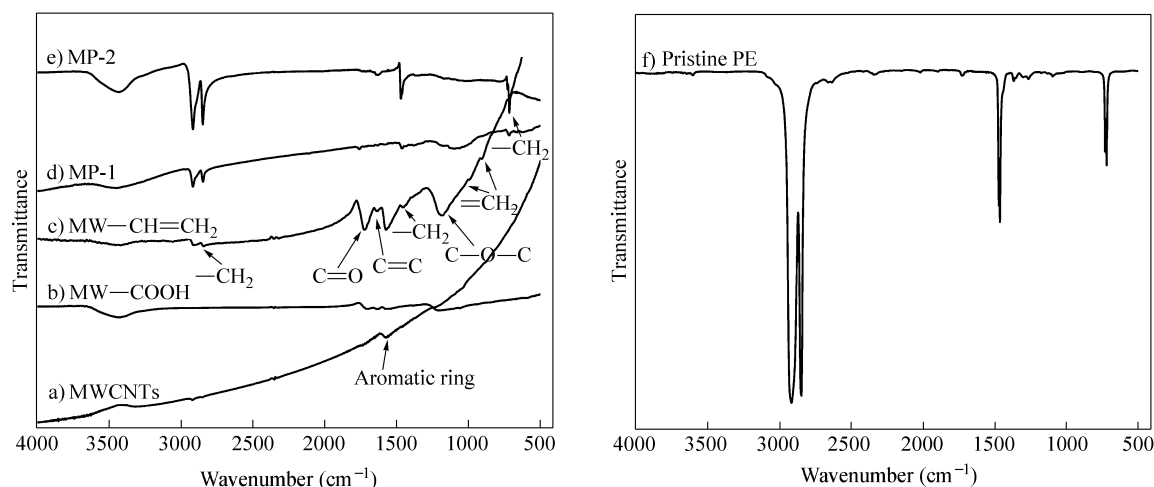


Fig. 3 FTIR results for (a) pristine MWCNTs, (b) MW-COOH, (c) MW-CH=CH₂, (d) MP-1, (e) MP-2 and (f) pristine PE

The absorptions around 720 cm⁻¹ are due to $-(CH_2)_n$ rock when $n \geq 4$. The new peaks in Fig. 3(c) definitely provide evidence for the presence of functional groups bonded to MWCNTs. The FTIR spectra of MWCNTs-PE nanocomposites (Figs. 3d and 3e) obtained from surface copolymerization show characteristic vibration peaks for PE (Fig. 3f). The characteristic bands of the vinyl group disappear. The absorption at 1468 cm⁻¹ is due to the deformation vibration of CH₂ and CH₃ groups. Moreover, with increasing PE quantity, the FTIR spectra of MWCNT-PE nanocomposites show a gradual increase of the transmissions associated with the PE moiety. Especially the absorption peaks at 2920 and 2850 cm⁻¹ due to the CH₂ framework vibration are significant. The FTIR results indicate that PE is successfully grafted from MWCNTs by surface copolymerization.

CONCLUSIONS

An *in situ* copolymerization method is successfully applied to functionalize the surface of MWCNT by grafting PE chains. Characterizations of the obtained core-shell MWCNTs-PE nanocomposites by ¹H-NMR, FESEM, TEM and FTIR revealed the covalent linkage between the PE and MWCNTs surface. The thickness of the PE layer increased with increasing the grafted PE layer quantity. Significantly, the uniform dispersion state of MWCNTs in PE matrix and the strong interaction between MWCNTs and PE open the way to a high number of opportunities, especially including the preparation of high performance polyolefin nanocomposites.

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