

This article was downloaded by:

On: 15 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Experimental Nanoscience

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t716100757>

Polymer grafted multiwalled carbon nanotubes via facile *in situ* solution radical polymerisation

Xueli Wu^a; Peng Liu^a

^a Institute of Polymer Science and Engineering, College of Chemistry and Chemical Engineering, Lanzhou University, Gansu 730000, People's Republic of China

Online publication date: 05 November 2010

To cite this Article Wu, Xueli and Liu, Peng(2010) 'Polymer grafted multiwalled carbon nanotubes via facile *in situ* solution radical polymerisation', Journal of Experimental Nanoscience, 5: 5, 383 – 389

To link to this Article: DOI: 10.1080/17458080903583956

URL: <http://dx.doi.org/10.1080/17458080903583956>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Polymer grafted multiwalled carbon nanotubes via facile *in situ* solution radical polymerisation

Xueli Wu and Peng Liu*

Institute of Polymer Science and Engineering, College of Chemistry and Chemical Engineering, Lanzhou University, Gansu 730000, People's Republic of China

(Received 8 September 2009; final version received 28 December 2009)

A facile strategy to graft polymers onto the surfaces of multiwalled carbon nanotubes (MWCNTs) was developed via the free radical addition process in the solution radical polymerisation of styrene in presence of the MWCNTs without any pretreatment so that the length of the original MWCNTs remained unchanged. The polystyrene grafted MWCNTs were characterised with Fourier transform infrared spectroscopy, Raman spectroscopy, thermogravimetric analysis (TGA) and transmission electron microscopy techniques. The effect of the amount of the initiator added and of the polymerising temperature on the percentage of grafting (PG%) and conversion of monomer (C%) were calculated from the TGA results. It was found that the maximum PG% of 15.6% was achieved with 0.5% initiator added and the higher polymerising temperature favoured the grafting polymerisation. The proposed method is expected to be extended to other vinyl monomers and offers another diverse way for the sidewall functionalisation of MWCNT.

Keywords: carbon nanotube; graft polymerisation; free radical addition; *in situ* polymerisation

1. Introduction

Carbon nanotubes (CNTs) have attracted more and more interest for wide applications because of their unique structure, mechanical and electrical properties [1]. But their poor solubility or dispersibility has imposed many barriers for their widespread use in many of these applications. Surface modification with polymers seems an efficient way to promote the solubility of CNTs in common solvents and organic polymeric matrices [2,3] and to improve the interfacial properties of the nanocomposites [4].

By far, there were many excellent works reported on the covalent surface functionalisation of MWCNTs with polymers with various strategies, such as ‘graft onto’ method [5–7], ‘graft from’ method, [8–12] ‘free radical addition’ method [13–19] and so on. Among the strategies for surface grafting polymers onto CNTs, the ‘free radical addition’ method is the simplest one because the MWCNTs must be functionalised with reactive or

*Corresponding author. Email: pliu@lzu.edu.cn

initiating groups before the polymerisation or reaction in the former two methods. As in the 'free radical addition' method, the MWCNTs could be used without any pretreatment.

In the 'free radical addition' method used, the polymer chain radicals which reacted with the C=C bonds of the MWCNTs were produced by the three main approaches: (i) the *in situ* radical polymerisation of the monomers in the presence of the MWCNTs by being initiated with initiator [9], ultrasonication assisted and microwave-induced [13], γ -ray irradiation [14] and thermo-initiation [15]; (ii) in the controlled/'living' radical polymerisation [16,17]; and (3) the polymer chain transfer reaction [18]. In most of the works reported, the MWCNTs were pretreated with acid.

In the present work, we reported the graft polymerisation of styrene (St) onto the pristine MWCNTs without any pretreatment via the free radical addition process in the solution free radical polymerisation. The effects of the initiator amount and the polymerising temperature on the percentage of grafting (PG%, mass ratio of the polymer grafted and MWCNTs) were also investigated.

2. Experimental details

2.1. Materials and reagents

MWCNTs with an average diameter of 20–40 nm and a purity of 95% were obtained from Shenzhen Nanotech Port Co., Ltd. (Shenzhen, P. R. China). The MWCNTs were used without any purification process. St was washed with dilute alkali solution, dried over barium oxide, and distilled twice under reduced pressure. 2,2'-Azobis(isobutyronitrile) (AIBN; Tianjin Chemicals Ltd Co. Tianjin, P. R. China) was re-crystallisation in ethanol. Toluene, ethanol and other solvents used were of analytical grade.

2.2. Solution polymerisation

MWCNTs (0.1 g), 10.0 ml St, 10.0 ml toluene and certain amounts of azobisisobutyronitrile (AIBN) (Table 1) were combined into a 100 ml round bottom flask. The mixture was heated at 90°C for 11 h. The product was precipitated in ethanol and dried at vacuum.

Table 1. Effect of the polymerising conditions on the C% and PG%.

MWCNTs-PS	Polymerising temperature (°C)	AIBN added (g)	C% of St	PG%
1	90	0.01	9.9	2.9
2	90	0.02	30.5	4.9
3	90	0.05	39.0	15.6
4	90	0.10	55.2	4.2
5	90	0.15	58.3	0.8
6	90	0.20	59.7	0.8
7	80	0.05	34.1	2.2
8	70	0.05	19.0	1.5
9	60	0.05	13.1	0.9
10	50	0.05	9.0	0.6

The polystyrene grafted MWCNTs (MWCNTs-PS) were separated from the free polystyrene via Soxhlet's extraction with toluene for 24 h [19].

2.3. Analysis and characterisation

A Bruker IFS 66 v/s infrared spectrometer was used for the Fourier transform infrared (FTIR) spectroscopy analysis. Raman measurements were carried out on the powder samples using a FT-Raman spectrometer (BRUKER RFS 100/S) with the excitation laser of Nd:YAG (wavelength: 1064 nm). Thermogravimetric analysis (TGA) was performed with a Perkin-Elmer TGA-7 system at a scan rate of $10^{\circ}\text{C min}^{-1}$ to 700°C in N_2 . The morphologies of the MWCNTs and MWCNTs-PS were characterised with a JEM-1200 EX/S transmission electron microscope (TEM). The powders were dispersed in toluene in an ultrasonic bath for 5 min, and then deposited on a copper grid covered with a perforated carbon film.

The conversion of monomer (C%) and the PG% were calculated according to the following relationships from the results of TGA analyses:

$$\text{C}\% = \frac{\text{Total PS (g)}}{\text{Monomer charged (g)}} \times 100\%$$

$$\text{PG}\% = \frac{\text{Grafted PS (g)}}{\text{MWCNTs charged (g)}} \times 100\%.$$

3. Results and discussion

In the present work, MWCNTs were used without any pretreatment including the purification process because that the MWCNTs might be cut into pieces in the acid-treatment process. Thus, the length of the MWCNTs remained unchanged.

After the *in situ* solution free radical polymerisation of St initiated with AIBN, the products precipitated in ethanol were extracted thoroughly with toluene. The asymmetrical and symmetrical stretching vibrations of $-\text{CH}_2$ at 2924 and 2854 cm^{-1} , the flexural vibrations of $-\text{CH}_2$ at 1440 cm^{-1} and the characteristic of C–C ring stretching vibration at 1630 cm^{-1} appeared in the FTIR spectrum (Figure 1) of the MWCNTs. It indicated that the polystyrene had been successfully grafted onto the surfaces of the MWCNTs by the proposed method.

Raman spectroscopy is useful to detect the extent of disorder in the functionalised MWCNTs [20]. As shown in Figure 2, the Raman spectrum of the pristine MWCNTs shows a characteristic D band at 1288 cm^{-1} (defects/disorder-induced modes) and a G band at 1601 cm^{-1} (in-plane stretching tangential modes) with an intensity ratio ($I_{\text{D}}/I_{\text{G}}$) of 0.74. As for the MWCNTs-PS, the $I_{\text{D}}/I_{\text{G}}$ intensity ratio increased to 1.97. The change in $I_{\text{D}}/I_{\text{G}}$ intensity can also be observed by the change of the peak height. For the pristine MWCNTs, the D band is slightly lower than the G band. However, for the MWCNTs-PS, the D bands are higher than the G bands. The results show that the *in situ* solution free radical polymerisation has led to an increase in the number of defects in the nanotubes.

The grafting of polystyrene onto MWCNTs enables the nanotubes to be dispersible in toluene. The pristine MWCNTs started to settle down soon after the sonication was

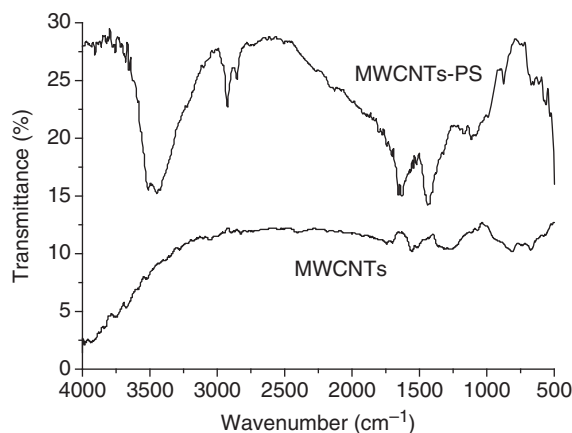


Figure 1. FTIR spectra of the pristine MWCNTs and MWCNTs-PS.

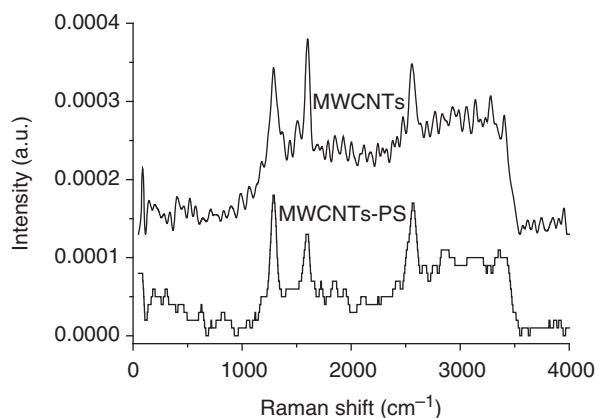


Figure 2. FT-Raman spectra of the pristine MWCNTs and MWCNTs-PS.

stopped and settled down completely within 1 h. However, the black solution of the MWCNTs-PS remained homogeneous upon standing, with no sedimentation observed after 3 days. The TEM images (Figure 3) also intuitively proved the graft polymerisation of St on the surfaces of MWCNTs. The MWCNTs were exfoliated into single nanotubes and dispersed perfectly in toluene. Furthermore, the diameters of the MWCNTs seemed to increase after the *in situ* radical graft polymerisation.

To determine the PG% and C%, TGA measurements were performed on the MWCNTs-PS samples prepared with different AIBN added as initiator and with the different polymerising temperature, as summarised in Table 1 (Figure 4). Slight weight losses were found at the temperature at 100°C, which is attributed to the release of the moisture and solvent adsorbed. Because the MWCNT participated in the polymerisation reaction and consumed AIBN [8], the effect of the initiator added on the PG% and C% were calculated from the weight loss at about 350–420°C of the TGA analysis, attributed

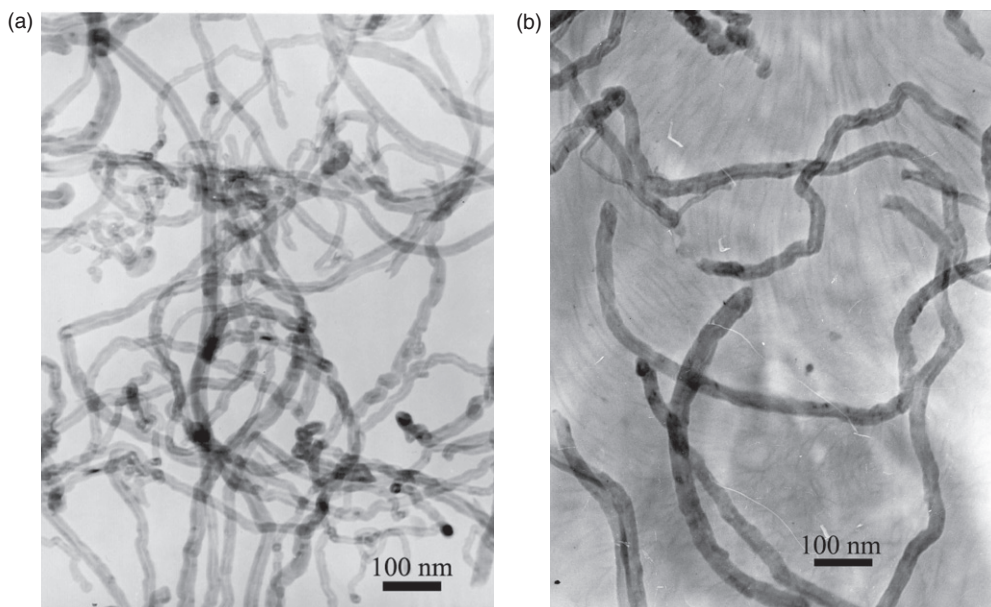


Figure 3. TEM images.

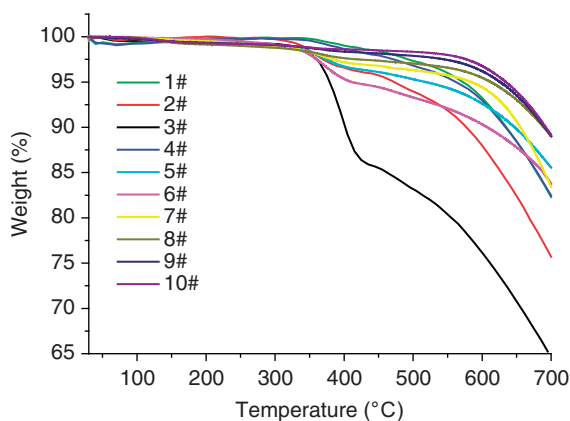


Figure 4. TGA curves of the MWCNTs-PS.

to the decomposition of the polymer grafted [21]. It was found that the C% of St increased with the increase in the amount of the initiator added. However, the highest PG% was achieved with 0.05 g AIBN. It was also found that the higher polymerising temperature was in favour of both the PG% and C%.

In the *in situ* grafting polymerisation, the coupling termination of the free radicals with each other and the addition of the free radicals onto the MWCNTs are rivalship. The more initiator added or at the higher polymerising temperature, the radicals were

formed faster, so the probability of the addition reaction of the free radicals onto the MWCNT increased. Therefore, the PG% achieved the highest value with more initiator (0.5%) added and at the higher polymerising temperature. However, with much more initiator (>0.5%) added, the coupling termination of the free radicals with each other might be the dominant reaction. So the PG% decreased. The PG% in the optimised polymerisation conditions in the present method was similar to those in the range of 12–16% reported. However, the present method was simple, convenient, and inexpensive.

4. Conclusions

In summary, a facile and effective method was developed for the grafting polymers onto the pristine MWCNTs via the *in situ* solution free radical polymerisation. The PG% and the C% were affected with the amount of the initiator added and the polymerising temperature. The proposed method was found to be simple, convenient and inexpensive and expected to be extended to other vinyl monomers.

References

- [1] D. Tasis, N. Tagmatarchis, A. Bianco, and M. Prato, *Chemistry of carbon nanotubes*, Chem. Rev. 106 (2006), pp. 1105–1136.
- [2] Y.P. Sun, K. Fu, Y. Lin, and W. Huang, *Functionalized carbon nanotubes: Properties and applications*, Acc. Chem. Res. 35 (2002), pp. 1096–1104.
- [3] P. Liu, *Modifications of carbon nanotubes with polymers*, Eur. Polym. J. 41 (2005), pp. 2693–2703.
- [4] M. Raja, A.M. Shanmugaraj, and S.H. Ryu, *Influence of surface functionalized carbon nanotube on the properties of polyurethane nanocomposites*, Soft Mater. 6 (2008), pp. 65–74.
- [5] D. Baskaran, J.R. Dunlap, J.W. Mays, and M.S. Bratcher, *Grafting efficiency of hydroxy-terminated poly(methyl methacrylate) with multiwalled carbon nanotubes*, Macromol. Rapid Commun. 26 (2005), pp. 481–486.
- [6] G. Mountrichas, S. Pispas, and N. Tagmatarchis, *Grafting-to approach for the functionalization of carbon nanotubes with polystyrene*, Mater. Sci. Eng. B 152 (2005), pp. 40–43.
- [7] H.M. Li, F.O. Cheng, A.M. Duft, and A. Adronov, *Functionalization of single-walled carbon nanotubes with well-defined polystyrene by “Click” Coupling*, J. Am. Chem. Soc. 127 (2005), pp. 14518–14524.
- [8] D. Baskaran, J.W. Mays, and M.S. Bratcher, *Polymer-grafted multiwalled carbon nanotubes through surface-initiated polymerization*, Angew. Chem. Int. Ed. 43 (2004), pp. 2138–2142.
- [9] X. Luo, C. Detrembleur, C. Pagnouille, R. Jerome, V. Bocharova, A. Kiriy, and M. Stamm, *Surface modification of multi-walled carbon nanotubes by poly(2-vinylpyridine): Dispersion, selective deposition and decoration of the nanotubes*, Adv. Mater. 16 (2004), pp. 2123–2127.
- [10] M. Dehonor, K. Masenelli-Varlot, A. Gonzalez-Montiel, C. Gauthier, J.Y. Cavaille, and M. Terrones, *Grafting of polystyrene on nitrogen-doped multi-walled carbon nanotubes*, J. Nanosci. Nanotechnol. 7 (2007), pp. 3450–3457.
- [11] H. Kong, C. Gao, and D.Y. Yan, *Controlled functionalization of multiwalled carbon nanotubes by in situ atom transfer radical polymerization*, J. Am. Chem. Soc. 126 (2004), pp. 412–413.
- [12] X.D. Zhao, X.H. Fan, X.F. Chen, C.P. Chai, and Q.F. Zhou, *Surface modification of multiwalled carbon nanotubes via nitroxide-mediated radical polymerization*, J. Polym. Sci.: Polym. Chem. 44 (2006), pp. 4656–4667.

- [13] S.J. Park, M.S. Cho, S.T. Lim, H.J. Choi, and M.S. Jhon, *Synthesis and dispersion characteristics of multi-walled carbon nanotube composites with poly(methyl methacrylate) prepared by in-situ bulk polymerization*, *Macromol. Rapid Commun.* 24 (2003), pp. 1070–1073.
- [14] H.X. Xu, X.B. Wang, Y.F. Zhang, and S.Y. Liu, *Single-step in situ preparation of polymer-grafted multi-walled carbon nanotube composites under γ -ray irradiation*, *Chem. Mater.* 18 (2006), pp. 2929–2734.
- [15] P. Liu, *Facile graft polystyrene onto multi-walled carbon nanotubes via in situ thermo-induced radical polymerization*, *J. Nanopart. Res.* 11 (2009), pp. 1011–1016.
- [16] Y.L. Hsin, J.Y. Lai, K.C. Hwang, S.C. Lo, F.R. Chen, and J.J. Kai, *Rapid surface functionalization of iron-filled multi-walled carbon nanotubes*, *Carbon* 44 (2006), pp. 3328–3335.
- [17] H.X. Wu, R. Tong, X.Q. Qiu, H.F. Yang, Y.H. Lin, R.F. Cai, and S.X. Qian, *Functionalization of multiwalled carbon nanotubes with polystyrene under atom transfer radical polymerization conditions*, *Carbon* 45 (2007), pp. 152–159.
- [18] D. McIntosh, V.N. Khabashesku, and E.V. Barrera, *Processing and mechanical properties of single-walled carbon nanotube-polypropylene composite fibers*, *J. Phys. Chem. C* 111 (2007), pp. 1592–1600.
- [19] P. Liu, J. Tian, W.M. Liu, and Q.J. Xue, *Surface graft polymerization of styrene onto nano-sized silica with a one-pot method*, *Polym. J.* 35 (2003), pp. 379–383.
- [20] M. Zhang, M. Yudasaka, A. Koshio, and S. Iijima, *Thermogravimetric analysis of single-wall carbon nanotubes ultrasonicated in monochlorobenzene*, *Chem. Phys. Lett.* 364 (2002), pp. 420–426.
- [21] Z.J. Jia, Z.Y. Wang, C.L. Xu, J. Liang, B.Q. Wei, D.H. Wu, and S.W. Zhu, *Study on poly(methyl methacrylate)/carbon nanotube composites*, *Mater. Sci. Eng. A* 271 (1999), pp. 395–400.