Polymer 50 (2009) 5901–5908

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Effect of radical grafting of tetramethylpentadecane and polypropylene on carbon nanotubes' dispersibility in various solvents and polypropylene matrix

Gholamali Farzi [a,b,c], Sohaib Akbar [a,b,c], Emmanuel Beyou [a,b,c,*], Philippe Cassagnau [a,b,c], Flavien Melis [a,b,c]

[a] Université de Lyon, Lyon, F-69003, France
[b] Université Lyon 1, Lyon, F-69003, France
[c] CNRS UMR5223, Ingénierie des Matériaux Polymères, Laboratoire des Matériaux Polymères et Biomatériaux, F-69622 Villeurbanne, France

ARTICLE INFO

Article history:
Received 24 July 2009
Received in revised form
23 September 2009
Accepted 8 October 2009
Available online 14 October 2009

Keywords:
MWCNTs
Polypropylene
Peroxide initiated radical grafting

ABSTRACT

Multiwalled carbon nanotubes (MWCNTs) have been functionalized by tetramethylpentadecane (TMP), 1-dodecanethiol (DT) and polypropylene (PP) through radical addition onto MWCNTs' surface using dicumyl peroxide as hydrogen abstractor. Surface functionalized MWCNTs were characterized by Raman, IR spectroscopy, elementary analysis (EA) and thermogravimetric analysis (TGA). We studied the effect of temperature, peroxide concentration and solvent on TMP grafting densities and it was found that this surface treatment lead to a fair solubility in various solvents. TMP-functionalized MWCNTs were also imaged by transmission electronic microscopy showing single long functionalized MWCNTs distinct from the starting pristine bundles. For the first time, PP was then grafted onto MWCNTs through a radical grafting reaction. However, scanning electronic microscopy images of PP-functionalized MWCNTs/PP composites did not show a significant improvement in MWCNTs dispersion within the PP matrix.

1. Introduction

Polymer nanocomposites containing carbon nanotubes (CNTs) have attracted much attention due to the excellent mechanical, electrical and thermal properties of CNTs [1–3]. Simple melt compounding is often difficult to achieve because CNTs tend to form agglomerates during processing of composites. Indeed, carbon nanotubes form clusters as very long bundles due to the high surface energy and the stabilization by numerous of π–π electron interactions among the tubes. Chemical modification of the CNTs' surface [4–6] and in situ polymerisation [7,8] have been used to achieve optimal enhancement in the properties of CNT/polymer composites. The use of "grafting to" [9–12] and "grafting from" [9,13–16] approaches, leading to chemical linkage between polymer and the surface of CNTs, have been also explored to improve the interfacial interaction between CNTs and polymer matrix. Polypropylene (PP) is one of the most widely used commercial polymer due to the excellent combination of mechanical resistance, chemical stability and excellent moisture barrier properties [17]. Although physical blending with CNTs is an economic way to modify polypropylene performance, compatibilizing agents are necessary for creating strong interface between filler particles and the polymer phase. Maleic anhydride grafted polypropylene (MA-g-PP) is often used as a compatibilizer which can improve the PP/CNTs composite properties by strong hydrogen bonding between hydroxyl groups located on the acidic-treated CNTs surface and anhydride groups of MA-g-PP [18,19]. A more promising way to disperse CNTs in polyolefins is the in situ polymerisation approach because homogenous metallocene catalysts are soluble in hydrocarbons. First, the co-catalyst methylaluminoxane (MAO) is anchored on the CNT surface through covalent bonding to –COOH or –OH groups which are inherent to partially oxidized CNTs. Then, the metallocene catalyst and the monomer are added yielding polyolefin chains attached directly to CNTs [17,20–22]. Another strategy for enhancing compatibility between nanotubes and polyolefins consists in the sidewall CNT functionalization with short alkyl chains [23,24]. This method involves thermal decomposition of an alkyl peroxide (radical initiator) at 100 °C in Toluene providing alkyl radicals which can react with unsaturated bonds located on the CNT surface. Peroxides are also used as hydrogen abstractors to chemically modify polyolefins in the molten state [25,26]. In this latter case, the radicals formed in the decomposition process must be able to abstract hydrogen atoms from polyolefin and to form radical centres that can react with unsaturated systems. This grafting reaction has been previously described [27–29] with a model compound approach involving a radical grafting reaction between peroxide-derived alkoxyl radicals, a set of low molecular weight alkanes and

---

[*] Corresponding author. CNRS UMR5223, Ingénierie des Matériaux Polymères, Laboratoire des Matériaux Polymères et Biomatériaux, F-69622 Villeurbanne, France.
E-mail address: beyou@univ-lyon1.fr (E. Beyou).

0032-3861/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2009.10.020

a monomer [27,28] or multiwall carbon nanotubes (MWCNTs) [29]. Herein, we use the radical mechanism for attaching tetramethylpentadecane (TMP) as model for PP, dodecanethiol (DT) and PP to multiwall carbon nanotubes (MWCNTs). Experiments reported here involve thermal decomposition of dicumyl peroxide (DCP), used as hydrogen abstractor, at temperatures above 130 °C.

The extent of grafting has been evaluated by thermogravimetric analysis, elemental analysis and scanning electronic microscopy (SEM) observations. We studied solubility behaviour of the formed TMP- and DT-grafted-MWCNTs in various solvents according to their grafting densities. In addition, PP coated MWCNTs were dispersed in a molten PP matrix before imaging by SEM.

2. Experimental

2.1. Materials

MWCNTs (Graphistrength™ C100, manufacturing: catalytic chemical vapour deposition (CCVD), average outer diameter: 10–15 nm, length: 0.1–10 μm, average number of walls: 5–15, C contents: 91%.) were kindly supplied by ARKEMA.

The low molecular weight hydrocarbon substrate, used as model for polypropylene, was 2,6,10,14-tetramethylpentadecane (TMP, 99%, Sigma–Aldrich-France). Dodecanethiol (DT, 99%, Acros) was used as received. A commercial grade of polypropylene (PPH7060) supplied by Atofina was used as the polymer matrix. Dicumyl peroxide (99%, Sigma–Aldrich-France) and all other solvents (dimethylformamide (DMF), dichlorobenzene (DCB)) were used without any further purification so as to fit the industrial conditions required in the melt processing.

2.2. Surface activation of MWCNTs

In this study, MWCNTs were oxidized in air at 450 °C for one hour. Air oxidized MWCNTs are used throughout this study and referred as pristine (p-MWCNTs).

2.3. Decomposition of DCP in presence of p-MWCNTs and hydrocarbon substrates

The thermolysis of dicumyl peroxide (DCP) in hydrocarbon substrates was performed in a glass reactor. For experiments conducted in solution, DCP (0.12 g/0.44 mmol) was first mixed in a mixture of p-MWCNTs (50 mg), TMP (1 g/3.73 mmol) and DMF (or DCB; 10 mL) and then sonicated for 15 min. Afterwards, the suspension was degassed by 3 freeze–pump–thaws, and then it was heated up to 160 °C for 6 h under stirring. The grafted MWCNTs were collected by centrifugation (11 K rpm, 20 min) and subsequent filtration. A similar procedure was employed to graft dodecanethiol and PP while maintaining the same molar ratio and using DCB as solvent for PP grafting reaction.

2.4. Recovery of free and tethered molecules/PP chains

The free molecules (TMP and DT) and PP chains were isolated from the grafted ones by exhaustive cleaning of the suspension by dialysis and Soxhlet extraction, respectively. In a typical process for the extraction of TMP (or DT), 30 mL of the MWCNTs' suspension was introduced into a cellulose membrane (Spectra/Por, MW cut-off, 1000 by Spectrum Medical Industries, Inc.) and repeatedly dialyzed against DCB (or DMF for DT) until no residual TMP (or DT) could be detected in the recovered solution (determined gravimetrically). Then, the alkane-grafted MWCNTs suspension was dried at 80 °C to evaporate the solvent prior to characterization.

PP is not soluble in any solvent at ambient temperature so it was necessary to use soxhlet extractor to recover free PP and tethered PP in DCB at elevated temperatures. In a typical procedure, 1 g of the solid fraction filtered from MWCNTs' suspension in DCB (after reaction) was put in a cellulose thimble (Macherey–Nagel GMBH & Co) and placed into the Soxhlet extractor refluxed with DCB at 140 °C for 4 days. The non-soluble PP-*g*-MWCNTs were collected from thimble and dried at 90 °C under vacuum.

2.5. PP/PP-g-MWCNTs nanocomposites processing

For processing, Haake Polylab Rheomixer fitted with "Rheomix 600" internal mixer with two rotors running in a contra-rotating way was used. Each batch was of ∼50 cm^3 (44 ± 1 g) to fill the

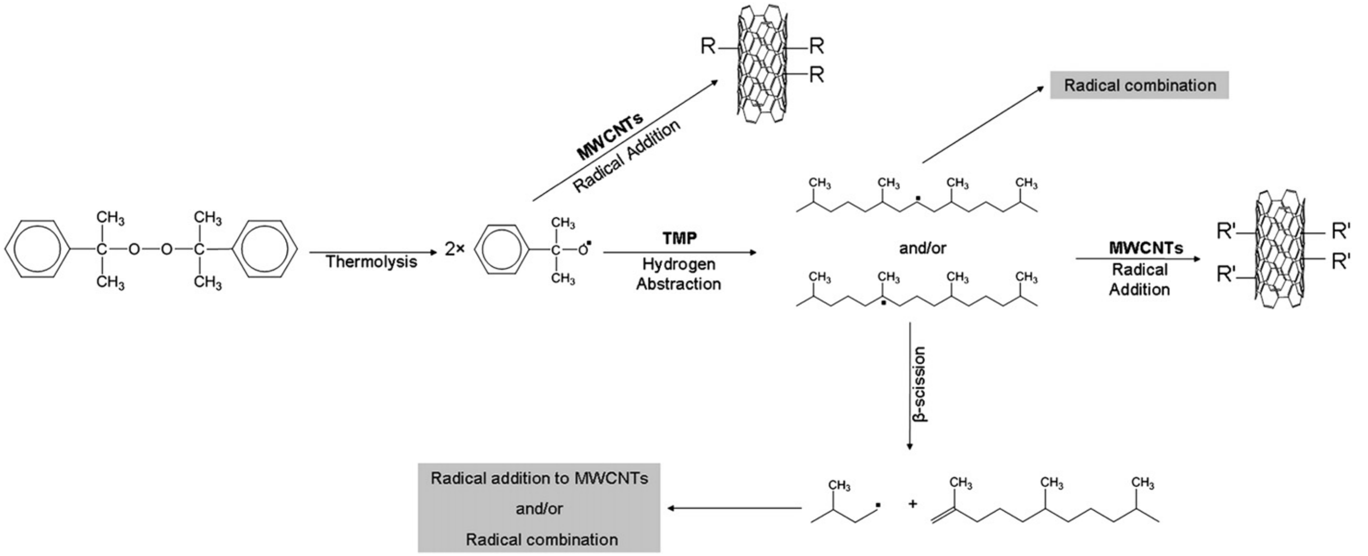

Fig. 1. Reaction scheme for the addition of TMP onto CNT in the presence of DCP.

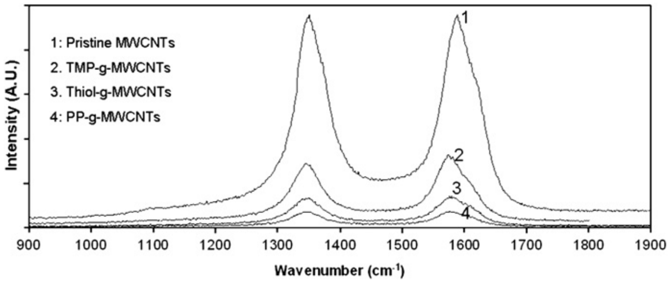

Fig. 2. Raman spectra of pristine and TMP-, DT- and PP-*g*-MWCNTs.

mixing chamber so as to receive the excellent shearing action to ensure the proven finest mixing. The amount of nanofiller in the final composites has been fixed to 3 wt%. Processing temperature was 200 °C and rotors rpm were 50.

2.6. Characterization

Gas chromatography–mass spectrometry (GC–MS) was performed with an Agilent 6890 series GC system equipped with a HP-5 ms (5%-phenyl)-methylpolysiloxane, ref. 19091S-433. The injector was at 250 °C and the temperature programme followed was: 50–310 °C at 20 °C/min. Injection and detection by MS was carried out at 280 °C.

Raman spectra were obtained by using a Raman spectrometer (RM1000, Renishaw, Wotton under Edge, U.K.). The sample was excited with Argon Laser at 514.5 nm.

FTIR spectra were recorded on a Perkin–Elmer spectrometer 2000 using powder-pressed KBr pellets. Specimens for the measurements were prepared by mixing 2 mg of the sample powder with 100 mg of KBr and pressing the mixture into pellets. FTIR spectra were obtained at a resolution of 2.0 cm^{-1} at room temperature in the range of 4000 to 400 cm^{-1} wavenumber and averaged over 16 scans.

Thermogravimetric analysis (TGA) were performed with a DuPont Instruments TGA 2950 thermobalance, controlled by a TC10A microprocessor. Samples were heated at 20 °C/min under a nitrogen flow (100 mL/min).

Elemental analysis (EA) was carried out (Analyzer: LECO SC144, Service central d'analyse du CNRS, Vernaison, France) to determine carbon and hydrogen contents. Transmission electron microscopy (TEM) was carried out with a Philips CM-120 microscope (Philips Consumer Electronics BV, Eindhoven, The Netherlands) operated at 80 keV. Scanning electron microscopy (SEM) was performed with a Hitachi S800 microscope operated at 15 KV.

Solubility was determined gravimetrically. In a typical experiment, saturated solutions of alkane-*g*-MWCNTs were prepared by sonication in vials. Sonication was done using S 40 H Elmasonic by Elma (Singem, Germany) for 30 min. Water bath temperature therein raised maximum to 35 °C. Vials were kept free standing over one month at room temperature and then the upper half aliquot part was carefully taken out with a syringe and heated to remove solvent under vacuum. All the weighting was carried out using an analytical balance with a sensitivity of 0.1 mg.

Table 1
Band Intensity ratios (I_D/I_G) of different samples in Raman spectra.

Sample	I_D/I_G
Pristine MWCNTs	0.99
TMP-g-MWCNTs	0.93
DT-g-MWCNTs	0.95
PP-g-MWCNTs	0.86

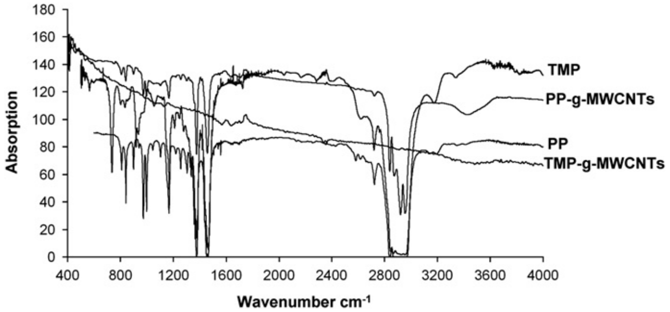

Fig. 3. FTIR spectra of TMP- and PP-*g*-MWCNTs, along with pure TMP and PP spectra for reference.

3. Results and discussion

3.1. Free radical grafting of TMP, DT and PP onto MWCNTs

We resorted to 2,6,10,14-tetramethylpentadecane (TMP, $C_{19}H_{40}$) as model for polypropylene. Indeed, high boiling points of long chain alkanes permit study under high temperature conditions, typically over 150 °C. It also gives clues about low viscosity at 150 °C; on top of that the formed products in the grafting experiment can hence be analysed more easily than in the polymer melt. Thermolysis of dicumyl peroxide initiator performed in TMP and in presence of MWCNTs is depicted in Fig. 1. Experiments as reported here involved decomposition of dicumyl peroxide (DCP) whose thermal decomposition is carried out in a range of temperatures close to the ones expected during reactive extrusion of polypropylene typically few minutes at 150–200 °C. As shown in Fig. 1, the formed peroxide radicals have a high tendency to react readily with unsaturated systems and are also prone to hydrogen abstraction from hydrocarbon substrates [30]. In this latter case, it is expected that the active species generated onto the hydrocarbon backbone react with unsaturated bonds located on the MWCNTs surface. The main drawback of free radical grafting is low selectivity of radical centres, especially at high temperature (150–200 °C for the extrusion of PP) causing side reactions such as chain scission for PP derivatives (Fig. 1) [30,31]. However, this method is a simple way to directly incorporate organic moieties onto the CNTs' surface leading to TMP and PP grafted MWCNTs. Dodecanethiol has been also grafted onto CNTs using the same procedure. The thiol family of compounds is widely used for controlling molar mass in free radical polymerizations via a chain transfer process. The chain transfer process displays two contiguous steps: transfer of the thiyl hydrogen to the growing polymer chain followed by re-initiation, whereby a thiyl radical adds to a monomeric double bond. In the presence of MWCNTs, thiyl radicals are expected to react by radical addition onto sp^2 carbon of the MWCNTs. First, according to our previous results [29] based on a study of the radical grafting of polyethylene derivatives onto MWCNTs, we investigated MWCNTs'

Table 2
Effect of temperature on grafting density for the preparation of TMP-*g*-MWCNTs (DCP conc.:1 wt%; DMF as solvent).

Experiment	Temperature (°C)	TGA (wt loss %)	Grafting density[a] (mg m^{-2})
1	130	3.2	0.15
2	140	3.0	0.14
3	150	7.8	0.38
4	160	8.9	0.43
5	170	6.3	0.30
6	180	5.5	0.26

[a] Based on calculations assuming a specific surface area of 225 $m^2 g^{-1}$ for MWCNTs.

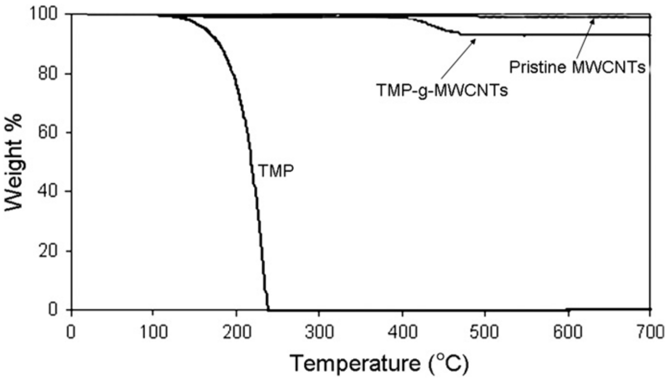

Fig. 4. TGA data (under N_2) for TMP-*g*-MWCNTs (experiment 3, Table 2) and the corresponding references of p-MWCNTs and pure TMP.

sidewall functionalization by TMP, DT and PP in the presence of 1 wt% DCP at 160 °C. DMF and DCB were used as solvents. For PP-based experiments, only DCB was used, as suitable hot solvent for PP. It is noteworthy that the unreacted molecules/polymer chains are removed from the grafted ones by dialysis/soxhlet extraction as mentioned in the experimental part. The efficient MWCNTs' sidewall functionalization by TMP, DT and PP has been confirmed with the aid of Raman and FTIR vibrational spectra. Raman spectra of p-MWCNTs and alkane-based derivatives-*g*-MWCNTs (Fig. 2) show two strong bands around 1340 cm^{-1} (D band) and 1590 cm^{-1} (G band). D-band is attributed to disorder or sp^3-hydridized carbons in the hexagonal framework of the nanotubes walls (typical sign for defective graphitic structures) and G-band is a characteristic feature of the graphitic layers and corresponds to the tangential vibration of the carbon atoms [29,32,33]. The ratio in intensities between the D band and G band is a good indicator of the changes in chemistry of CNTs. We can observe a relatively low intensity of the D band relative to G band ($I_D/I_G < 1$) for all the alkane-based derivatives-*g*-MWCNT samples (Fig. 2, Table 1) in comparison with that of p-MWCNT (i.e. $I_D/I_G \approx 1$, Fig. 2, Table 1) whatever are the grafting experimental conditions. This behaviour could be interpreted as an indication of the increase in the number of sp^3 hybridized carbon atoms after polymer functionalization.

TMP-*g*-MWCNTs and PP-*g*-MWCNTs were additionally analysed by FTIR spectroscopy (Fig. 3). The emergence of nearly identical series of vibrational bands for both grafted and non-grafted species suggest the successful grafting of TMP and PP onto MWCNTs. Then, we found it interesting to see whether the temperature, the peroxide concentration and the solvent could modify the TMP grafting density and the solubility of the resulting products.

3.2. *Effect of temperature, DCP concentration and solvent on TMP grafting density*

In order to increase the understanding of the cumyloxyl radicals behaviour, experiments from 1 to 6 (Table 2) correspond to the ones performed with TMP and 1 wt% DCP relative to TMP in DMF as solvent at temperatures varying from 130 °C to 180 °C. The TGA traces for both the starting pure TMP and the TMP-grafted nanotubes are shown in Fig. 4. Pure TMP sample completely decomposes in the temperature range between 180 and 250 °C. For TMP-grafted nanotubes, one decomposition event is clearly visible at ca. 450 °C attributed to the loss of TMP (Fig. 4). In Fig. 4, we estimate the weight of grafted TMP to be around 8%. The TMP weight loss increases from 3.2% to 8.9% by increasing the reaction temperature from 130 °C to 160 °C (experiments 1–6, Table 2). The corresponding grafting densities can be calculated using the theoretical specific surface area (SSA) of MWCNTs defined as the following equation [34]:

$$\mathrm{SSA}\left(\mathrm{m}^2\cdot\mathrm{g}^{-1}\right) = \frac{1315 * d_\mathrm{e}}{n d_\mathrm{e} - 0.68\left[\sum_{i=1}^{n-1} i\right]}$$

where d_e is the external diameter in nm and n is the number of shells.

For our Graphistrength™ C100 MWCNTs, we obtain an average SSA of 225 $m^2\,g^{-1}$.

The calculated grafting densities are varying from 0.15 mg m^{-2} to 0.43 mg m^{-2} (Table 2). The grafting density decreases from 0.43 mg m^{-2} to 0.26 mg m^{-2} for reaction temperatures above 160 °C (i.e. 170 °C and 180 °C, Table 2), suggesting that shorter half time life of DCP initiator favours competitive reactions which might lead to combination reactions.

Peroxide concentration is also a key parameter in a radical grafting reaction so experiments with various DCP content (1 wt%–18 wt%, Table 3) were conducted at 160 °C (optimal temperature for TMP grafting density). Experiments from 1 to 9 (Table 3) show that the TMP weight loss determined by TGA slightly increases from 8% to 15% by increasing initiator concentration from 1 wt% to 12 wt%. Comparable weight losses have been recently reported by Koval'chuck [23] for undecanyl-*g*-MWCNTs but the current functionalization is feasible for a wider compound range. The corresponding grafting densities increase from 0.39 mg m^{-2} to 0.78 mg m^{-2} respectively (Table 3). Elemental analysis (EA) is also an indicator of degree of grafting and a good agreement between grafting densities calculated from EA and TGA analysis was obtained (e.g. 0.72 mg m^{-2} and 0.78 mg m^{-2} respectively, experiment 7, Table 3). For peroxide concentration higher than 12 wt%, the grafting density decreases from 0.78 mg m^{-2} to 0.55 mg m^{-2}

Table 3
Effect of DCP concentration on grafting density for the preparation of TMP-*g*-MWCNTs (160 °C, with DMF as solvent).

Experiment	DCP (wt% of TMP)	EA (H content, %)	EA (C content, %)	Percent grafting (TGA weight loss)	Grafting density[a] ($mg\,m^{-2}$)	
					EA	TGA
1	1	–	–	8	–	0.39
2	1.5	3.25	88.75	8.9	0.52	0.43
3	3	3.55	88.44	12	0.62	0.61
4	4.5	3.71	88.3	13	0.67	0.66
5	6	3.75	88.26	13	0.69	0.66
6	9	3.78	88.21	13.5	0.70	0.69
7	12	3.84	88.16	15	0.72	0.78
8	15	3.79	88.20	13	0.70	0.66
9	18	3.31	88.70	11	0.54	0.55

EA of pristine MWCNTs shows: carbon ~90%, hydrogen ~1.4%.
[a] Based on calculations assuming a specific surface area of 225 $m^2\,g^{-1}$ for MWCNTs.

Table 4
Influence of solvent on TMP grafting density onto MWCNTs (DCP conc.:1.5 wt%).

Solvent	EA (H content, %)	TGA (wt loss %)	Grafting density ($mg\ m^{-2}$)	
			EA	TGA
DMF	3.25	8.9	0.52	0.43
DCB	3.81	14.4	0.71	0.75
TMP ("bulk" = "Master-batch")	4.15	17.2	0.83	0.92

upon increasing DCP concentration up to 18 wt% (Table 3). It suggests that the presence of higher concentration of radicals changes the reaction kinetics, possibly leading to combination reactions (Fig. 1). We can also speculate on the various radicals that can add to MWCNTs. However, according to the literature [19,35], the efficiency of addition of carbon radicals to MWCNTs is expected to be greater than that of oxygen radicals.

The optimal DCP concentration for the TMP radical grafting reaction is 12 wt% at 160 °C. However, the following experiments involve a usual low concentration of DCP (1.5 wt%) in order to prevent PP from degradation [36,37].

In order to check the influence of solvent onto TMP grafting density, experiments were therefore conducted at 160 °C with 1.5 wt% DCP in two kinds of solvents: DMF and DCB, which is a good solvent for PP at high temperatures. The initial visual aspect of the MWCNTs dispersions in DMF and in DCB is somewhat different. The dispersion of MWCNTs is totally unstable in DMF due to poor hydrogen bonding ability whereas MWCNTs take some time before settling down in DCB solution showing an affinity (though very low) with this solvent. After the radical grafting reaction in these solvent, it is observed that DCB ensures better TMP grafting density than DMF ($0.75\ mg\ m^{-2}$ and $0.43\ mg\ m^{-2}$ from TGA respectively, Table 4) which may be attributed to the better miscibility of TMP with DCB. Using TMP as solvent, the grafting density increases to $0.92\ mg\ m^{-2}$ suggesting a poorer TMP-based radical attack onto the sp^2 carbon of the MWCNTs in dilute media.

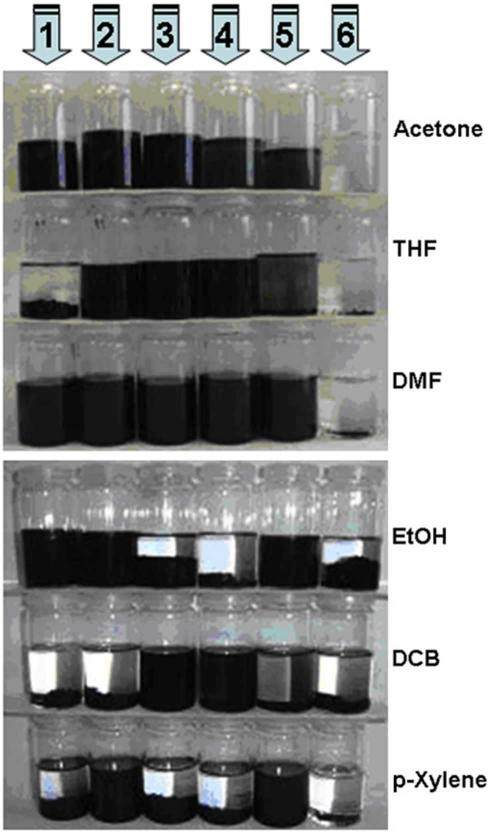

Fig. 5. Solubility behaviour of (1) DT-g-MWCNTs, (2) DCP-g-MWCNTs, (3) TMP-g-MWCNTs ($0.92\ mg\ m^{-2}$), (4) TMP-g-MWCNTs ($0.75\ mg\ m^{-2}$), (5) TMP-g-MWCNTs ($0.43\ mg\ m^{-2}$), (6) MWCNTs in various solvents.

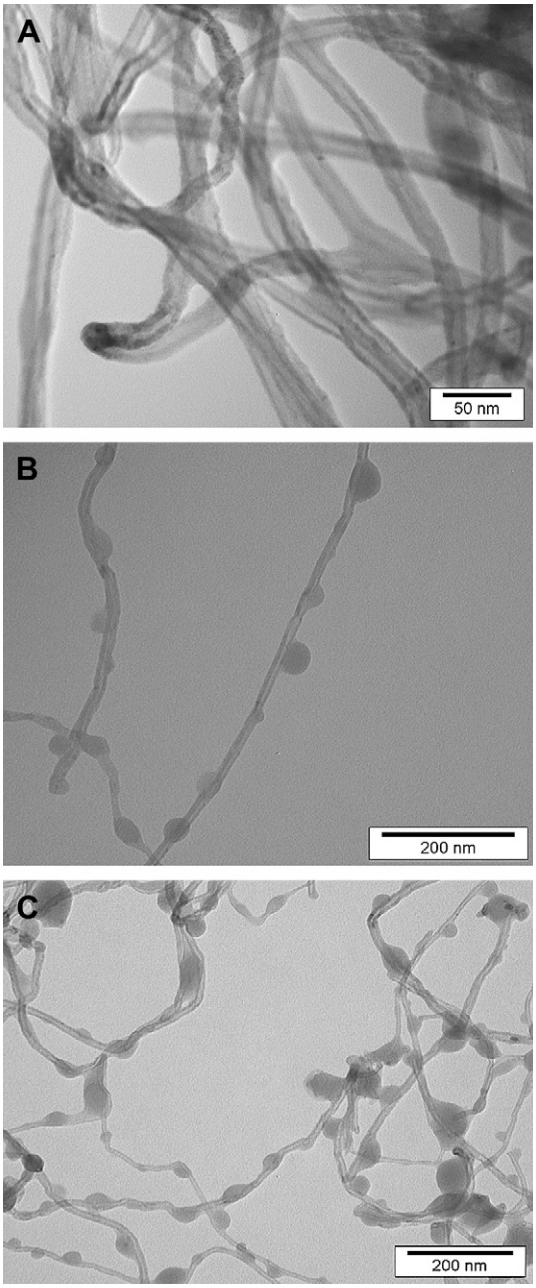

Fig. 6. TEM micrographs of (A) bare MWCNTs, (B) TMP-g-MWCNTs, (C) PP-g-MWCNTs

In the presence of a thiol (i.e. DT), a hydrogen transfer process is required between cumyloxyl radicals and/or radicals located onto the MWCNTs and the thiol derivative. Then, the generated thiyl radicals can react with unsaturated compounds, such as MWCNTs, leading to DT-g-MWCNTs. The experiment was conducted at 160 °C in DMF with 1.5 wt% DCP and a grafting density of $0.20\ mg\ m^{-2}$ was

Table 5
Room temperature solubilities (in mg. mL^{-1}) of TMP- and DT-*g*-MWCNTs in various solvents at given grafting densities.

Solvent	DT-*g*-MWCNTs 0.20 mg m^{-2}	TMP-*g*-MWCNTs 0.92 mg m^{-2}	TMP-*g*-MWCNTs 0.75 mg m^{-2}	TMP-*g*-MWCNTs 0.43 mg m^{-2}
Acetone	5.4	23.2	13.1	9.2
THF	N/D	20.9	13.1	8.3
DMF	5.1	8.7	6.6	6.3
ETOH	26.5	N/D	N/D	4.8
DCB	N/D	18.2	12.2	5.8
Xylene	N/D	N/D	N/D	18.8

N/D: not determinable.
N.B. Pristine MWCNTS are not soluble in any of these solvents.

calculated from TGA. This value is approximately lowered by a factor 2 in comparison with the TMP grafting density (e.g. 0.43 mg m^{-2}, Table 4) suggesting that the efficiency of addition of carbon radicals to MWCNTs is greater than that of sulfur radicals, which is well-known for C_{60} [19,35] and a low occurrence of hydrogen transfer reactions between DT and radical species.

It is expected that this functionalization approach will provide convenience and versatility in building up PP architecture on CNTs. For the first time, PP has been grafted onto MWCNTs through this radical grafting reaction, carried out under similar experimental conditions (1.5 wt% DCP, 160 °C) and using 1,2-dichlorobenzene (DCB) as solvent able to solubilize PP partially at elevated temperature. The corresponding PP-grafted nanotubes were analysed by TGA after a purification by soxhlet extraction in DCB. However, it was not possible to obtain reproductible results with weight losses varying from 50% to 80% for the above-mentioned experiment. This behaviour may be attributed to the purification procedure which does not permit to remove all the free PP chains. One may also speculate on the degradation behaviour of PP through the well-known β-scission reaction occurring in the presence of radical species therefore we were not able to give a PP grafting density. Nevertheless, the microstructure of the corresponding nanocomposites in PP matrix is discussed ahead in Section 3.4.

3.3. Morphology and solubility

As an additional evidence for the functionalization of TMP and PP onto MWCNTs, TEM pictures of the sonicated p-MWCNTs, TMP-*g*-MWCNTs and PP-*g*-MWCNTs are shown in Fig. 6. TEM analysis of TMP- and PP-*g*-MWCNTs exhibit predominant individual CNTs completely separated from the starting bundle. It demonstrates that the functionalization leads to better debundling of MWCNTs. Moreover, the surface of the p-MWCNTs seems to be smooth without any extra phase adhering to them (Fig. 6a) whereas the surface of TMP- and PP-*g*-MWCNTs is rough (Fig. 6b and c). Images reveal the presence of bumps on the sidewalls of the tubes. According to the literature [29,32,38–40], this morphology can be attributed to alkyl moieties attached to the tube wall.

Organic solubility can be achieved by appending DT and TMP alkyl chains onto the MWCNTs and the morphology might better be understood considering the behaviour of raw- and functionalized MWCNTs in various solvents. The visual aspect of the dispersions is significantly different depending on the solvent and covalent functionalization. Solutions were prepared by adding 20 mg of the samples into the same amount of various solvent followed by sonication for 15 min at 20 W and then leaving them free standing for one month. Room temperature solubility in various solvent were determined for TMP-*g*-MWCNTs with grafting densities varying from 0.43 mg m^{-2} to 0.92 mg m^{-2} and DT-*g*-MWCNTs with a grafting density of 0.20 mg m^{-2} (Table 5). While raw MWCNTs form aggregates/bundles and settled down in most solvents, MWCNTs covered with TMP chains form stable colloidal

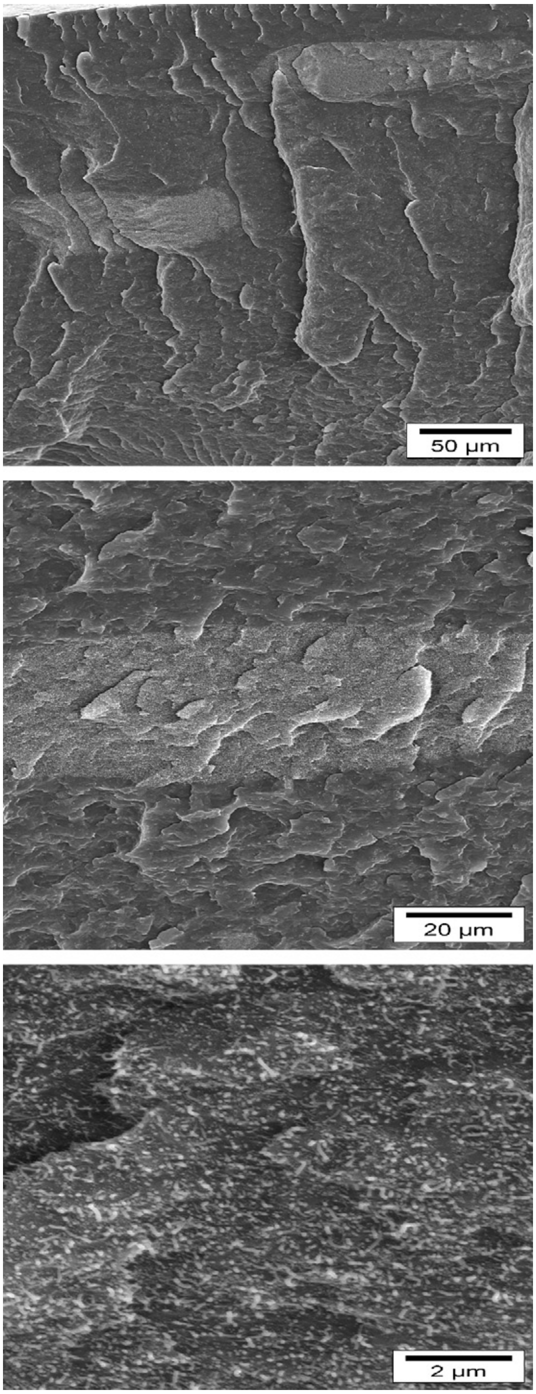

Fig. 7. SEM micrographs of PP/MWCNTs composites with MWCNTs loading of 3 wt%.

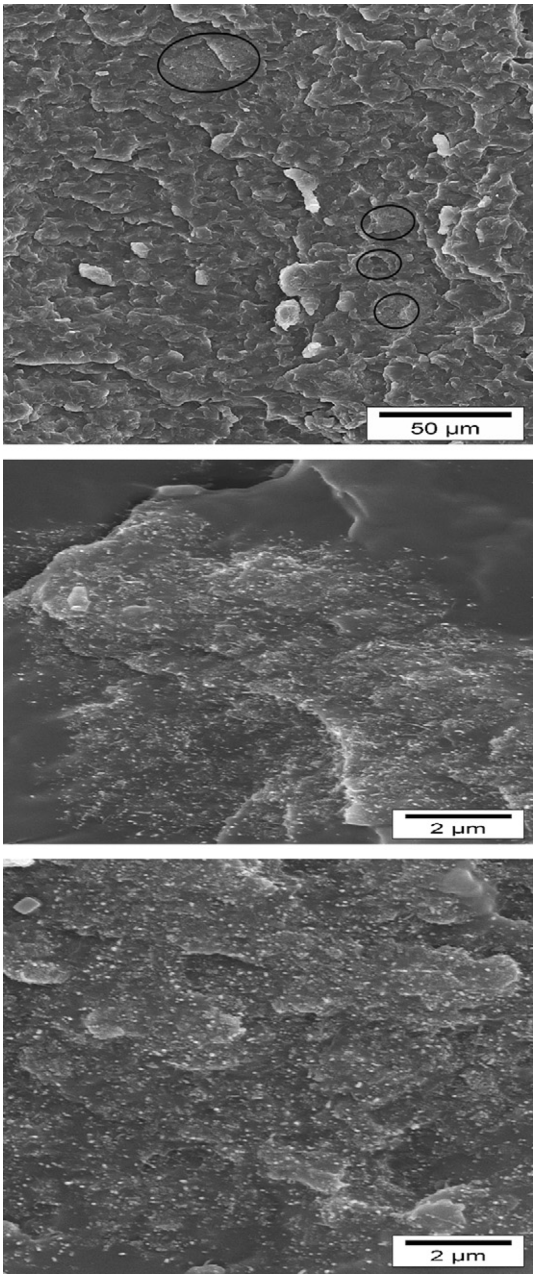

Fig. 8. SEM micrographs of PP/PP-*g*-MWCNT composites with MWCNTs loading of 3 wt%.

suspensions in Acetone, THF, DMF and DCB (Fig. 5). These suspensions are very little disturbed with time indicating that the long alkane organic groups covalently linked onto the sidewalls of MWCNTs ensure fine dispersion. In addition, contrary to TMP-*g*-MWCNTs, DT-*g*-MWCNTs give stable suspensions in EtOH suggesting that DT-*g*-MWCNTs suspension contains less remaining nanotubes aggregates in hydrophilic solvent. In this latter case, the thiyl grafting groups may slightly increase the polarity of the MWCNTs. The unstable DT-*g*-MWCNTs suspension in both THF and DCB solvents may be attributed to the lower DT grafting density in comparison with the TMP one (e.g. 0.20 mg m^{-2} and 0.43 mg m^{-2}, respectively) while various accounts suggest that surface tension [29,41,42] and dielectric constant [29,43] of the solvent are key parameters to make stable suspensions. The reported solubilities in Table 5 highly depend on degree of functionalization and solvent. For TMP grafted MWCNTs, the best solubilities are obtained for samples prepared from a radical grafting reaction in bulk. In the latter case, we assume that the higher TMP grafting density (e.g. 0.92 mg m^{-2}, Table 5) explains this result. As a general rule, in most solvent the solubility of TMP-*g*-MWCNTs increases with increasing the TMP grafting density. These solubility values are higher than those of pentadecane-*g*-MWCNTs [29] and octadecylamine modified MWCNTs [43] in polar solvent (e.g. Acetone, DMF and THF). For example, the high grafting density of TMP onto MWCNTs (e.g. 0.92 mg m^{-2}) permit to obtain solubilities of 8.7, 23.2 and 20.9 mg mL^{-1} in DMF, Acetone and THF, respectively while pentadecane-*g*-MWCNTs display a solubility of 1.1 mg mL^{-1} in Acetone and are not soluble in THF [29]. Surprisingly, we found unstable TMP-*g*-MWCNTs dispersions in xylene when the TMP grafting density is higher than 0.43 mg m^{-2}. In addition, the solubility of the DT-*g*-MWCNTs is lower than that of TMP-*g*-MWCNTs in all solvent except in ethanol, as described above.

3.4. PP/PP-g-MWCNTs nanocomposites

PP coated MWCNTs have been dispersed within a commercially available PP matrix using a contra-rotating Haake Rheomixer. The amount of nanofiller in the final composites has been fixed to 3 wt%. Morphological analysis is very important for the evaluation of dispersion and it was examined by using scanning electron microscopy (SEM). For a simple melt blend of PP with untreated MWCNTs, SEM images of the resulting material only show clusters of a few tens micrometers of diameter (Fig. 7) evidencing a poor interfacial adhesion in the material, as reported by Lee [19] for untreated MWCNT/PP composites MWCNTs containing of 2 wt%. In some areas, the concentration of neat-MWCNTs is high and the nanotubes are entangled together whereas none of neat-MWCNTs can be found in other areas. The interfacial bonding at the interface PP/MWCNTs composite is expected to prevent MWCNTs from agglomeration. SEM images of the PP/PP-*g*-MWCNTs composites MWCNTs containing of 3 wt% (Fig. 8) demonstrate that there are still some areas where PP-*g*-MWCNTs are not found which is obviously connected with improper filler distribution. Nevertheless, sizes of the aggregates are slightly reduced in comparison with those of untreated MWCNT/PP composites indicating that the agglomerates have been partly destroyed through the functionalization. It is then clear from these results that the grafting of PP onto MWCNTs provides a low steric barrier against the strong intermolecular Van der Waals interactions among nanotubes within the PP matrix.

4. Conclusion

MWCNTs were successfully functionalized through a simple radical grafting approach based on the use of dicumyl peroxide as an alkane hydrogen abstractor. Raman, FTIR and TGA data attested for successful functionalization of MWCNTs by TMP and DT. For experiments conducted in DMF at 160 °C with 1.5 wt% DCP, TMP and DT grafting densities were as high as 0.43 and 0.20 mg/m^2, respectively. The lower grafting density obtained for DT may be attributed to the lower efficiency of addition of sulfur radicals to MWCNTs. Moreover, TEM images showed the presence of individual MWCNTs with a characteristic rough surface. TMP grafted MWCNTs exhibited dispersibility in various organic solvents with solubilities varying from 4.8 mg/mL in ethanol to 23.2 mg/mL in acetone. SEM images of the PP-*g*-MWCNTs nanocomposites with filler loadings of 3 wt% in PP matrix did not show a significant improvement in MWCNTs dispersion within the PP matrix although sizes of the aggregates were slightly reduced. Future work will focus on the influence of melt processing conditions (shear/

stress, mixing time…) on PP-*g*-MWCNTs dispersibility in order to obtain deep insight into the microstructural features.

Acknowledgment

The authors would like to thank ADEME for providing financial support and close collaboration for this research work and the “Centre Technologique des Microstructures de Lyon1” for imaging nanocomposites.

References

[1] Poole CP, Owens FJ. Introduction to nanotechnology. Weinheim: Wiley-Interscience; 2003.
[2] Connell MO. Carbon nanotubes: properties and applications. CRC Press; 2006.
[3] Gogotsi Y. Carbon nanomaterials. CRC Press; 2006.
[4] Liu J, Rinzler AG, Dai H, Hafner JH, Bradley RK, Boul PJ, et al. Science 1998;280:1253–6.
[5] Wang C, Guo Z, Fu S, Wu W, Zhu D. Prog Polym Sci 2004;29(11):1079–141.
[6] Moniruzzaman M, Winey KI. Macromolecules 2006;39(16):5194–205.
[7] Zhao CG, Hu GJ, Justice R, Schaefer DW, Zhang S, Han CC. Polymer 2005;46(14):5125–32.
[8] Trujillo M, Arnal ML, Muller AJ, Laredo E, Bredeau S, Bonduel D, et al. Macromolecules 2007;40(17):6268–76.
[9] Qin S, Qin D, Ford WT, Resasco DE, Herrera JE. Macromolecules 2004;37(3):752–7.
[10] Sun YP, Huang WJ, Lin Y, Fu KF, Kitaygorodskiy A, Riddle LA, et al. Chem Mater 2001;13(9):2864–9.
[11] Huang WJ, Lin Y, Taylor S, Gaillard J, Rao AM, Sun YP. Nano Lett 2002;2(3):231–4.
[12] Lin Y, Zhou B, Fernando KAS, Liu P, Allard LF, Sun YP. Macromolecules 2003;36(19):7199–204.
[13] Shaffer MSP, Koziol K. Chem Commun 2002:2074–5.
[14] Kong H, Gao C, Yan DY. J Mater Chem 2004;14(9):1401–5.
[15] Gao C, Muthukrishnan S, Li WW, Yuan JY, Xu YY, Muller AHE. Macromolecules 2007;40(6):1803–15.
[16] Kong H, Gao C, Yan DY. J Am Chem Soc 2004;126(2):412–3.
[17] Kaminsky W. Macromol Chem Phys 2008;209(5):459–66.
[18] Wang Y, Wu J, Wei F. Carbon 2003;41:2939–48.
[19] Lee SH, Cho E, Jeon SH, Youn JR. Carbon 2007;45:2810–22.
[20] Bonduel D, Mainil M, Alexandre M, Monteverde F, Dubois P. Chem Commun 2005:781–3.
[21] Park S, Yoon SW, Lee KB, Kim DJ, Jung YH, Do Y, et al. Macromol Rapid Commun 2006;27(1):47–50.
[22] Koval'chuk AA, Shevchenko VG, Shchegolikhin AN, Nedorezova PM, Klyamkina AN, Aladyshev AM. Macromolecules 2008;41(9):3149–56.
[23] Koval'chuk AA, Shevchenko VG, Shchegolikhin AN, Nedorezova PM, Klyamkina AN, Aladyshev AM. Macromolecules 2008;41(20):7536–42.
[24] Umek P, Seo JW, Hernadi K, Mrzel A, Pechy P, Mihailovic DD, et al. Chem Mat 2003;15(25):4751–5.
[25] Robin JJ, Boyer C, Boutevin B, Loubat C. Polymer 2008;49(21):4519–28.
[26] Hoight AH, Meijer J, Jelenic J. Reactive modifiers for polymers. London: Al-Malaïka S; 1997. p. 84, and references therein.
[27] Badel T, Beyou E, Bounor-Legare V, Chaumont P, Flat JJ, Michel A. J Polym Sci Part A Polym Chem 2007;45(22):5215–26.
[28] Badel T, Beyou E, Bounor-Legare V, Chaumont P, Flat JJ, Michel A. Macromol Chem Phys 2009;210(13–14):1087–95.
[29] Akbar S, Beyou E, Cassagnau P, Chaumont P, Gholamali F. Polymer 2009;50(12):2535–43.
[30] Russell KE. Prog Polym Sci 2002;27(6):1007–38.
[31] Hettema R, Van Tol J, Janssen LPBM. Polym Eng Sci 1999;39(9):1628–41.
[32] Bahr JL, Yang J, Kosnykin DV, Bronikowski MJ, Smalley RE, Tour JM. J Am Chem Soc 2001;123(27):6536–42.
[33] Osswald S, Havel M, Gogotsi Y. J Raman Spectrosc 2007;16(6):728–36.
[34] Peigney A, Laurent C, Flahaut E, Bacsa R, Rousset A. Carbon 2001;39(4):507–14.
[35] Krusic PJ, Wasserman E, Parkinson BA, Malone B, Holler ER. J Am Chem Soc 1991;113(16):6274–5.
[36] Ratzsch M, Arnold M, Borsig E, Bucka H, Reichelt N. Prog Polym Sci 2002;27(7):1195–282.
[37] Bahu RR, Singha NK, Nashar K. J Appl Polym Sci 2009;113(3):1836–52.
[38] Hudson JL, Jian HH, Leonard AD, Stephenson JJ, Tour JM. Chem Mat 2006;18(11):2766–70.
[39] Stephenson JJ, Sadana AK, Higginbotham AL, Tour JM. Chem Mat 2006;18(19):4658–61.
[40] Dyke AC, Tour JM. Nano Lett 2003;3(9):1215–8.
[41] Meuer S, Braun L, Schilling T, Zentel R. Polymer 2009;50(1):154–60.
[42] Shuhui W, Shanks RA. J Appl Polym Sci 2004;93(3):1493–9.
[43] Qin Y, Liu L, Shi J, Wu W, Zhang J, Guo Z-X, et al. Chem Mater 2003;15(17):3256–60.