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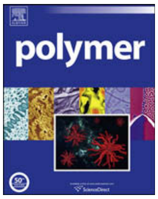

Radical grafting of polyethylene onto MWCNTs: A model compound approach

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ABSTRACT

Covalent functionalization of pentadecane-decorated multiwalled carbon nanotubes (MWCNTs) has been studied as a model compound approach for the grafting of poly(ethylene-co-1-octene) onto MWCNTs by reactive extrusion. It was accomplished through radical addition onto unsaturated bonds located on the MWCNTs' surface using dicumyl peroxide as hydrogen abstractor. It was found that this surface treatment results into the break-up of the native nanotube bundles and increases solubility in various solvents. Raman spectroscopy was utilized to follow the introduction of pentadecane on the MWCNTs' surface; while thermogravimetric analysis and elemental analysis indicated the extent of this grafting. Pentadecane functionalized MWCNTs were imaged by transmission electronic microscopy showing single long functionalized MWCNTs distinct from the starting pristine bundles.

1. Introduction

Carbon nanotubes (CNTs) are extremely promising for applications in materials science and engineering. Much attention has been paid to CNT-based nanocomposites for the preparation of high-performance materials exhibiting improved or unusual mechanical and physical properties. The combination of a soft polymer matrix with nanosized rigid filler particles can provide new nanocomposite materials with largely improved modulus and strength. However, the homogeneous dispersion of raw CNTs within a polymeric matrix is relatively difficult to achieve, especially in apolar matrixes such as polyolefins. Indeed, carbon nanotubes tend to aggregate as very long bundles due to the high surface energy and the stabilization by numerous of π–π electron interactions among the tubes. Several methods for preparing polymer/CNTs nanocomposites have been explored to achieve good dispersion and load transfer, such as noncovalent [1–3] and covalent [4,5] approaches. The noncovalent methods, including solution mixing [6], melt mixing [7] and *in situ* polymerization [8] are simple and convenient; however, the dispersion of CNTs and the interfacial interaction between CNTs and polymer matrix are poor, especially in the case of melt mixing. In contrast, the covalent approaches, including "grafting to" [4,9] and "grafting from" [9,10], leading to chemical linkage between polymer and the surface of CNTs, improve the dispersion of CNTs in polymer matrices. However, the synthesis of end-functionalized polyethylene (PE), which is necessary in the "grafting to" approach, is difficult [11]. Otherwise, the grafting procedure can be achieved by *in situ* polymerization of ethylene as catalyzed directly from the nanotubes surface treated by a highly active metallocene-based complex [8,12]. Another promising route for a chemical modification of MWCNTs by PE is to use free radical initiators such as peroxides. The general mechanism of free radical grafting of vinyl compound from hydrocarbon chains detailed by Russell [13], Chung [14] and Moad [15] seems to express a widespread view. The grafting reaction starts with hydrogen abstraction by alkoxyl radicals generated from thermal decomposition of the peroxide. Then, the active species generated onto the hydrocarbon backbone react with unsaturated bonds located on the MWCNTs surface. This chemical modification is thus conceivable during reactive extrusion because the radicals' lifetimes (in the range of few milliseconds) are compatible with typical residence time in an extruder (around 1 min). Nevertheless, the main drawback of the free radical grafting is the low selectivity of the radical center, specially at high temperatures (in the range of 150–200 °C, required for extrusion of polyethylene), leading to side reactions such as coupling and chain scission [13,16]. Moreover, performing this chemical modification by reactive processing brings in many constraints inherent to the processing (e.g. short reaction time, viscous dissipation and high temperature). For instance, the difference of viscosity between the monomer and the molten polymer could enhance these side reactions. So, to separate

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Table 1
Characteristics of Graphistrength™ C100.

Manufacturing	CCVD
Apparent density	50–150 kg/m^3
Mean agglomerate size	200–500 μm
C contents	~90 wt%
Mean number of walls	5–15
Outer mean diameter	10–15 nm
Length	0.1–10 μm

these physical influences from the chemical modification, the grafting reaction is, in this work, predicted with a model compound approach based on a radical grafting reaction between peroxide-derived alkoxyl radicals, and a low molar mass alkane representing characteristics moieties of PE. We resorted to pentadecane ($C_{15}H_{32}$) as model for polyethylene. 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.

Table 2
List of samples according to the experimental conditions.

Sample	Constituents	Reaction conditions	Principal product
A	MWCNTs (50 mg) + DCP (0.23 g) + pentadecane (7.69 g)	150 °C for 6 h	Penta-g-MWCNTs
B-1	Blank experiment: DCP (0.23 g) + pentadecane (7.69 g)	150 °C for 6 h	Interlinked pentadecane
B-2	Blank experiment: MWCNTs (50 mg) + DCP (0.23 g) + DMF (5 mL)	150 °C for 6 h	Cumyloxyl-g-MWCNTs
C	MWCNTs (50 mg) + DCP (0.23 g) + pentadecane (7.69 g)	At different temperatures for 6 h	Penta-g-MWCNTs
D	MWCNTs (50 mg) + DCP (different ratios) + pentadecane (7.69 g)	150 °C for 6 h	Penta-g-MWCNTs

Scanning the factors influencing the selectivity toward hydrogen abstraction and radical grafting reaction is of particular interest and dicumyl peroxide (DCP) has been selected to generate alkoxyl radicals in presence of the alkane model. Experiments reported here involve decomposition of DCP. Its thermal decomposition is carried

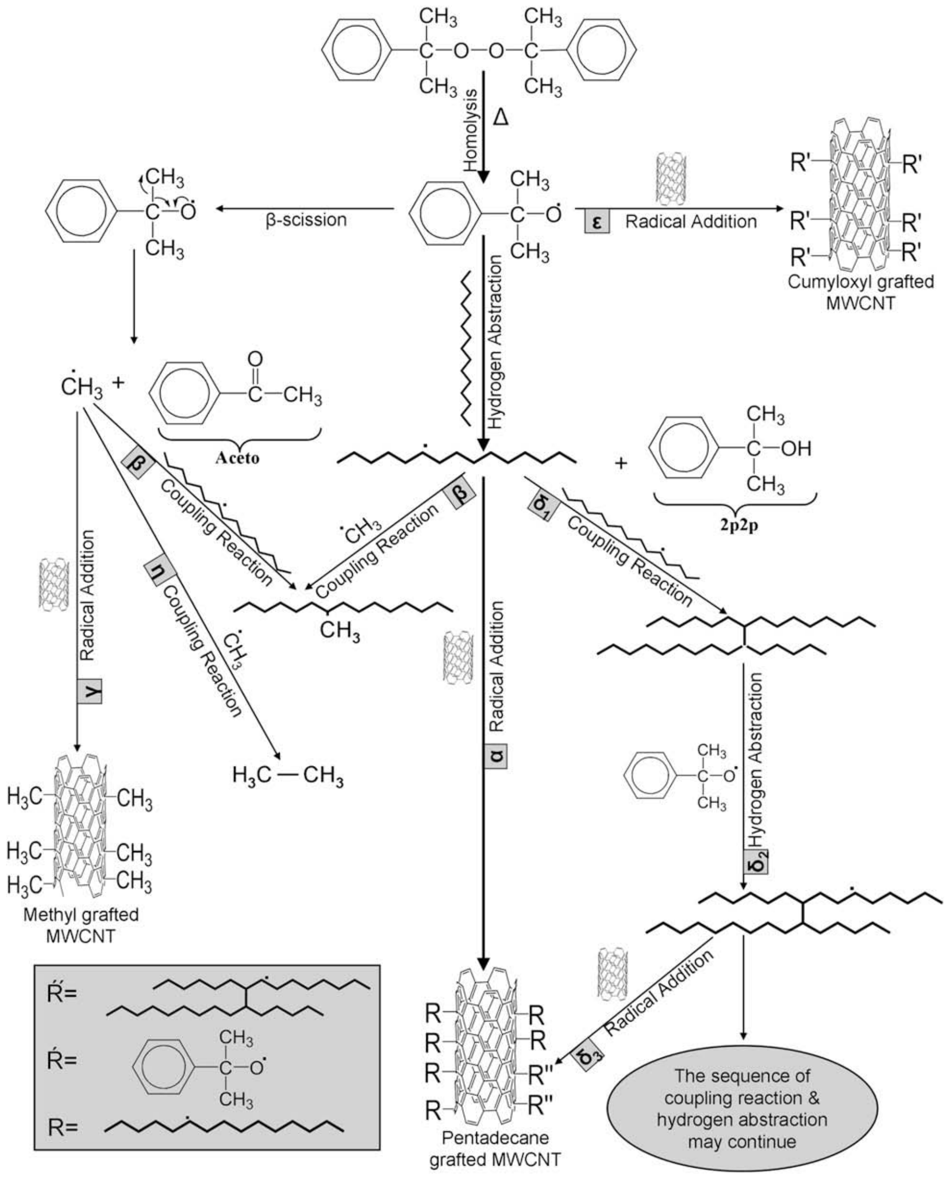

Fig. 1. General reactive pathways of free radical grafting of pentadecane onto MWCNTs.

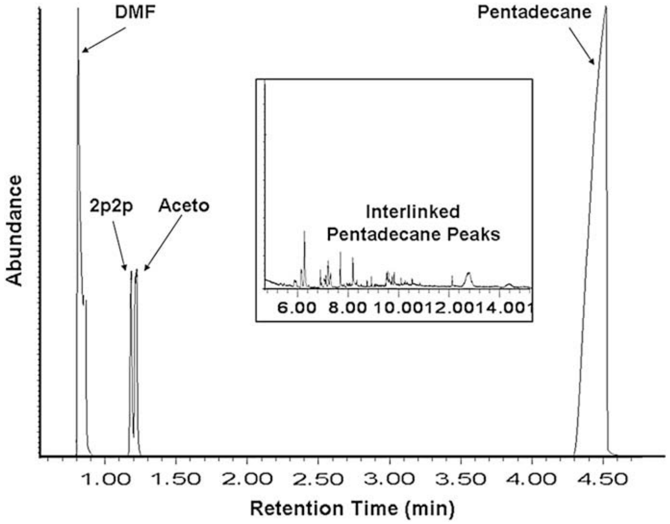

Fig. 2. GC–MS chromatogram of the liquid phase of the blank sample B-1 (diluted with DMF after reaction); inset: a myriad of small pentadecane peaks observed after ca. 6 min.

out in a range of temperatures close to the ones expected during reactive extrusion of poly(ethylene-co-1-octene) typically few minutes at 150–200 °C.

This manuscript aims at describing the course of the generated radical species and the extent of the grafting reaction in regards to the DCP concentration and temperature. This chemical functionalization approach leads to high degree of functionalization which influences solubility behaviour of the formed pentadecane-grafted MWCNTs in various solvents. In addition, pentadecane-grafted MWCNTs were analysed by Raman spectroscopy, transmission electronic microscopy, thermogravimetric analysis and elemental analysis.

2. Experimental

2.1. Materials

MWCNTs (Graphistrength™ C100: see salient characteristics in Table 1) were kindly supplied by ARKEMA.

The low molecular weight hydrocarbon substrate, used as model for poly(ethylene-co-octene), was pentadecane (99%, Sigma–Aldrich – France). Initiator was dicumyl peroxide (99%, Sigma–Aldrich – France) and all other solvents were used without any further purification so as to fit with the industrial conditions required in the melt processing.

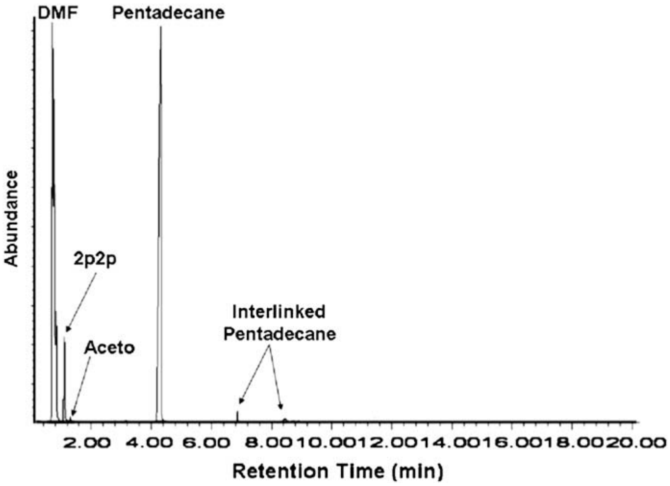

Fig. 3. GC–MS chromatogram of the liquid phase of the sample A (diluted with DMF after reaction).

Table 3
Area ratios of different constituents in GC analysis.

Ratio	Fig. 1, sample B-1	Fig. 2, sample A
A_{2p2p}/A_{Aceto}	~0.9	~10
A_{Penta}/A_{Aceto}	~4	~30
A_{Penta}/A_{2p2p}	~5	~4

2.2. Surface activation of MWCNTs

In this study, MWCNTs were oxidized in air at 450 °C for 1 h. 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 alkanes

The thermolysis of dicumyl peroxide (DCP) in pentadecane was performed in a glass reactor. In a typical grafting experiment, DCP (0.23 g/0.85 mmol), as a radical initiator, was first mixed in with p-MWCNTs (50 mg) and pentadecane (7.69 g/36.26 mmol) and then sonicated for 15 min. After that, the suspension was degassed by 4 freeze-pump-thaws, and then it was heated to 150 °C under stirring. After 6 h, the reaction mixture was cooled down quickly and diluted in DMF for characterization through gas chromatography analysis. The grafted MWCNTs were collected by centrifugation (11K rpm, 20 min) and subsequent filtration.

2.4. Recovery of free and tethered pentadecane molecules

The free pentadecane molecules were isolated from the grafted MWCNTs by exhaustive cleaning of the suspension by dialysis. In a typical process, 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 DMF until no residual pentadecane could be detected in the recovered solution (determined gravimetrically). Then, the pentadecane-grafted MWCNTs suspension was dried at 80 °C to evaporate the solvent prior to characterization. Details of the specimens prepared and tested are given in Table 2.

2.5. Characterization

Gas chromatography–mass spectrometry (GC–MS) was performed with an Agilent 6890 series GC system equipped with an HP-5ms (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 were 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.

Thermogravimetric analysis (TGA) was carried out 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 the contents of C and H.

Transmission electron microscopy (TEM) was carried out with a Philips CM-120 microscope (Philips Consumer Electronics BV, Eindhoven, The Netherlands) operated at 80 keV.

Solubility was determined gravimetrically. In a typical experiment, saturated solutions of penta-g-MWCNTs were prepared by

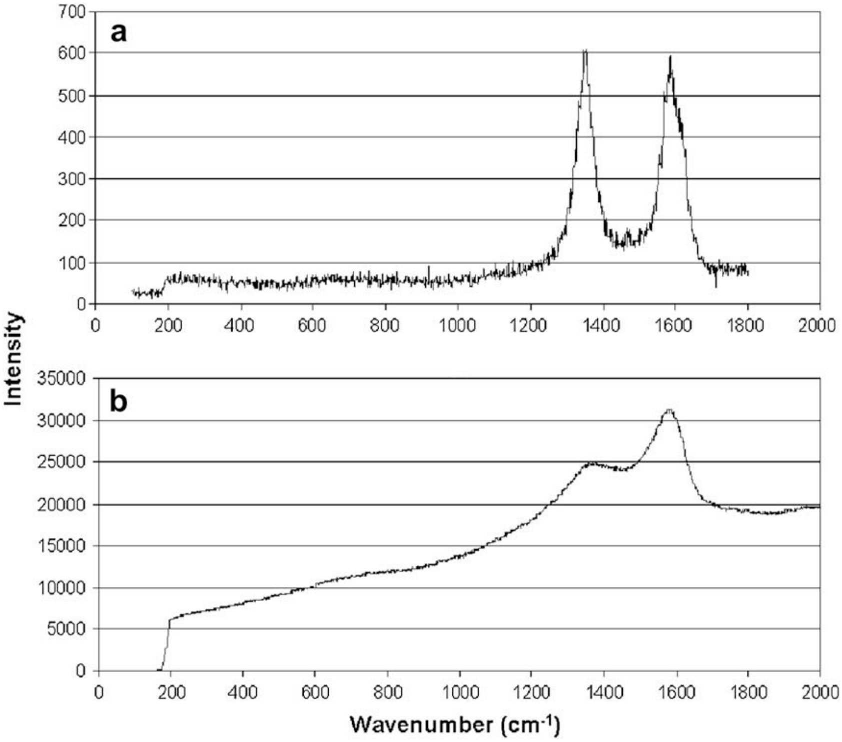

Fig. 4. Raman spectra of: p-MWCNTs (a) and penta-g-MWCNTs (b).

sonication in vials. Sonication was done using S 40 H Elmasonic by Elma (Singem, Germany) for 15 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.

3. Results and discussion

3.1. Free radical grafting of pentadecane onto MWCNTs

Fig. 1 sums up main reactive pathways of free radical grafting of pentadecane onto MWCNTs with dicumyl peroxide as initiator. The hydrogen abstraction reaction from alkyl hydrocarbon bonds was studied starting from the reaction of DCP-derived radicals with pentadecane. However, the alkoxy radicals can undergo additional reactions including β-scission leading to the formation of methyl radicals [17]. These latter preferentially induce coupling reaction (Fig. 1, route β and η) or attack onto the sp^2 carbon of the MWCNTs (Fig. 1, route γ) whereas cumyloxyl radicals are more prone to hydrogen abstraction from pentadecane [15]. The formed pentadecyl radicals through hydrogen abstraction are able to react with MWCNTs by radical addition onto sp^2 carbon of the MWCNTs (Fig. 1, main route α) and with other radical species via the common radical coupling reactions (Fig. 1, routes δ_1 and β). According to the results of Johnston [18,19], based on a study of the crosslinking reaction of poly(ethylene-co-1-octene) in the presence of DCP at 160 °C, coupling reactions are four times more prone to happen than scission reactions so we assume that pentadecyl radicals do not undergo scission reactions. First, we investigated the selectivity of cumyloxyl radicals, coming from the thermal decomposition of DCP, to find out the chemical structure of the formed species. As described in Fig. 1, the cumyloxyl radical, can undergo two main reactions leading to the formation of 2-phenyl-2-propanol (2p2p) through H-abstraction from the hydrocarbon substrate, or acetophenone (aceto) by intramolecular β-scission. We found it interesting to see whether the presence of the MWCNTs could modify the radical species course.

First, products arising from the reaction involving a solution of DCP in pentadecane (blank, sample B-1, Table 2) were analysed by GC–MS (Fig. 2). Three main peaks corresponding to 2p2p, aceto and pentadecane are observed in Fig. 2 confirming H-abstraction from

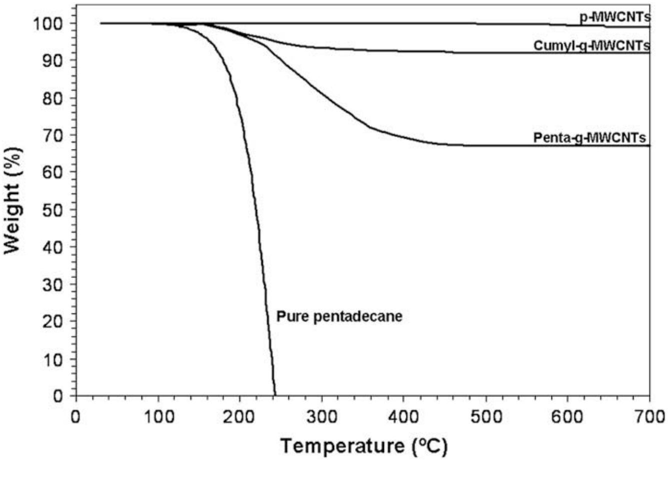

Fig. 5. TGA data (under N_2) for cumyl-g-MWCNTs and penta-g-MWCNTs with that of p-MWCNTs and pure pentadecane for corresponding reference.

Table 4
Carbon and hydrogen contents determined by elemental analysis.

Sample	Element	%
p-MWCNTs	C	87–90
	H	0.3–0.66
Penta-g-MWCNTs (A)	C	87–90
	H	5–6

Table 5
Effect of reaction temperature on the degree of grafting with 3% DCP.

Experiment	Reaction temperature (°C)	A_{2p2p}/A_{Aceto}	A_{Penta}/A_{2p2p}	Percent grafting[a] (weight loss in TGA)	Chains per CNT[b]	Grafting density[b]	
						mg m^{-2}	mmol g^{-1}
C1	140	~9	~4	25	62,800	0.108	1.180
C2	150	~10	~4	31	77,900	0.134	1.463
C3	160	~9	~5	27	67,800	0.117	1.278
C4	170	~4	~9	16	40,200	0.069	0.754
C5	180	~3	~15	10	25,100	0.043	0.470

[a] Based on TGA results.
[b] Based on calculations assuming avg. CNT length of 5 μm and OD of 13 nm. Number of chains includes interlinked chains as well.

pentadecane and β-scission reaction from cumyloxyl radicals respectively. The small peaks observed from 6 min to 14 min are attributed to interlinked pentadecane molecules and are believed to be synthesized by combination of the formed pentadecane radicals.

For the reaction procedure where MWCNTs are included in the solution of DCP in pentadecane (sample A, Table 2), GC–MS analysis of the formed products (Fig. 3) mainly displays a big peak corresponding to 2p2p and a smaller one attributed to aceto. Assuming that the A_{2p2p}/A_{Aceto} area ratio of the corresponding peaks is directly linked to the [2p2p]/[aceto] concentration ratio [17], we investigated the course of pentadecane radicals through the calculations of A_{2p2p}/A_{Aceto}, A_{Penta}/A_{aceto}, A_{Penta}/A_{2p2p} area ratios (Table 3). The A_{2p2p}/A_{Aceto} area ratio is ten times higher in the case of sample A than in the case of sample B-1, suggesting that presence of MWCNTs favorably changes the course of reaction by limiting β-scission reaction and attracting cumyloxyl radicals. In a similar way, the area ratio A_{Penta}/A_{aceto} is higher for sample A and no significant change is observed for the A_{Penta}/A_{2p2p} ratio in any of the samples (Table 3). Moreover, GC-MS chromatogram of sample A (Fig. 3) only displays two other peaks assigned to interlinked pentadecane molecules. On contrary, chromatogram of sample B-1 displays a large number of such peaks (Fig. 2) giving an evidence that most radical pentadecane chains are grafted onto MWCNTs surface in case of sample A. Besides, no DCP traces were detected in any of the samples (A and B-1).

Direct evidence for covalent sidewall functionalization can be also found by Raman spectroscopy [20–22]. G band is a characteristic feature of the graphitic layers and corresponds to the tangential vibration of the carbon atoms. The second characteristic mode is a typical sign for defective graphitic structures (D band). The ratio between the G band and D band is a good indicator of the changes in chemistry of CNTs. Interestingly, Raman spectra of p-MWCNTs (Fig. 4a) and penta-g-MWCNTs (Fig. 4b) show two main peaks around 1350 cm^{-1} (D band) and 1586 cm^{-1} (G band). The relatively high intensity of the G band relative to D band ($I_G/I_D = 1.25$) for penta-g-MWCNT sample in comparison with that of p-MWCNT (i.e. $I_G/I_D = 0.95$) could be designated as an indicator of grafting species.

Table 6
Effect of amount of peroxide on degree of grafting at 150 °C.

Experiment	DCP (wt% of pentadecane)	Percent grafting[a] (weight loss in TGA)	Chains per CNT[b]	Grafting density[b]	
				mg m^{-2}	mmol g^{-1}
D1	0.5	5	12,600	0.021	0.229
D2	1	9	22,600	0.039	0.426
D3	2	15	37,700	0.065	0.710
A/D4[c]	3	31	77,900	0.134	1.464
D5	4	12	30,200	0.052	0.568
D6	5	8	20,100	0.034	0.371

[a] Based on TGA results.
[b] Based on calculations assuming avg. CNT length of 5 μm and OD of 13 nm. Number of chains includes interlinked chains as well.
[c] Samples A and D4 are basically same; here ‘A’ is named as ‘D4’ to keep the sequence.

To gain a more quantitative picture of the extent of nanotube functionalization, thermogravimetric analysis was performed on the reaction products. Indeed, it is well known that heating functionalized nanotubes in an inert atmosphere removes the organic moieties and restores the pristine nanotubes structure [23–25]. It is noteworthy that the adsorbed molecules can be removed from the grafted ones by dialysis as mentioned in the experimental part. As shown in Fig. 5, the amount of organic functionalities physically and/or covalently attached to the initial MWCNTs can be neglected (weight loss $< 1.5\%$). After treatment with DCP (blank experiment B-2), the weight loss increases to 8% (Fig. 5) as expected for MWCNTs with more organic moieties on the surface. In addition, TGA results show that pure pentadecane can be completely decomposed at a temperature of 450 °C; therefore, the amount of pentadecane that covalently attached to the p-MWCNTs is estimated by the weight loss of pentadecane-grafted MWCNTs sample between 180 °C and 450 °C. In Fig. 5, we estimate the weight of grafted pentadecane to be around 30%. It is notable here that this degree of functionalization is higher than those reported earlier for MWCNTs derivatized through the billups reaction (10–20%) [26]. The weight losses of blank sample B-2 and sample A, which are 8% for cumyloxyl groups and 30% for pentadecyl groups correspond to a surface coverage of approximately 31,600 cumyloxy groups per nanotube and 75,400 pentadecyl groups per nanotube (the calculations are based on a 5 mm long and 13 nm wide nanotube with a surface of 2.04×10^5 nm^2 and a volume of 8.8×10^5 nm^3). The average density of the nanotubes is 100 kg/m^3 so there are around 1.13×10^{13} nanotubes present per mg). Therefore, adsorptions of 0.08 mg cumyloxy group/mg CNTs (0.59 mmol/g) and 0.3 mg pentadecyl group/mg CNTs (1.42 mmol/g) suggest a grafting density of 0.034 mg/m^2 and 0.13 mg/m^2 respectively. Comparable grafting densities have been recently reported for pyrene polymer functionalized MWCNTs [27].

We can conclude that the grafting efficiency is higher for the pentadecyl radicals than for other radical species. These consequences might have originated because of two factors: (1) the increase of grafting efficiency suggests poor attack onto the sp^2 carbon of the MWCNTs by the cumyloxyl radicals; (2) the high molecular weight of the grafted molecules, i.e. pentadecane. Elemental analysis (Table 4) is also an indicator of degree of grafting. We can observe that carbon content does not increase after the grafting procedure and hydrogen content increases from the range of 0.3–0.6 wt% for neat MWCNTs to the range of 5–6 wt% for the pentadecane-grafted MWCNTs. The hydrogen content of the grafted species, calculated from TGA, gives a value close to the one found from elemental analysis: a weight loss of 30% for the pentadecane-grafted MWCNTs (sample A) corresponds to 4.7 wt% H contents.

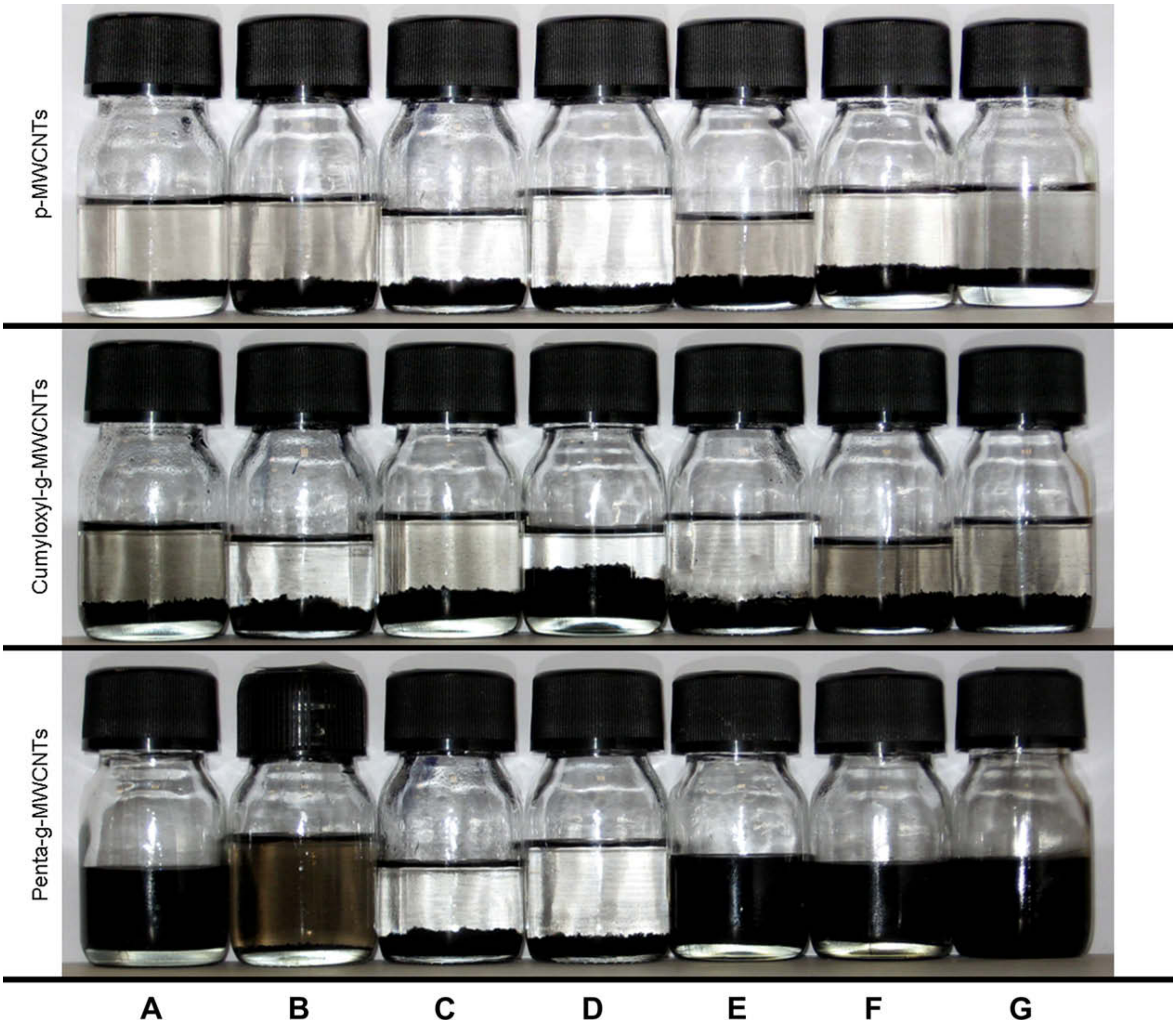

Fig. 6. Solubility behaviour of pristine carbon nanotubes (p-MWCNTs) after 5 min, cumyloxy grafted CNTs (cumyloxy-g-MWCNTs) after 30 min and pentadecane-grafted MWCNTs (penta-g-MWCNTs) after 2 months in DMF (A); acetone (B); chloroform (C); THF (D); toluene (E); DCB (F); xylene (G).

3.2. *Influence of temperature*

As discussed earlier, DCP generates methyl radicals through β-scission reaction (Fig. 1). This reaction is characteristic to tertiary peroxides, which undergo a unimolecular reorganisation of the primary alcoxyl radical into an alkyl radical (usually a methyl radical). It is also strongly sensitive to temperature as its driving force is entropic [28]. In order to increase the understanding of the cumyloxyl radicals' behaviour, the experiments C1 to C5 (Table 5) correspond to the ones performed with 3 wt% DCP, as hydrogen abstractor, at temperatures varying from 140 °C to 180 °C. For temperatures lower than 170 °C (samples C1–C3), the number of pentadecyl groups per CNT, calculated through thermogravimetric analysis, varies from 62,800 to 77,900. The highest grafting density is obtained for sample C2 (i.e. 1.464 mmol/g). For temperatures greater than 160 °C (i.e. 170 °C and 180 °C), the grafting density

Table 7
Room temperature stability and solubility of 'penta-g-MWCNTs' (sample A/D4) in various solvents.

Solvent	Solubility (mg mL^{-1})	Stability	Dielectric constant	Surface tension (20 °C in mN m^{-1})
n-Hexane	–	Suspension; complete precipitation with time	2	18.43
n-Heptane	–	Suspension; complete precipitation with time	1.9	20.14
n-Octane	–	Suspension; complete precipitation with time	1	21.62
Acetone	1.1	Metastable; high precipitation with time	20.7	25.2
THF	–	Suspension; complete precipitation with time	7.5	26.4
n-Pentadecane	–	Suspension; complete precipitation with time	2.2	26.9
Chloroform	–	Suspension; complete precipitation with time	4.8	27
Toluene	14.6	Stable over months; negligible precipitation with time	2.4	28.4
Xylene	16.3	Stable over months; negligible precipitation with time	2.6	30
DCB	19.2	Stable over months; negligible precipitation with time	2.8	33.6
DMF	13.9	Metastable; little precipitation with time	38	37.1

N.B. MWCNTs are reported in literature to have surface tension in the range of 40–80 mN m^{-1}.

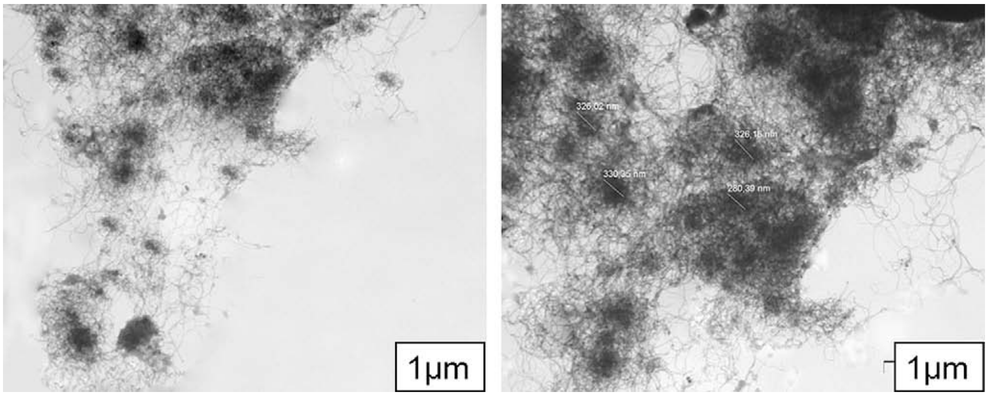

Fig. 7. TEM images of p-MWCNTs.

dramatically decreases from 1.278 mmol/g (weight loss = 27%) to 0.470 mmol/g (weight loss = 10%) and a fraction of insoluble product is detected. Moreover, the A_{2p2p}/A_{Aceto} area ratio (calculations are based on GC analysis of the resulting mixture) decreases by increasing temperature, while A_{Penta}/A_{2p2p} area ratio increases (Table 5). These results confirm that the β-scission reaction of cumyloxyl radical also increases as the temperature increases, leading to the formation of methyl radicals. These latter preferentially react by combination whereas cumyloxyl radicals are more prone to hydrogen abstraction from pentadecane [15].

3.3. Influence of DCP concentration

Maximum pentadecane grafting density was observed at 150 °C while on higher temperatures the amount of insoluble product was increased so experiments were conducted at 150 °C with various concentrations of DCP.

Experiments from D1 to D4 (Table 6) show that, for initiator concentration up to 3%, the more the DCP concentration is used the higher the grafting density is achieved (from 0.229 mmol/g to 1.464 mmol/g). For initiator concentration higher than 3 wt%, the grafting density decreases from 1.464 mmol/g to 0.371 mmol/g upon increasing DCP concentration up to 5%. Thus, to get high grafting efficiency, one should opt for optimal initiator concentration, i.e. 3 wt%, and choose the most favourable reaction temperature, i.e. 150 °C. Upon using higher amount of DCP yields a major part of MWCNTs that are not soluble in various solvents. This result is due to the fact that the presence of higher concentration of radicals changes the reaction kinetics, possibly leading to combination reactions (Fig. 1). This particular aspect needs further investigation in future studies.

3.4. Solubility behaviours of cumyl-g-MWCNTs and penta-g-MWCNTs

To investigate the stability of the p-MWCNTs and the functionalized MWCNTs in organic solutions, we prepared solutions by adding 200 mg of the samples into the same amount of various solvents followed by sonication for 15 min at 20 W and then leaving them free standing for 5 min to 2 months. As illustrated in Fig. 6, for p-MWCNTs (unfunctionalized), we found unstable dispersions in both polar and nonpolar solvents meaning that it is not possible to well disperse p-MWCNTs in these solvents even after sonication. Two phenomena affect p-MWCNTs dispersion: nanotube morphology and attractive forces between the tubes. Not only the tube surfaces are attracted to each other by molecular forces, but the extremely high aspect ratios coupled with the flexibility also dramatically increase the possibilities for entanglements. For the cumyloxyl grafted MWCNTs (grafting density = 0.371 mmol/g), similar behaviour is observed suggesting that the grafting density is not high enough to ensure a good dispersion. In contrast, for pentadecane-grafted MWCNT, we found stable dispersions in DMF, toluene, DCB and xylene where the CNTs could not be centrifuged down easily (Fig. 6). The obvious improvement in the suspension stability of the penta-g-MWCNTs confirms that the long alkane organic groups are covalently linked onto the sidewalls of MWCNTs that ensure fine dispersion. Three states of dispersion could be found in Fig. 6: sedimented—as in case of p-MWCNTs in all solvents despite sonication; swollen—as in case of cumyloxyl-g-MWCNTs

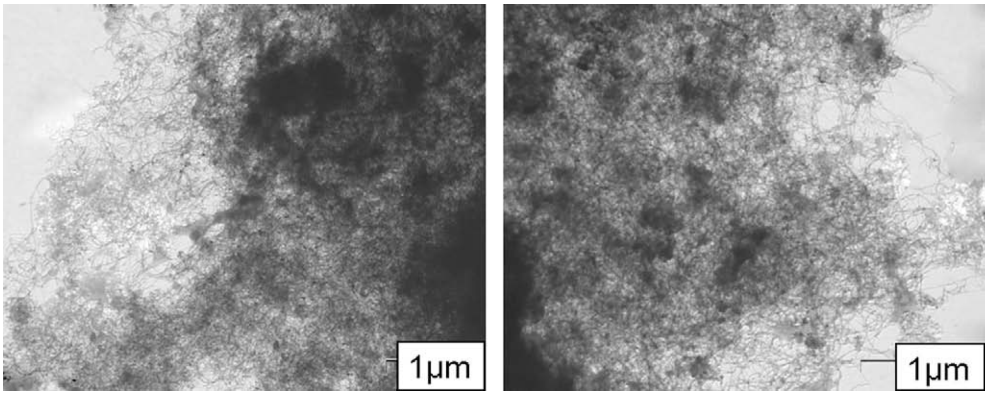

Fig. 8. TEM micrographs of MWCNTs coated with cumyloxy groups.

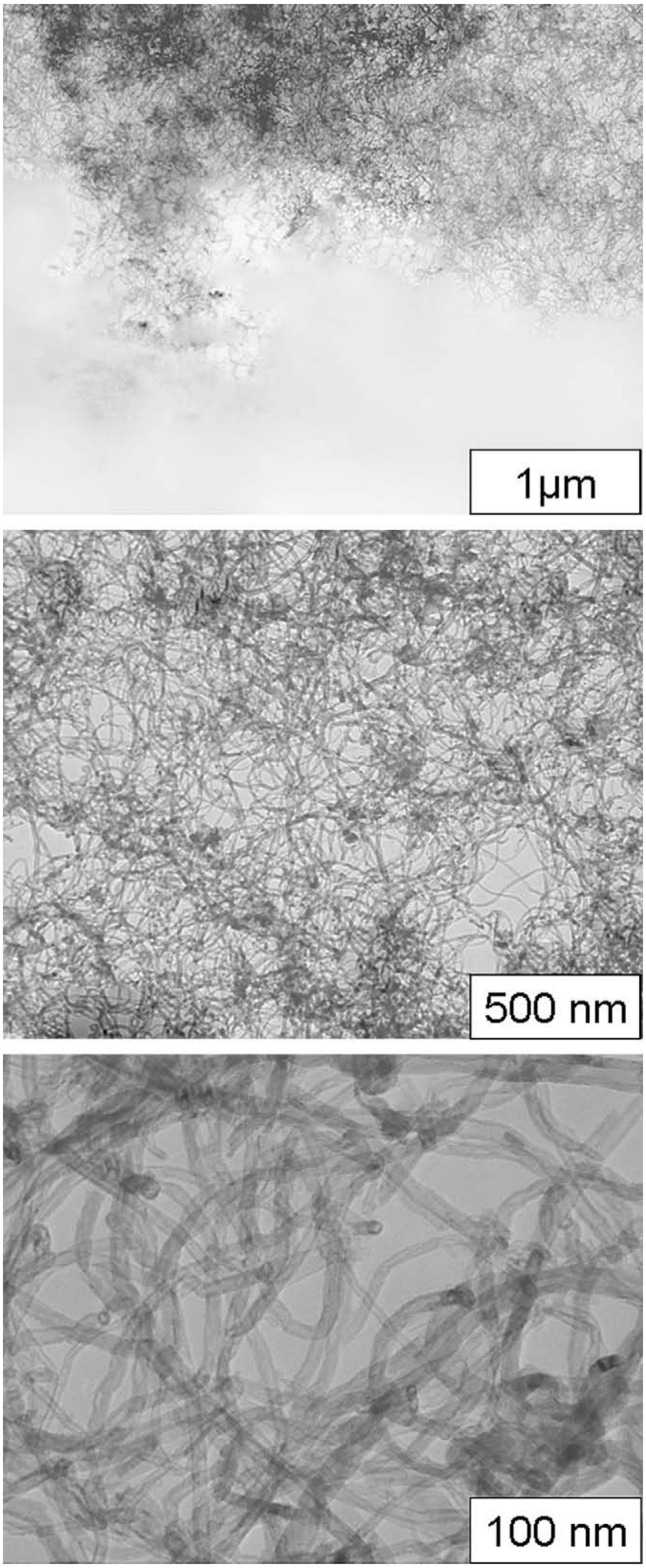

Fig. 9. TEM micrographs of pentadecane-grafted MWCNTs.

and penta-g-MWCNTs in chloroform and THF; and dispersed—as in case of penta-g-MWCNTs in DMF, toluene, DCB and xylene. The stability of pentadecane-grafted MWCNTs is disturbed in polar solvents such as acetone, chloroform and THF, however, pretty good solubility in DMF, toluene, DCB and xylene. The usual methods to separate the solubilized CNTs from those that are insoluble are vacuum filtration and Soxhlet extraction [29]. The solubility of these pentadecane stabilized dispersions was achieved according to the following procedure. At first, 200 mg of accurately weighed functionalized MWCNTs was added in 5 mL of the selected solvent under study in order to obtain a saturated solution. Then, the solution was sonicated, separated into three portions and left free standing for one month at room temperature. Then their upper half aliquot parts were carefully taken out with a syringe and solubility of pentadecane-grafted MWCNTs was finally calculated by an average weighing of the three samples after removing the solvent under vacuum at 100 °C for 12 h. The solubility values of pentadecane-grafted MWCNTs in typical organic solvents are given in Table 7. The reported solubilities highly depend on degree of functionalization and values reported in Table 7 correspond to solutions of penta-g-MWCNTs with a grafting density of 1.464 mmol/g (sample A). Depending on the solvent, solubilities vary from 1.1 mg/mL to 19.2 mg/mL. As shown in Table 7, penta-g-MWCNTs show the best solubility in dichlorobenzene (i.e. 19.2 mg/mL). These solubility values are close to those of octadecylamine modified MWCNTs reported by Guo [29] with solubilities varying from 9 mg/mL to 14.3 mg/mL in aromatic solvents and determined through UV/Vis absorption spectroscopy. As discussed by Guo [29], the relatively high solubilities of pentadecane-grafted MWCNT in various solvents provide the possibility to easily disperse MWCNTs which allows preparing MWCNTs/polymer composites.

It is evident from Table 7 that the classic principle of “like dissolves like” is no longer applicable here and does not explain well the solubility of functionalized nanotubes. Amazingly, even being nonpolar, penta-g-MWCNTs are not soluble in some nonpolar solvents like hexane, heptane, octane, and even in pentadecane; however soluble in toluene and xylene that are nonpolar as well. On the other hand these functionalized CNTs are soluble in one polar-aprotic solvent, i.e. DMF, but not soluble in the others like THF and acetone. Various accounts suggest surface tension [27,30] and dielectric constant [31,32] are better indexes of polarity; hence might be used to investigate this strange solubility behaviour. Table 7 shows an interesting correlation of solubility of penta-g-MWCNTs with surface tension and dielectric constant of the solvents. As a rule of thumb, penta-g-MWCNTs make stable suspensions in all those solvents having surface tension and dielectric constant greater than those of pentadecane (i.e. grafted species).

When it comes to chloroform, its surface tension is almost equal to that of pentadecane and dielectric constant, too, not higher enough making it insoluble. Stephenson et al. [26] have also reported a meagre value of solubility (0.12 mg mL^{-1}) for alkyl chains grafted MWCNTs in chloroform.

In addition, a transmission electronic microscope was used to evaluate the local state of debundling of functionalized MWCNTs. TEM pictures of the sonicated p-MWCNTs, cumyl-g-MWCNTs and penta-g-MWCNTs are shown in Figs. 7–9, respectively.

Figs. 7 and 8 are shown at 1 μm scale, since it is hard to take close up photos by TEM in the presence of large accumulated mass that do not let the light to pass through.

Apparently, TEM observations demonstrate that the functionalization leads to better debundling of MWCNTs. Fig. 7 shows the morphologies of p-MWCNTs and illustrates the heavily entangled nature of CNTs within these agglomerates leading to the presence of large bundles and ropes scattered around. However, it is not easy to distinguish the differences between the number and the size of agglomerates in p-MWCNTs and cumyl-g-MWCNTs from the TEM micrographs (Figs. 7 and 8 respectively). TEM micrographs of cumyl-g-MWCNTs (Fig. 8) seem not to show agglomerates as big as visible in Fig. 7 for p-MWCNTs. Here loosely entangled swelled mass shows that the functionalization has untied the otherwise tightly held bundles of p-MWCNTs. This morphology might better be understood considering the behaviour of cumyl-g-MWCNTs in various solvents (Fig. 6). Contrary to p-MWCNTs, cumyl-g-MWCNTs are precipitated as a swollen mass at the bottom of the vials, especially in toluene (Fig. 6) suggesting that functionalization has succeeded in unfastening the p-MWCNTs bundles, despite the low grafting density of cumyloxy groups.

In contrast, for the penta-g-MWCNTs sample, with a high grafting density, TEM micrographs at nanoscale show CNTs mostly debundled into individual tubes (Fig. 9) leading to a fine nanodispersion in various solvents (Fig. 6). Even at microscale, the image shows a large amount of light passing through TEM sample which gives an evidence of spacing between the individual nanotubes.

These results highlight that radical grafting of long alkane molecules onto the sidewalls of MWCNTs is a promising way to chemically graft polyethylene onto MWCNTs.

4. Conclusion

Thermolysis of dicumyl peroxide initiator performed in pentadecane and in presence of MWCNTs (depending on the melt conditions set up to chemically modify polyethylene) appeared to induce alkane grafting onto MWCNTs. This method is a simple way to directly incorporate organic moieties onto the CNTs' surface leading to pentadecane-grafted MWCNTs with a grafting density as high as 1.46 mmol/g at 150 °C. At higher temperatures, the grafting density decreases because the β-scission reaction of cumyloxyl radical accelerates as the temperature increases, leading to the formation of methyl radicals. These latter preferentially react by combination whereas cumyloxyl radicals are more prone to hydrogen abstraction from pentadecane.

Pentadecane-grafted MWCNTs have exhibited good dispersibility in various organic solvents and we showed that a grafting density of 1.464 mmol/g leads to a solubility of 19.2 mg/mL in dichlorobenzene.

Moreover, TEM images clearly indicated that the pentadecane coating grafted on the sidewalls allows debundling of MWCNTs to a high exfoliation degree.

We believe that this functionalization approach will provide convenience and versatility in building up polyolefin architectures on CNTs in future work.

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