

Tandem Action of Early–Late Transition Metal Catalysts for the Surface Coating of Multiwalled Carbon Nanotubes with Linear Low-Density Polyethylene

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The homogeneous surface coating of multiwalled carbon nanotubes with linear low-density polyethylenes, containing from 3 to 34 branches per 1000 carbon atoms, has been achieved for the first time by combining the polymerization-filling technique (PFT) with tandem copolymerization catalysis. This method, which takes advantage of the use of ethylene as single monomer feed, allows for the breakup of the native nanotube bundles and provides an effective way to control the branching in the PEs produced at the nanotube surface. TEM micrographs of the composite materials have shown an interesting dependence of the PE-coating morphology on the experimental parameters of the tandem system.

Introduction

Since their discovery in the early 1990s by Iijima,¹ carbon nanotubes (CNTs)² have attracted increasing attention in nanotechnology because of their outstanding high mechanical, thermal, and electrical properties.³ At present, technological applications of CNTs are being studied in a wide range of areas, spanning from construction to automotive and aerospace engineering, to alternative energy production, and to medicine, just to mention a few.⁴ Recently, much attention has been paid to CNT-based nanocomposites for the preparation of high-performance materials exhibiting improved or unusual mechanical and physical properties, even at very low nanofiller loading.⁵ It has been established that the combination of a soft polymer matrix with nanosized rigid filler particles can provide new nanocomposite materials with largely improved modulus and strength.⁶ Melt blending and solution blending are frequently used methods for the preparation of a variety of polymer/clay nanocomposites.⁷ However, the homogeneous dispersion of native CNTs within a polymeric matrix is relatively difficult to achieve under

classical melt blending conditions, especially in apolar matrixes such as polyolefins. Indeed, this kind of one-dimensional nanofillers tends to aggregate as very long bundles due to the high surface energy and the huge number of π – π electron interactions among the tubes, which may result in defect sites in the resulting composites.⁸ Therefore, a key factor to get appropriate materials consists in breaking down the native bundles of the aggregated CNTs to reach a high level of nanofiller dissociation, while maintaining a strong CNT–polymer interfacial adhesion for a good load transfer.

Several techniques have been developed to achieve a homogeneous and fine dispersion of the CNTs in polymer

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matrixes, for example in situ polymerization, ultrasonication, and chemical functionalization of the nanotube surface.^{9–14} The in situ polymerization and copolymerization of monomers by metallocene complexes activated by either physico-chemically^{14–16} or covalently¹⁷ anchored cocatalysts onto the nanotube surface is a recent method to obtain a homogeneous coating of the nanofillers with a polymeric matrix, leading to an effective breakup of the native nanotube bundles. This protocol is actually a variation of the polymerization-filling technique (PFT) originally developed for Ziegler–Natta polymerization^{18,19} and more recently applied in metallocene catalysis in conjunction with a large variety of microfillers such as kaolin, silica, wollastonite, and graphite.^{20–23} As a result, CNTs can be homogeneously coated by polyolefin chains grown on the external surface, leading to deaggregation of the CNTs. Some of us have successfully applied the PFT to the homogeneous or textured coating of CNTs (depending on the catalytic system used) with either semicrystalline HDPE^{14,15} or ethylene–norbornene copolymers.¹⁶ This procedure would allow for the economically viable production of high-performance nanocomposites via their dispersion in commercially available model polymer matrixes.^{5,24}

Even though catalytic systems based on metallocene/alkylaluminumoxane are excellent tools for the production of ethylene/ α -olefin copolymers, their extensive use in PFT still remains a challenge, in particular for the coating with structurally tailored materials. Indeed, the high cost of the monomers, largely dictated by their purification, limits the application of PFT to coatings derived from controlled ethylene/ α -olefin copolymerizations. This drawback can be overcome by replacing a traditional copolymerization process with a tandem protocol. Tandem copolymerization catalysis, using two or more different single-site catalysts in the same reactor, is a relatively recent technique for the production of branched polyethylene (PE) from ethylene as a single monomer feed.^{25,26} Some of us have recently described an efficient early–late tandem polymerization protocol based on the Ti^{IV} CG (constrained geometry) copolymerization

catalyst (TiCl₂[(η ⁵-C₅Me₄)SiMe₂(^tBuN)]) in combination with different bis-halide Co^{II} iminopyridyl complexes²⁷ as oligomerization systems.²⁸ Depending on the cobalt molar fraction (χ_{Co}), these Ti–Co systems can produce a variety of branched copolymers spanning from linear low-density polyethylene (LLDPE) to ultralow-density polyethylene (ULDPE), to amorphous ethylene/ α -olefin elastomers with T_g values as low as -60 °C. LLDPEs with an excellent branching selectivity have been also prepared using a zirconocene copolymerization catalyst selective for exclusively 1-butene incorporation.^{28d}

In this paper, we report an original approach for the preparation of multiwalled carbon nanotubes (MWCNTs) coated with structurally tailored linear low-density polyethylene (LLDPE) via the in situ tandem action of early–late transition metal complexes activated by MMAO-pretreated (modified methylaluminumoxane) CNTs. This procedure allows for the production of deaggregated and periodically LLDPE-coated MWCNTs, whose coating morphology can be finely tuned by varying the experimental conditions.

Experimental Section

General Considerations. All manipulations of air- and/or moisture-sensitive materials were carried out under a dry argon atmosphere, in a glovebox or using standard Schlenk-type techniques. Argon ($\geq 99.999\%$ from Rivoira) was dried through a CaCl₂ column and deoxygenated with an Oxisorb cartridge from Messer Griesheim prior to use. Prior to use, Ethylene N35 (Air–Liquide, $\geq 99.95\%$) was deoxygenated and dried through two columns containing the BASF catalyst R3-11 and activated molecular sieves (10 Å), respectively. Anhydrous toluene was obtained by means of a MBraun Solvent Purification System, and *n*-heptane was dried and distilled over Na prior to use. The imino(pyridine) cobalt complex CoCl₂(N₂)^{2Th} was synthesized according to published procedures.²⁷ Cp₂ZrCl₂ and TiCl₂[(η ⁵-C₅Me₄)SiMe₂(^tBuN)] were purchased from Sigma-Aldrich and MCAT GmbH, respectively, and used as received. MMAO-3A (7.0 wt % solution in *n*-heptane, $d = 0.734$, modified with isobutyl groups (CH₃/*i*-C₄H₉ = 2.3), was purchased from AkzoNobel and used as received. The purified multiwalled carbon nanotubes were kindly supplied by Nanocyl S.A. and were previously dried at 110 °C under reduced pressure (1.3×10^{-5} bar) overnight and then stored under N₂ atmosphere. The copolymerization reactions were performed with a 700 mL stainless steel reactor, constructed at the ICCOM-CNR (Firenze, Italy), equipped with a mechanical stirrer, a Parr 4842 temperature

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and pressure controller, a mass flow meter (Bronkhorst HI-TEC, F111C-AAB), equipped with a digital control for the connection to the PC, and an external jacket for the temperature control. The reactor was connected to an ethylene reservoir to maintain a constant gas pressure during the catalytic runs.

Carbon Nanotube Surface Activation. A 250 mL Schlenk flask was charged with 0.3 g of MWCNTs and heated at 110 °C under high vacuum for 1 h. The flask was then filled with nitrogen and cooled to room temperature. CNTs were suspended in 10 mL of dry and degassed toluene (or 1:1 toluene/*n*-heptane) and heated under stirring at 50 °C in an oil bath. The suspension was then treated under nitrogen with 8.2 mL of MMAO-3A and maintained under vigorous stirring for 1 h. The solvent was distilled off under reduced pressure, and the resulting solid was heated at 150 °C under vacuum for a further 90 min to remove all volatiles. The solid was handled in a glovebox and finely crushed by means of a flexible doctor blades spatula before being transferred into the reactor.

In Situ Tandem Copolymerization Processes. Tandem system A: $\text{CoCl}_2\text{N}_2^{\text{Th}}$ (**1**) and Cp_2ZrCl_2 (**2**) A 0.7 g sample of MMAO-pretreated MWCNTs (see above for the CNT activation) were suspended in 50 mL of dried toluene directly in a 700 mL stainless steel reactor equipped with a magnetic drive stirrer and temperature controller. The reactor was filled with argon, and then it was heated to 50 °C by means of an external circulating bath and purged with ethylene (15 s) to remove argon. Finally, the reactor was pressurized with ethylene (2 bar) and stirred at 450 rpm. After complete temperature and pressure equilibration, a toluene solution (8.6 mM) of $\text{CoCl}_2(\text{N}_2^{\text{Th}})$ (**1**) (0.75 mL for $\chi_{\text{Co/Zr}} = 0.8$ or 0.81 mL for $\chi_{\text{Co/Zr}} = 0.9$) and a toluene solution (1.6 mM) of Cp_2ZrCl_2 (**2**) (0.92 mL for $\chi_{\text{Co/Zr}} = 0.8$ or 0.62 mL for $\chi_{\text{Co/Zr}} = 0.9$, $[\text{Al}]/[\text{M}] = 750$) were added to the reactor in sequence. Ethylene was continuously fed to maintain the reactor pressure at the desired value all over the catalytic run. The reactions were terminated after a fixed ethylene consumption (from 0.5 to 1 bar). Afterward, the reactor was depressurized and cooled to 20 °C. The final material was precipitated using 100 mL of methanol acidified with hydrochloric acid, under stirring for 30 min. After filtration and washing with small portions of MeOH and *n*-pentane, the resulting material was dried at 30 °C under vacuum overnight.

Tandem System B: $\text{CoCl}_2\text{N}_2^{\text{Th}}$ (**1**) and $[(\eta^5\text{-C}_5\text{Me}_4)\text{SiMe}_2(\text{N}^i\text{Bu})]\text{TiCl}_2$ (**3**). The polymerization using reaction method **B** was carried out following the procedure described above, except for using a 1:1 toluene/*n*-heptane solution (1.2 mM) of $\text{CoCl}_2(\text{N}_2^{\text{Th}})$ (**1**) (0.25 mL for $\chi_{\text{Co/Ti}} = 0.2$ or 0.5 mL for $\chi_{\text{Co/Ti}} = 0.4$) and a 1:1 toluene/*n*-heptane solution (2.6 mM) of $[(\eta^5\text{-C}_5\text{Me}_4)\text{SiMe}_2(\text{N}^i\text{Bu})]\text{TiCl}_2$ (**3**) (0.46 mL for $\chi_{\text{Co/Ti}} = 0.2$ or 0.35 mL for $\chi_{\text{Co/Ti}} = 0.4$, $[\text{Al}]/[\text{M}] = 4000$), as copolymerization protocol.

Materials Characterization. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the extracted polymer materials were recorded on a Bruker Avance 300 MHz instrument (100.6 MHz) at 110 °C. Polymer samples of 80–200 mg were dissolved in 2 mL of 1,1,2,2-tetrachloroethane- d_2 ($\delta = 74.24$ ppm) in 10 mm NMR tubes (pulse width, 30°; pulse delay, 5 s; acquisition time, 0.65 s; number of scans, 6144). The differential scanning calorimetry (DSC) analysis of the LLDPE-coated MWCNTs and of the extracted materials was carried out by means of either a Mettler Toledo DSC 821^e instrument equipped with an intracooler and calibrated with the melting transition of indium (156.1 °C) or a Q 200-TA instrument under nitrogen atmosphere using 5–10 mg samples. Any thermal history in the polymers was eliminated by first heating the specimen at a heating rate of 20 °C min⁻¹ to 200 °C, cooling at 20 °C min⁻¹ to -70/-100 °C, and then recording the second scan from -70 to 200 °C. The results of the second heating run were used to determine the melting points. The molecular weight (M_w) and the molecular

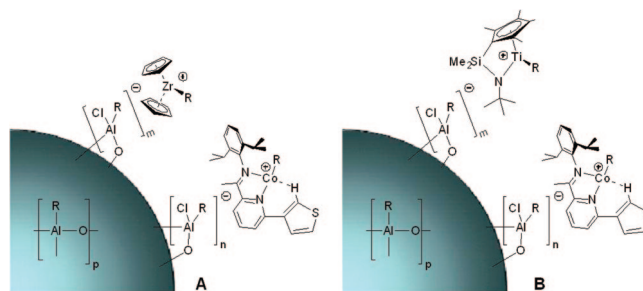


Figure 1. (A) Active species generated at the CNT surface with a tandem system made of $\text{CoCl}_2\text{N}_2^{\text{Th}}$ (**1**)/ Cp_2ZrCl_2 (**2**)/MWCNT-MMAO-3A. (B) Active species generated at the CNT surface with a tandem system comprising $\text{CoCl}_2\text{N}_2^{\text{Th}}$ (**1**)/ $[(\eta^5\text{-C}_5\text{Me}_4)\text{SiMe}_2(\text{N}^i\text{Bu})]\text{TiCl}_2$ (**3**)/MWCNT-MMAO-3A.

weight distribution (M_w/M_n) of the polymers were evaluated by gel permeation chromatography (GPC) with a Waters GPC 2000 system equipped with a set of three columns Styragel HT6, HT5, and HT3, and refractive index detector. The analyses were performed at 140 °C using 1,2,4-trichlorobenzene as solvent with an elution rate of 1 mL min⁻¹ and standard polystyrene as the reference. The thermogravimetric analysis (TGA) was carried out using a Q 50-TA instrument under He or air atmosphere. The samples were heated from 30 to 850 °C at 20 °C min⁻¹ under a He flow or from 30 to 950 °C at 20 °C min⁻¹ under an air flow. The morphology of the PE-coated MWCNTs was determined by transmission electron microscopy (TEM) (Philips CM 200 at 120 kV).

Results and Discussion

The tandem copolymerization catalysis applied to the PFT for the coating of CNTs with LLDPE can be conveniently described as a four-step process which involves (i) the physicochemical anchoring of the cocatalyst, MMAO, onto the CNT surface; (ii) the addition of the oligomerization and copolymerization precatalysts and their subsequent activation at the surface of the nanofillers; (iii) the surface-initiated tandem copolymerization of ethylene and α -olefins; and (iv) the growth and precipitation of LLDPE onto the CNTs leading to their coating and separation. This technique, recently applied for the preparation of polyethylene (PE) as well as ethylene/norbornene (E/N) coated CNTs, has been now employed to synthesize a new class of nanocomposites characterized by tailored polyolefin microstructure.

The cocatalyst fixation onto the surface of the CNTs has been achieved by reacting dried MWCNTs with MMAO-3A in toluene at 50 °C for 1 h, followed by solvent evaporation to dryness. Keeping the solid under high vacuum at 150 °C for prolonged times resulted in the complete removal of the volatiles and ultimately in the immobilization of the cocatalyst over the nanofiller surface. Such a treatment was found to maintain the cocatalyst physicochemically anchored to the surface of the nanotubes even after several washings with hot toluene.¹⁵ These MMAO-pretreated CNTs were then placed in contact with the tandem copolymerization systems (either system **A** or system **B**), to form alkyl-cationic oligomerization/copolymerization species located in close proximity to the nanotube surface via electrostatic interaction between the cationized metal centers and the MMAO anions anchored to the nanofiller surface (Figure 1).

Two different tandem copolymerization protocols, involving an (imino)pyridine cobalt(II) dichloride as oligomeriza-

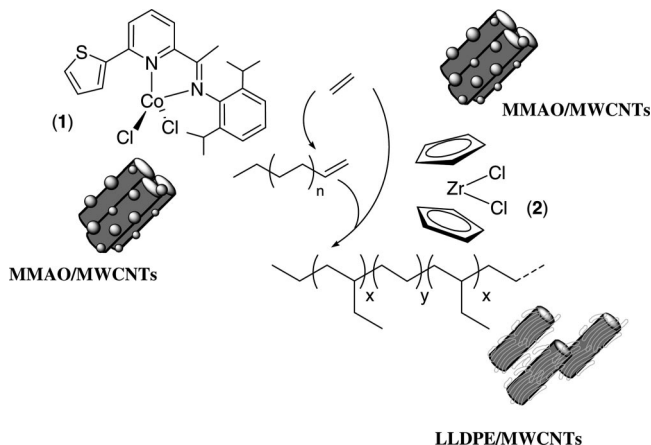


Figure 2. In situ tandem copolymerization catalysis by tandem system A.

tion precursor and an early metallocene as copolymerization system (either the bis(cyclopentadienyl)zirconium(IV) dichloride or the half-sandwich metallocene complex $[(\eta^5\text{-C}_5\text{Me}_4)\text{SiMe}_2(\textit{t}\text{BuN})]\text{TiCl}_2$), have been used to control the number and type of branches of the LLDPE coating. To this purpose, the cobalt molar fraction (χ_{Co}) proved to be a parameter of crucial importance.

The ethylene/ α -olefin copolymerization catalysts are generally very active but not selective. Therefore, when the oligomerization catalyst produces different types of α -olefins, for example mixtures featured by a Schulz–Flory distribution, the LLDPE microstructure, especially in terms of length and distribution of the branches, is hardly reproducible and is difficult to control.^{28,29} In order to avoid this problem, the copolymerization catalysts may be flanked by oligomerization catalysts that are able to produce a unique α -olefin.²⁷ As an alternative to the use of a selective ethylene oligomerization catalyst, one may employ a copolymerization system that exhibits different kinetics of α -olefin incorporation into the growing copolymer chain as a function of the α -olefin length and concentration as well as other experimental parameters.

The first tandem system described in this paper (hereafter named as tandem system A) comprises CoCl_2 modified with a 6-thienyl-2-(imino)pyridine ligand, known to produce α -olefins with a Schulz–Flory α -value of about 0.08 (butenes 92.0%, hexenes 7.4%), and Cp_2ZrCl_2 as copolymerization catalyst. Both catalyst precursors were activated at the surface of MMAO-3A pretreated MWCNTs (Figure 2).

Previous studies have demonstrated that, upon activation by MAO (methylaluminumoxane) in toluene, tandem system A allows one to convert ethylene into LLDPE with exclusively ethyl branches, melting temperatures as low as 82 °C, and productivities as high as 25 400 kg (mol of Zr)⁻¹ h⁻¹.^{28d} The excellent branching selectivity is controlled by the metal-

locene catalyst that, under certain experimental conditions and in spite of the α -olefins produced by the Co complex, does not copolymerize higher α -olefins than 1-butene. A similar trend has been also observed using as activator the MMAO-3A pre-coated MWCNTs. The exclusive presence of ethyl branches in the LLDPEs produced at the nanofiller surface was unambiguously demonstrated by recording $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the polyolefin materials obtained after extraction with toluene from the nanocomposites with a 50 mL Kumagawa extractor. The analysis of the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra has also shown the formation of LLDPEs with a number of ethyl branches per 1000 carbon atoms varying from 3.5 to 13.5 at 0.8 and 0.9 χ_{Co} 's, respectively.^{28,30}

From a perusal of the data reported in Table 1, one may readily realize the importance of χ_{Co} , hence of the instantaneous concentration of the oligomers in the reactor, to control both the productivity and the characteristics of the LLDPE product. A positive “comonomer effect”^{28,31} was obtained at 0.8 and 0.9 values of χ_{Co} (runs 1–3). At χ_{Co} of 0.9, however, the “comonomer effect” was less marked, likely due to the huge instantaneous concentration of 1-butene, which can hamper the regular and continuous ethylene uptake by the copolymerization catalyst. No branches were observed for polymer composites prepared at χ_{Co} 's lower than 0.8. Finally, we have observed a close relationship between the high concentration of free short-chain α -olefins and the morphology of the coating (vide infra).

Replacing Cp_2ZrCl_2 with $[(\eta^5\text{-C}_5\text{Me}_4)\text{SiMe}_2(\textit{t}\text{BuN})]\text{TiCl}_2$ (Ti^{IV} CGC, DOW) (3) has been found to generate a new tandem system (hereafter named as tandem system B), capable of producing PEs with higher degrees of ethyl and butyl branching (Figure 3).

The DOW complex 3 represents a milestone in catalytic ethylene homopolymerization and copolymerization with α -olefins.^{32,33} As such, it constitutes the ingredient of many successful tandem processes in conjunction with both early and late metal catalysts.^{28,29,34–36} As previously mentioned, the χ_{Co} value can greatly influence the characteristics of the resulting copolymers. Indeed, the tandem system B, upon activation by MAO in toluene, is able to produce not only semicrystalline LLDPE but also completely amorphous

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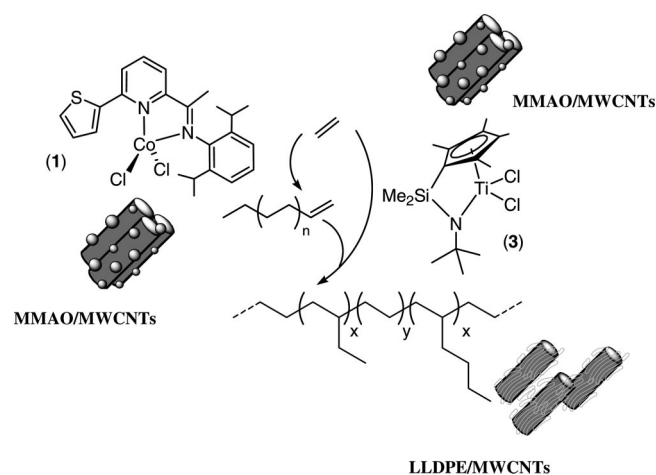
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Table 1. Tandem Copolymerization Catalysis Applied to the Polymerization-Filling Technique Using Tandem Systems A and B

run ^a	tandem system	Co (μmol)	Zr (μmol)	Ti (μmol)	[Al]/[M] ^b	χ_{Co} ^c	A^d	total branch ^e (%)	C ₂ br (%)	C ₄ br (%)	PE ^f (%)	T_m ^g (°C)		ΔH_m (J g ⁻¹)	X^h (%)	M_w (kg mol ⁻¹) ⁱ	M_w/M_n
												LLDPE-NT composites	extracted LLDPEs				
1	—	—	1.5	—	750	0	1860	—	—	—	73.0	135.3	135.0	124.2	46.01	67	10.49
2	A	6.5	1.5	—	750	0.8	9980	3.5	100	—	81.4	130.9	129.1	122.8	45.5	55	3.11
3	A	7	1	—	750	0.9	2690	13.5	100	—	70.8	126.1	124.0	114.6	42.46	48	2.72
4	—	—	—	1.5	4000	0	906	—	—	—	68.8	134.2	133.1	125.7	46.57	67	2.73
5	B	0.3	—	1.2	4000	0.2	770	23	62.43	37.57	66.2	116.3	114.2	97.7	36.20	35	2.67
6	B	0.6	—	0.9	4000	0.4	713	29.8	69.31	30.69	35.3	107.6	101.7	88.0	32.62	41	3.21
7	B	0.6	—	0.9	4000	0.4	500	34.5	72.56	27.44	26.4	102.3	93.4	93.8	34.75	35	3.13

^a Reaction conditions: stainless steel reactor, 700 mL; 0.7 g of MMAO-3A precoated MWCNTs; 50 mL toluene, stirrer rate, 450 rpm; C₂H₄ pressure, 2 bar; 1 bar ethylene consumption; temperature, 50 ± 2 °C. ^b [M] = [Zr] + [Co] or [Ti] + [Co]. ^c $\chi_{\text{Co}} = [\text{Co}]/([\text{Co}] + [\text{Zr}])$ for system A or $\chi_{\text{Co}} = [\text{Co}]/([\text{Co}] + [\text{Ti}])$ for system B. ^d Activity expressed as kg of polymer (mol of Zr·h)⁻¹ for system A or as kg of polymer (mol of Ti·h)⁻¹ for system B. ^e Number of branches per 1000 C atoms calculated from ¹³C NMR. ^f Determined by TGA under He flow (20 °C min⁻¹). ^g Determined by DSC (second heating scan at 20 °C min⁻¹). ^h Crystallinity calculated as $(\Delta H_f / \Delta H_{f0}) \times 100$, where ΔH_{f0} is 269.9 J g⁻¹. See refs 37 and 38. ⁱ Determined by GPC.

**Figure 3.** In situ tandem copolymerization catalysis by tandem system B.

materials with T_g values as low as -60 °C by simply varying the χ_{Co} from 0.05 up to 0.75.^{28a}

In the presence of MMAO-3A precoated MWCNTs, the tandem system B produced branched PE starting from $\chi_{\text{Co}} = 0.2$ (23 total branches per 1000 carbon atoms, 62.4% ethyl branches and 37.6% butyl branches) (run 5). Increasing χ_{Co} to 0.4 resulted in the formation of LLDPE with a number of ethyl and butyl branches per 1000 carbon atoms as high as 34.5 (72.6% ethyl branches and 27.4% butyl branches) (runs 6 and 7).

Beyond this χ_{Co} value, partially soluble low-density PE was produced. Despite the use of a solvent comprising toluene and *n*-heptane in a 1:1 (v/v) ratio, the hyperbranched PE, due to its higher solubility, gave nanocomposites with no effective coating. Indeed, the TEM analysis of these materials (not reported here) showed only a close contact between the polyolefin and the surface of the nanotube.

A slight decrease in productivity, as compared to the homopolymerization catalysis by **3**, was observed for the tandem system B, with 0.2 and 0.4 χ_{Co} 's. This "negative comonomer effect"³⁹ may be due to the too-high efficiency of the oligomerization catalyst^{28a} that rapidly consumes most of the ethylene feed.

The influence of χ_{Co} on the copolymer properties has been also evaluated for either tandem system by means of DSC and GPC analyses (Table 1). The thermal characteristics of the LLDPE-coated MWCNTs as well as that of the extracted LLDPE were determined by DSC (Figure 4). Melting points between 135 and 102 °C were in line with the formation of materials spanning from HDPE to semicrystalline LLDPE with increasing branching.⁴⁰ The T_m value decreased from 135.3 °C for the PE produced by **2** (run 1) to 126.1 °C for the LLDPE produced by the tandem system A with $\chi_{\text{Co}} = 0.9$ (run 3), and from 134.2 °C for the PE produced by **3** (run 4) to 102.3 °C for the LLDPE produced by the tandem system B with $\chi_{\text{Co}} = 0.4$ (run 7).

Interestingly, the T_m values measured for the PE composites were invariably higher (from a minimum of 0.4 °C to a maximum of 8.5 °C) than the values observed for the extracted PE counterparts. Such a difference, particularly evident at a low coating (Table 1, run 7, and Figure 4) and ascribed to the action exerted by the CNTs on the mobility of the polyolefin chains, can be ultimately related to a good adhesion of the latter to the CNT surface.¹⁶ A similar effect has been recently observed by some of us for HDPE-coated MWCNTs and attributed to a remarkable nucleating effect of the CNTs on the polyolefin matrix, leading ultimately to a "bottle-brush" morphology of the nanocomposites.^{24b}

The GPC experiments showed lower molecular weights (M_w) for the copolymers compared to the homopolymers. A significant change on the M_n values was also observed by varying χ_{Co} . The high concentration of free short-chain α -olefins was found to control the polydispersity of the resulting copolymers (Table 1, run 1 vs runs 2 and 3) by favoring chain transfer over chain propagation. In all cases, the GPC curves were consistent with a monomodal distribution of the molecular weights.

In order to characterize the extent of the LLDPE coating around the carbon nanotubes and the coating morphology as well, the composite materials were studied by transmission electron microscopy (TEM). In all cases, the TEM analyses showed a relatively good deaggregation of the native CNT

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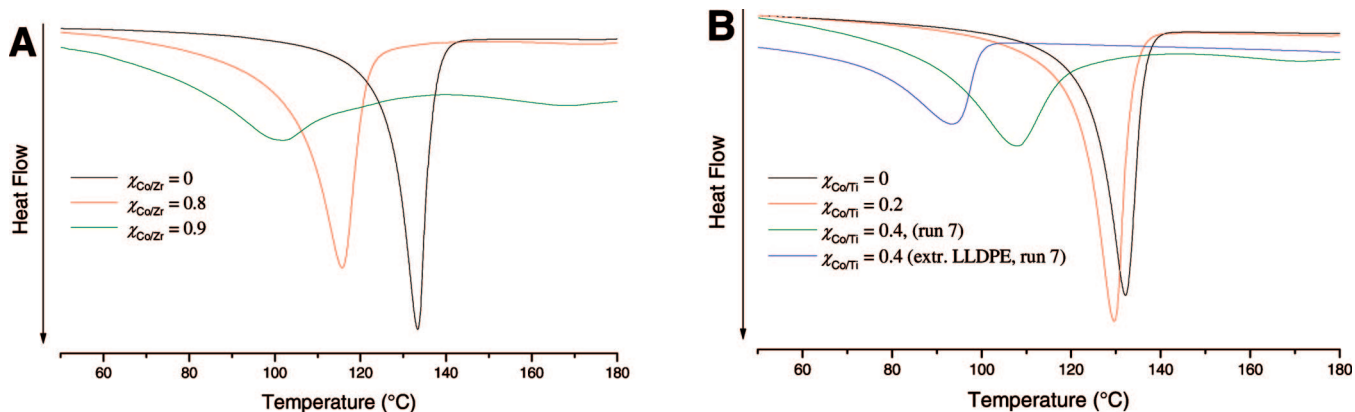


Figure 4. DSC curves of the LLDPE-coated MWCNTs as obtained by the PFT technique using the tandem system **A** (A) or the tandem system **B** (B) at different χ_{Co} values.

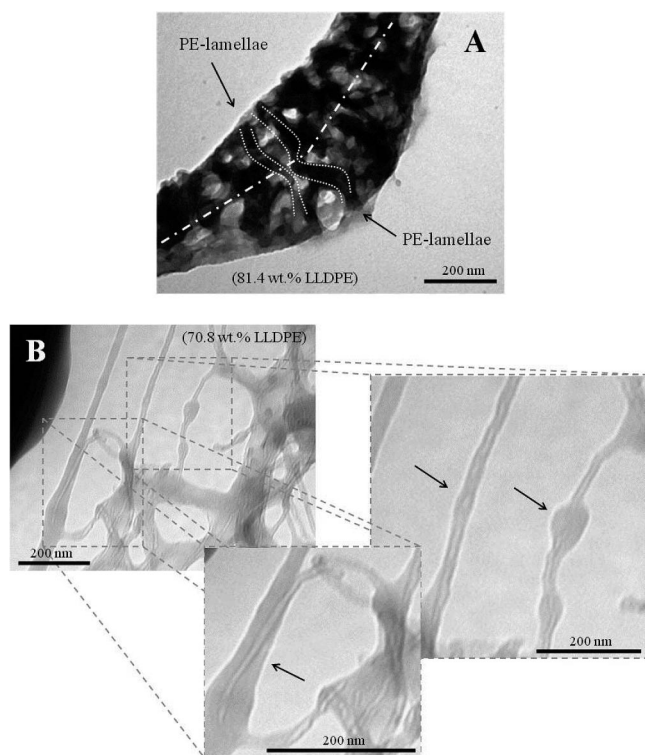


Figure 5. TEM micrographs of tandem system **A**. (A) $\chi_{Co} = 0.8$; (B) $\chi_{Co} = 0.9$.

bundles together with a homogeneous polyolefin coating of the tubes. The tandem system **A** was found to produce nanocomposites with a strictly χ_{Co} -dependent coating morphology. Figure 5A, which refers to the tandem system **A** at $\chi_{Co} = 0.8$, shows a typical crystalline coating morphology made of disk-shaped objects, corresponding to LDPE single-crystal lamellae grown all around the NT (dashed lines) and arranged in a new nanohybrid morphology, the so-called “shish-kebab”-like structure. The central *shish* is the carbon nanotube while the *kebabs* are formed by the PE chains. Such a morphology has already been obtained by Li et al.⁴¹ using a controlled HDPE crystallization method from a solution to obtain such a periodically patterned polymeric material on individual carbon nanotubes. Finally, it should be noted that most of the kebabs adopt a nearly perpendicular

orientation to the MWNT surface, thus favoring the growth of LLDPE into larger crystals.^{15b}

Figure 5B shows a nanohybrid obtained with the same tandem system at $\chi_{Co} = 0.9$, with a continuous and relatively smooth coating (see arrows), which is typical of a “sausage-kebab”-like structure and consistent with a more amorphous PE produced at the nanotube surface (see Table 1, run 2 vs run 3). A great number of other factors may affect the morphology of the PE coating, including the reaction temperature, the type of cocatalyst, and the solvent used, just to mention a few.^{14,15} The solvent is most likely responsible for the changes observed in the coating morphology of the two nanocomposites prepared at 0.8 and 0.9 χ_{Co} 's, respectively. Indeed, the reduced crystallinity of the sample prepared at $\chi_{Co} = 0.9$ is likely caused by both a higher extent of α -olefin incorporation in the growing polymer and a “cosolvent” effect generated by a high concentration of the free oligomers in the reactor.

The simultaneous occurrence of these two effects was confirmed by a comparison of the coating morphologies observed for the samples prepared by the two tandem systems. Indeed, typical TEM micrographs for the three samples obtained by the tandem system **B** at $\chi_{Co} = 0$, 0.2, and 0.4, respectively, showed that a crystalline “shish-kebab”-like structure of the LLDPE-coating was maintained irrespective of the more amorphous PE produced (see Table 1, runs 5 and 6) at any cobalt loading (Figure 6).

Finally, no significant agglomeration was shown by the TEM micrographs of the two series of nanocomposites, indicating that the original MWCNTs are separated into individual tubes by the MMAO-3A/tandem system-induced polymerization.

Conclusions

The in situ tandem copolymerization catalysis for the homogeneous coating of CNTs with linear low-density polyethylene represents a real breakthrough for controlling the microstructures of the growing polyolefin chains at the nanofiller surface. Textured surface coating of MWCNTs, as evidenced by TEM micrographs, was conveniently achieved by the in situ tandem copolymerization catalysis of ethylene and α -olefins using ethylene as a single monomer feed. This approach allows for an effective control of the

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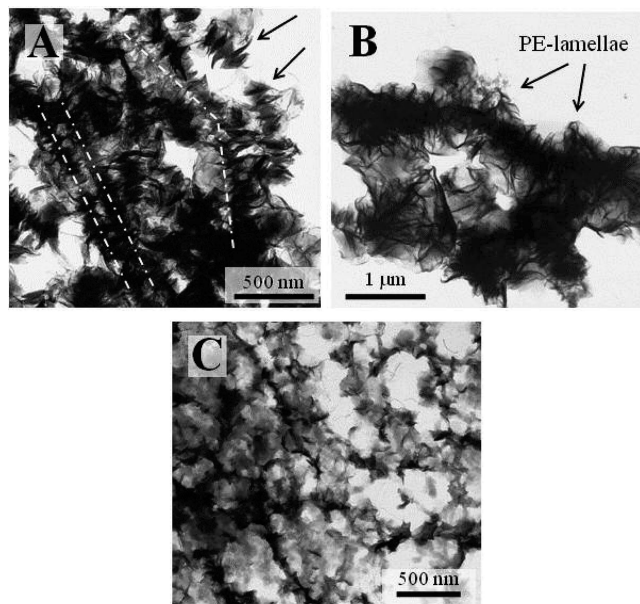


Figure 6. TEM micrographs of tandem system **B**. (A) $\chi_{Co} = 0$ (68.8 wt % LLDPE); (B) $\chi_{Co} = 0.2$ (66.2 wt % LLDPE); (C) $\chi_{Co} = 0.4$ (35.3 wt % LLDPE).

polyolefin microstructure in terms of number and type of branches. As such, it provides a valuable alternative to traditional copolymerization catalysis. In particular, control

of the number of branches has been conveniently achieved by varying the molar fraction of the oligomerization catalyst, while the type of branching (ethyl, butyl, etc.) has been tuned by selecting the appropriate copolymerization system. Our results contribute to define PFT as an efficient process both for the surface modification of nanotubes (e.g., LLDPE coating) and deaggregation from the native nanofiller bundles. The different coating morphologies of the two series of composites obtained are expected to affect their macroscopic properties, particularly the electrical conductivity, as well as their usability as “masterbatches” in the preparation of MWCNT nanocomposites, based on commercial thermoplastic matrixes.⁵

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