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Ethylene–Norbornene Copolymerization by Rare-Earth Metal Complexes and by Carbon Nanotube-Supported Metallocene Catalysis

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Summary: E–N copolymerization with a number of half-sandwich rare-earth metal compounds $[M(\eta5\text{-}C_5Me_4SiMe_2R)(\eta1\text{-}CH_2SiMe_3)_2(L)]$ (M = Sc, Y, Lu) has been achieved. Mainly atactic alternating E–N copolymers are obtained with all catalytic systems. Interestingly, copolymers arising from $[Sc(\eta5\text{-}C_5Me_4SiMe_2C_6F_5)(\eta^1\text{-}CH_2SiMe_3)_2(THF)]/[/[Ph_3C][B(C_6F_5)_4]$ possess narrower molar mass distributions than those from $[Sc(\eta^5\text{-}C_5Me_4SiMe_3)(\eta^1\text{-}CH_2SiMe_3)_2(THF)]/[Ph_3C][B(C_6F_5)_4]$. In addition, homogeneous surface coating of multi-walled carbon nanotubes is accomplished for the first time by in situ E–N copolymerization as catalyzed by *rac*-Et(Ind)$_2$ZrCl$_2$/MMAO-3A anchored onto the carbon nanotube surface. The copolymerization reaction allows for the destructuration of the native nanotube bundles. The relative quantity of E–N copolymer can be tuned up as well as the norbornene content in the formed copolymers and accordingly their glass transition temperature. By melt blending with an ethylene-vinyl-*co*-acetate copolymer (27 wt.-% vinyl acetate comonomer) matrix, high performance polyolefinic nanocomposites are obtained.

Keywords: ethylene–norbornene copolymers; living polymerization; metallocene catalysts; polymer nanocomposites; rare earth metal catalysts

Introduction

Ethylene (E) – norbornene (N) copolymers compose one of the most interesting novel class of polymer materials industrially produced by metallocene catalysts.[1–6] They are commercialized as high performance engineering polymers due to a good combination of many desirable properties. To our knowledge only one report on the E–N copolymerization by alkyl rare-earth metal complexes has appeared in the literature.[7] These systems are of special interest since they can yield active polymerization systems without or with a low amount of aluminum alkyls, which are responsible of important chain transfer reactions. Thus, the design of such systems could allow to achieve living polymerization.

Carbon nanotubes (CNTs) have extraordinary properties such as extremely high mechanical strength, high electrical and thermal conductivity. As a result of these outstanding properties, CNTs are expected to have potential applications in a wide range of areas, including construction, mechanical, automotive, aerospace engineering, electrochemical, biomedical, and electrical applications.[8–11] Separation of CNTs, which have very strong tendency to

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aggregation, is essential for these applications.

Here we report on:

A) E–N copolymerization with a number of half-sandwich rare-earth metal compounds [$M(\eta^5$-$C_5Me_4SiMe_2R)(\eta 1$–$CH_2SiMe_3)_2(L)$].
B) Homogeneous surface coating of multi-walled carbon nanotubes achieved for the first time by in situ E–N copolymerization as catalyzed by *rac*-Et(Ind)$_2$Zr-Cl$_2$/MMAO-3A anchored onto the carbon nanotube surface.

Results

Ethylene–Norbornene Copolymerization by Rare-Earth Metal Complexes

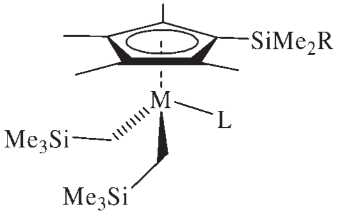
A number of rare-earth metal compounds were synthesized by some of us[12–13] to evaluate the influence of metal size and different electronic properties on the catalyst activity of the system [$M(\eta^5$-$C_5Me_4SiMe_2R)(\eta^1$-$CH_2SiMe_3)_2(L)$]/[Al]/[Ph_3C][$B(C_6F_5)_4$] (M = Sc, Y, Lu; [Al] = AlR'_3, MAO) (Scheme 1).

Variation on the silyl group of the tetramethylcyclopentadienyl ring allows examination of steric and electronic effects of the ligand on the complex geometry and the resulting polymerization activity. A protocol had been found to activate these systems for styrene and other α-olefin polymerization.[14] The influence of the kind and stoichiometry of various aluminum alkyl cocatalysts on the polymerization activity of selected catalyst systems was investigated.

Here we report on the tests of some of half-sandwich rare-earth metal compounds for E–N copolymerization. All copolymers have been characterized by ^{13}C NMR, GPC, and DSC. Table 1 reports a selection of experiments. The first screening has been performed on scandium complexes of general formula [$Sc(\eta^5$-$C_5Me_4SiMe_2R)(\eta^1$-$CH_2SiMe_3)_2(L)$] (R = Me (**1**), Ph (**2**), C_6F_5(**3**), 2-pyridyl (**4**); L = THF (**1, 2 3**), 2-pyridyl (**4**)). Copolymerizations were performed in toluene solution, with [Ph_3C][$B(C_6F_5)_4$] as activator in the presence of $AlBu^i_3$ (TIBA) or dried methylaluminoxane (MAO) as scavenger (Scheme 2). The aluminum activators have been selected on the basis of previous experiments on styrene polymerization[14] and in order to reduce the probability to have chain transfers.

In the initial experiments (# 1–8) optimal conditions required a greater amount of catalyst than in the second series (# 9–12) and both [Ph_3C][$B(C_6F_5)_4$] and [Al] in 1:1 ratio with the catalyst. The experiments with TIBA (# 1–4) were performed at 50 °C, while tests of the catalytic systems with MAO (# 5–8) were performed at lower temperature (25 °C), that is, under better controlled conditions since the system **1** with MAO resulted more active.

Catalyst **1** (R = Me) is the most active one, showing the maximum activity in the presence of MAO (# 5), while those with R = C_6F_5 (**3**) and py (**4**) are more active in the presence of TIBA (# 3 and 4). The complex bearing Ph (**2**) is not active under any condition used so far. Activity values with catalyst **1** are more than one order of magnitude higher than with the other tested



1 M = Sc, R = Me, L = THF
2 M = Sc, R = Ph, L = THF
3 M = Sc, R = C_6F_5, L = THF
4 M = Sc, R = 2-py, L = 2-py
5 M = Y, R = C_6F_5, L = THF
6 M = Lu, R = C_6F_5, L = THF

Scheme 1.
Catalysts precursors investigated.

Table 1.
E/N copolymerizations results.[a]

Entry	Complex	μmol	[Al]	N/E	T	Time	Yield	Activity[b]	N polymer content[c]	M_n[d]	M_w/M_n[d]	T_g[e]
				mol/mol	°C	min	mg		mol%	10^4Da		°C
1	**1**	20	TIBA	9.83	50	30	800	80	46	3	2.70	93
2	**2**	20	TIBA	9.83	50	30	–	–	–	–	–	–
3	**3**	20	TIBA	9.83	50	30	182	14	43	7	1.33	88
4	**4**	20	TIBA	9.83	50	30	198	20	34	12	1.23	–
5	**1**	20	MAO	5.63	25	30	900	180	45	4	2.06	113
6	**2**	20	MAO	5.63	25	30	–	–	–	–	–	–
7	**3**	20	MAO	5.63	25	30	12	1.2	–	–	–	–
8	**4**	20	MAO	5.63	25	30	83	8	24	–	–	–
9	**1**[f]	10	–	2.52	25	5	450	540	38	7	1.41	103
10	**3**[f]	10	–	5.63	25	5	263	315	34	6	1.17	89
11	**5**[f]	10	–	5.63	25	20	125	37	31	–	–	70
12	**6**[f]	10	–	5.63	25	15	–	–	–	–	–	–

[a] Conditions: V = 20 mL, [**complex**]/[$Ph_3CB(C_6F_5)_4$]/[Al] = [1]/[1]/[1].
[b] Kg P(E-co-N)*mol^{-1}Sc*h^{-1}.
[c] Determined by ^{13}C NMR.
[d] Determined by DSC.
[f] Accurately dried toluene and norbornene stored on sodium mirror covered glasses.

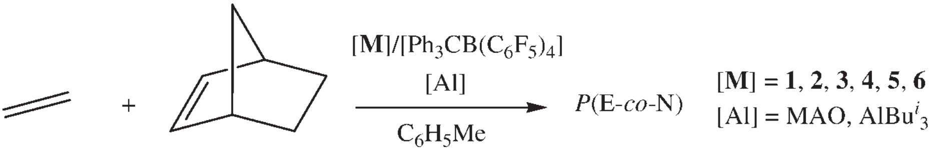
systems. This could be due both to steric hindrance and to electronic factors.

The fraction of norbornene incorporated in the copolymer has been determined by ^{13}C NMR spectra analysis.

Mainly atactic alternating[15–16] E–N copolymers are obtained with all catalytic systems, with an average norbornene content of about 40 mol% (see Figure 1). By comparing entries 1 and 5 it could be noticed that there is no evidence of an effect of the nature of scavenger in the norbornene incorporation. With catalyst **1** norbornene is better incorporated into the copolymer (46 mol%), while incorporation decreased with catalyst **4**. This behaviour is probably due to the bite of chelating ligand in complex **4** that decreases the accessibility of norbornene to metal centre.

Molar mass distributions of E–N copolymers (50 °C) are narrower than those of polystyrenes (room temperature) obtained with the same catalysts. The narrower molar mass distributions have been obtained with catalyst **3** and **4** at 50 °C (Table 1, # 3 and 4). However, the copolymer obtained by **4** has shown a low value in intrinsic viscosity (η = 0,1 dl/g). Very interestingly copolymers arising from **3**/[Ph_3C][$B(C_6F_5)_4$] possess narrower molar mass distributions than those from **1**/[Ph_3C][$B(C_6F_5)_4$] maintaining high norbornene incorporation. The T_g values of entries 1 and 3 prepared at 50 °C are lower than those at 25 °C (#5) at parity of norbornene content and molar masses. This seems to arise from the presence of species of low molar masses or with branches as visible in the ^{13}C NMR spectra (starred signals in Figure 1- bottom).

These catalysts revealed to be very sensitive to experimental conditions: normal reactants purification protocol, suitable for olefins polymerization by standard



Scheme 2.
Copolymerization of ethylene and norbornene with rare-hearth metal catalysts.

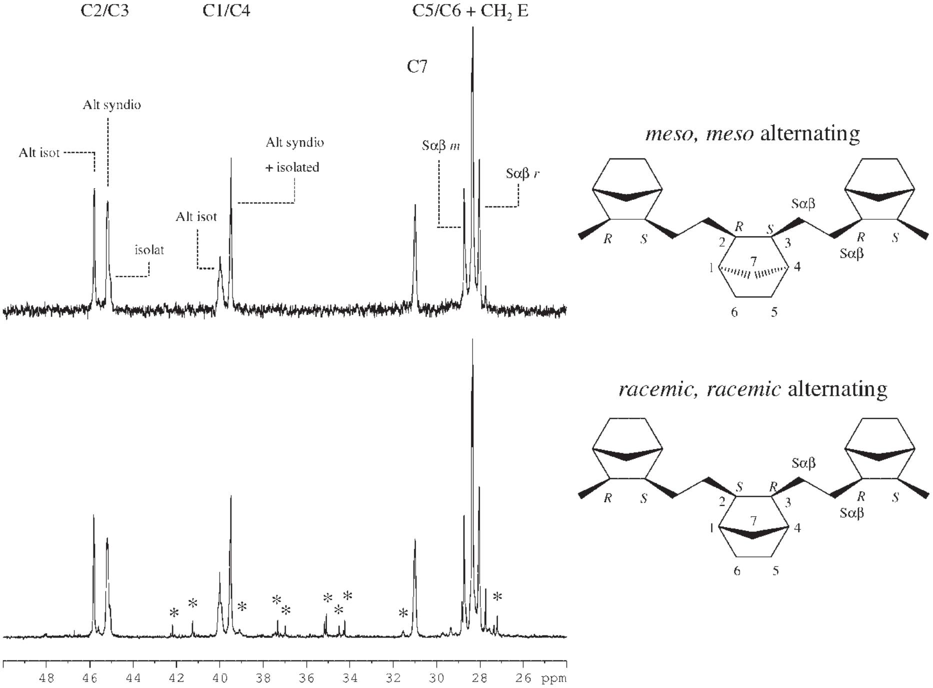


Figure 1.
^{13}C NMR spectra of E–N copolymers obtained in entries 1 and 5. Chemical shifts are referenced to HMDS. The spectra were measured in $C_2D_2Cl_4$ at 105 °C. Top: copolymerization in the presence of MAO at 25 °C. Bottom: copolymerization in the presence of TIBA at 50 °C.

metallocene catalysts, does not work with these compounds. Thus, we have dedicated some efforts in finding best conditions for their manipulation. Improvement in toluene and norbornene purification technique and their storage on sodium mirror covered glasses lead to successful ethylene and norbornene copolymerization without any aluminium scavenger (MAO or TIBA) in reaction medium (# 9–12). The new experiments have been performed by using complexes **1** and **3** for their promising results in terms of activity and livingness, respectively. The catalytic activities are much higher than in the previous experiments, it is possible to avoid the use of scavenger, and to decrease the amount of catalyst in solution (# 9 and 10). The increase in activity of **3** is even higher, and under these new conditions catalyst **3** is almost as active as **1**. Therefore for further studies we have chosen complex **3** as best compromise for activity, norbornene incorporation ability and above all because this system approaches most the livingness.

Under these new conditions we have also investigated the yttrium catalyst **5**. Results show that the yttrium catalyst yields both worse activities and norbornene incorporation than scandium catalysts (# 11). GPC data reveal a complex molecular weight distribution. Attempts to use lutetium catalyst (**6**) indicated that this catalyst is much less active than scandium and yttrium catalysts in ethylene–norbornene copolymerizations. Only polymer traces have been obtained at longer polymerization time (entry 13).

In order to demonstrate the potential of catalyst **3** in living E–N polymerization we have performed kinetics experiment by sampling aliquots of reaction medium at different time Yields increase linearly within the first three minutes (Figure 2).

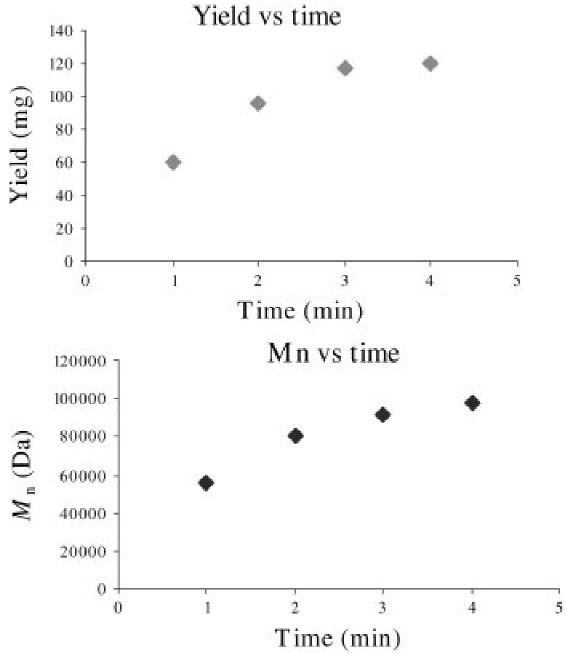


Figure 2.
Plots of kinetics experiments with catalyst **3** (Table 2).

Very interesting is that GPC analysis shows that also the molar masses increase with time and that molar mass distributions are as low as 1.19. This indicates that E–N copolymerizations with catalyst **3** is under good control. Further experiments with different polymerization time confirmed these results.

Ethylene–Norbornene Copolymerization by Carbon Nanotube-Supported Metallocene Catalysis

The techniques employed to achieve homogeneous and fine dispersion of CNTs in polymer matrices include optimum physical blending, ultrasonication and chemical functionalization of the nanotube surface,[17–23] which can perturb the extended delocalized electronic system responsible for the special properties displayed by carbon nanotubes. Some of us have recently applied an original method derived from the Polymerization-Filling Technique (PFT) to coat CNTs with semi-crystalline high density polyethylene (HDPE) chains.[24] We have been able to apply this method to E–N copolymerization for the first time. A series of E–N copolymerization as catalyzed by *rac*-Et(Ind)$_2$ZrCl$_2$/MMAO-3A anchored onto the carbon nanotube surface has been performed.[25] The surface of multi-walled carbon nanotubes (MWNTs) has been treated with modified methylaluminoxane (MMAO-3A) first by reaction in heptane at 50 °C for 1 hour. After solvent evaporation and high temperature treatment (1.5 hour at 150 °C), most of the MMAO remains anchored onto the carbon nanotube surface and cannot be extracted in solution. Then the treated MWNTs are dispersed in heptane followed by the addition of 2-norbornene solution (in toluene or heptane), ethylene saturation and addition of metallocene catalyst. The metallocene by reaction with the anchored MMAO forms an alkylated cationic species (*rac*-Et(Ind)$_2$ZrR$^+$) which is immobilized at the vicinity of the nanotubes surface by electrostatic interactions with the counter-anion. Ethylene–norbornene copolymeri-

Table 2.
Kinetics experiments.[a)]

Entry	Time min	Yield mg	M_n [b)] Da	M_w/M_n [b)]
13	1	60	55786	1,19
14	2	96	80323	1,26
15	3	117	91765	1,38
16	4	120	97382	1,39

[a)] Conditions: T = 25 °C, *p*E = atm; V_{tot} = 50mL, $V_{aliquot}$ = 5mL, **3** = 20 μmol, $[Ph_3C]B(C_6F_5)_4]$ = 20μmol.

[b)] Determine by GPC.

zations have been carried out by varying time reaction, ethylene pressure, and solvent. A portion of the composites have been extracted by Soxhlet method with boiling toluene. The extracted fractions have been analyzed by ^{13}C NMR spectroscopy to determine the norbornene content in the copolymer, and by SEC and DSC to estimate molecular masses and T_g, respectively. The characteristics of some selected and most representative copolymers are displayed in Table 3.

Figure 3 shows the ^{13}C NMR spectrum of an ethylene–norbornene copolymer containing 47.5 mol-% of N (Table 3, # 1), which is similar to those of E–N copolymers prepared with the same catalytic system "not supported on CNTs" under similar conditions. It is worth noting that the T_g values of the extracted fractions (Table 3, entries 4 and 5) are considerably lower than those of E–N-copolymer coated MWNT composites. These observations indicate a good interaction between the in situ grown copolymers and nanotubes surface (see TEM observations hereafter). Molar masses and molar mass distributions of the extracted E–N copolymer measured are similar to those of E–N copolymers prepared with catalyst not supported on MWNTs.

TEM micrographs of the composites (Figure 4) give evidence that MWNTs are relatively well separated from the starting highly entangled bundle-like associations and covered by a rather homogeneous ethylene–norbornene copolymer layer (determination of coating average diameter is ca. 15 nm). Thus, homogeneous surface coating of multi-walled carbon nanotubes with a thin layer of poly(ethylene-co-norbornene) is achieved for the first time by in situ copolymerization. The copolymerization reaction allows for the destructuration of the native nanotube bundles. The relative quantity of E–N copolymer and T_gs can be tuned up as well as the norbornene content in the formed copolymers and accordingly their glass transition temperature.

E–N copolymer-coated CNTs (cMWNTs) have been used as a predispersed "masterbatch" and melt-blended with a commercially available model polymer matrix, e.g., ethylene-co-vinyl acetate copolymer (EVA with 27 wt.-% of vinyl acetate comonomer),

Table 3.
Ethylene–Norbornene (E–N) copolymerization and thermal characteristics of co-E–N-MWNTs nanocomposites as obtained by PFT with the catalyst *rac*-Et(Ind)$_2$ZrCl$_2$ (ethylene pressure: 1.3 bar).

Entry	Activity[a)]	N (mol-%)[b)]	M_n [c)]	M_w/M_n [c)]	E–N content[d)](wt.-%)	T_g [e)] (°C)	
1	120	47.5	n.d.	n.d.	47.0	140.0[f)]	135.1[g)]
2	215	n.d.	n.d.	n.d.	83.0	138.0[f)]	n.d.
3[h)]	65	41.8	55840	1.7	69.7	108.3[f)]	107.3[g)]
4[i)]	44	51.5	20700	1.8	36.8	154.0[f)]	134.3[g)]
5[i)]	35	43.7	23100	1.6	28.4	165.7[f)]	128.1[g)]

[a)] Activity = kg polymer/(mol Zr h bar).

[b)] Mol-% of 2-norbornene calculated by analysis of ^{13}C NMR spectra.

[c)] Measured by SEC at 145°C in 1,2-dichlorobenzene.

[d)] as determined by TGA (weight loss recorded under helium flow with a heating ramp of 20K/min).

[e)] T_g = glass transition temperature determined by DSC (2nd heating scan at 20K/min).

[f)] co-E–N-MWNTs nanocomposites.

[g)] Extracted E–N copolymers.

[h)] Ethylene pressure: 2.7 bar.

[i)] Starting norbornene solution in heptane.

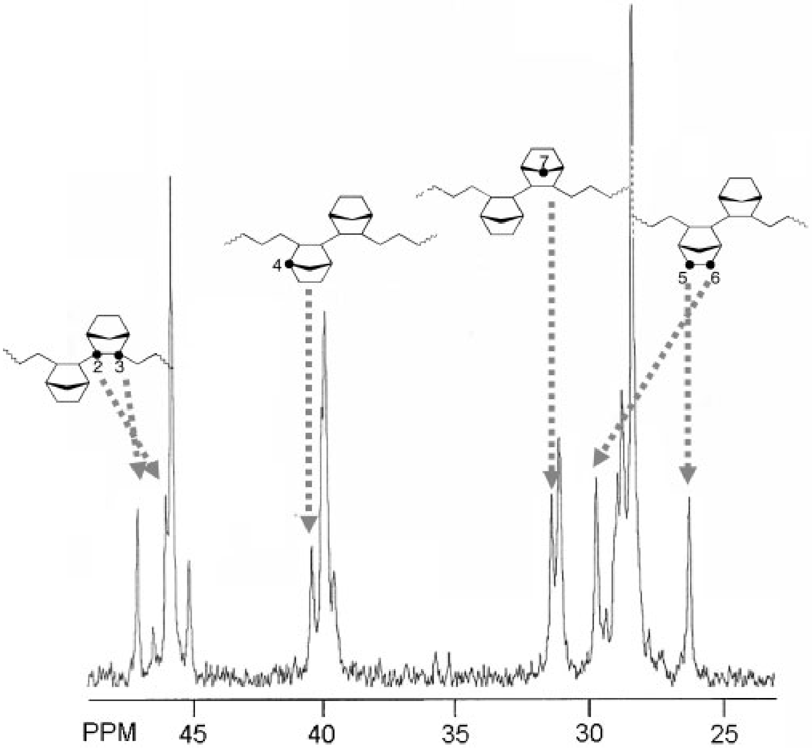


Figure 3.
^{13}C NMR spectrum of the extracted fraction of the E–N copolymer-coated CNTs (cMWNTs) sample, prepared with *rac*-Et(Ind)$_2$ZrCl$_2$, with N content of 47.5 mol-%.

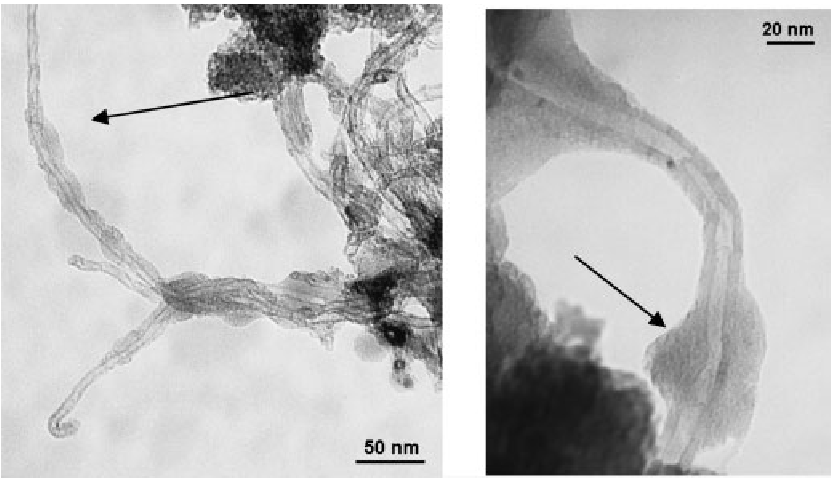


Figure 4.
TEM micrographs of MWNTs coated by in situ grown E–N copolymers (highlighted by the arrow) with 47 wt.-% E–N as obtained by the Polymerization-Filling Technique (entry 1 Table 3).

using a co-rotating twin-screw mini-extruder. Highly dispersed MWNTs/polymer nanocomposites have been prepared containing 1 and 3 wt.-% of the nanofiller as shown from TEM images in ref 25. Thus, the combination of the PFT technique and melt blending is an efficient method for the disruption of the native nanotubes bundles and for achieving an exceptional state of dispersion of CNTs.[26]

To assess the effect of the MWNTs dispersion on the final properties of the resulting materials, their mechanical properties have been evaluated using dynamic mechanical thermo-analysis (DMTA) in tensile mode. For the sake of comparison, unfilled EVA and EVA filled with 1 and 3 wt.-% of pristine CNTs (pMWNTs) have been processed under the same conditions. By melt blending with an ethylene-vinyl acetate copolymer (27 wt.-% vinyl acetate) matrix, high performance polyolefinic nanocomposites were obtained with much improved elastic modulus (almost a threefold increase in the presence of only 3wt.-% of cMWNTs).

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