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The First Molecularly Characterized Isotactic Polypropylene-*block*-polyethylene Obtained via "Quasi-Living" Insertion Polymerization

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The rapidly expanding research on "post-metallocene" catalysts[1] has already provided access to a variety of novel polyolefin architectures via Ziegler−Natta chemistry under living conditions.[2] The drawback inherent in living catalysis that one polymer chain (at most) can be obtained per metal center, often coupled with a high catalyst cost, makes industrial applications not yet at hand; possible exceptions are high-added-value materials such as for example diblock copolymers to be used as phase compatibilizers in poorly miscible polyolefin blends.[3] In terms of market significance, blends of isotactic polypropylene (iPP) unquestionably represent the elective target;[4] ironically, a number of old[2,5] and new[2,6,7] coordination catalysts allow the synthesis of sPP-*block*-polyolefin (sPP = syndiotactic polypropylene), whereas no living catalysts for the production of iPP-*block*-polyolefin have been documented until now.[2]

In this communication, we report on the synthesis of iPP-*block*-PE (PE = polyethylene) with a Zr-based post-metallocene catalyst and present—as far as we know—the first direct and complete ^{13}C NMR evidence of a true block nature for a polyolefin-based material containing a polypropylene block of any tacticity.

Highly isotactic and living polymerization of 1-hexene at room temperature was recently achieved by Kol and co-workers using the C_2-symmetric Zr complex of Chart 1 (**1**; Bn = benzyl), activated with $B(C_6F_5)_3$.[8] In the framework of a more general project on single-center octahedral C_2-symmetric column 4 catalysts for ethene and propene polymerization, we prepared and tested **1** in the polymerization of such monomers.[9] Our attempts to activate **1** with $B(C_6F_5)_3$ as described in ref 8 were unsuccessful; on the other hand, reasonable productivities were observed when using either methylalumoxane (MAO) or $[HMe_2N(C_6H_5)]$ $[B(C_6F_5)_4]$, in the latter case with Al(isobutyl)$_3$ as a scavenger. The presence of an Al−alkyl in the reaction medium resulted in fast chain transfer to Al, with corresponding loss of the living character; both **1**/MAO and **1**/$[HMe_2N(C_6H_5)][B(C_6F_5)_4]$/Al(isobutyl)$_3$, however, turned out to produce a polypropylene of fairly high isotacticity, with a microstructure typical of enantiomorphic sites control (at 25 °C, [*mmmm*] = 0.80, [*mrrm*] = 0.037).[9]

It has been shown[10] that the propensity of Al−trialkyls to promote chain transfer from transition metal catalysts can be decreased by replacing one or two alkyl residues with bulky alkoxide ones; this can be easily achieved, e.g., by reaction of AlR_3 with stoichiometric amounts of a sterically hindered phenol. We prepared the 1:1 reaction product of Al(isobutyl)$_3$ with 2,6-di(*tert*-butyl)phenol (**2**) and used it as a scavenger in the place of Al(isobutyl)$_3$ in ethene and propene polymerization with **1**/$[HMe_2N(C_6H_5)][B(C_6F_5)_4]$.

Chart 1

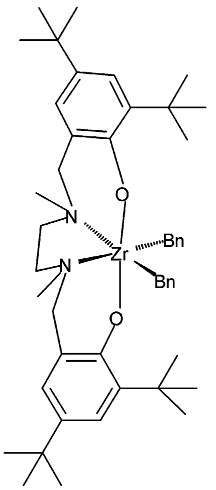

Table 1. Dependence of Average Molecular Mass on Reaction Time for Polyethylene Samples Prepared at 25 °C in the Presence of 1/$[HMe_2N(C_6H_5)][B(C_6F_5)_4]$/2

run no.	t_p, min	$P_n \times 10^{-2}$	M_n, kDa	M_w/M_n
1	1.5	1.2	3.5	1.3
2	3	2.4	6.7	1.5
3	6	3.3	9.2	1.6
4	15	4.6	12.9	1.9
5	20	5.0	14.0	1.8

In Table 1, we report the results of a GPC characterization of a series of polyethylene samples prepared at 25 °C and $p(C_2H_4) = 1.5$ bar, with increasing polymerization time (t_p) in the range 1.5−20 min. The data are typical of what Keii and co-workers defined a "quasi-living" kinetic regime,[11] i.e., of a polymerization process in which chain transfer is not truly negligible but is slow in the time scale of the experiment. Indeed, the asymptotic plot of M_n vs t_p (Figure 1), which extrapolates to a limiting M_n value of 1.8×10^4 Da, is almost linear up to 5 min. The M_w/M_n ratio was 1.3 and 1.5 for polyethylene samples obtained at $t_p = 1.5$ and 3 min, respectively, and only at t_p of ca. 15 min it approached the value of 2.0, typical of a Schultz−Flory distribution.

The plot can be linearized in terms of the following equation:[11]

$$1/P_n = M_1/M_n = f_t/(k_p[M]) + 1/(k_p[M]t_p) \qquad (1)$$

where P_n is the number-average degree of polymerization, M_1 the molar mass of the monomer, [M] the monomer concentration, k_p the kinetic constant of chain propagation, and f_t the frequency of chain transfer. By applying eq 1 to the data of Table 1, we obtained best-fitting values of $k_p = 11$ mol L^{-1} s^{-1} and $f_t = 0.0026$ s^{-1}.

A "quasi-living" character was observed also in propene polymerization, with even lower values of k_p (= 0.045 mol L^{-1} s^{-1}) and f_t (= 0.0006 s^{-1}). In an iPP sample prepared with $t_p = 1.0$ h, we detected by ^{13}C

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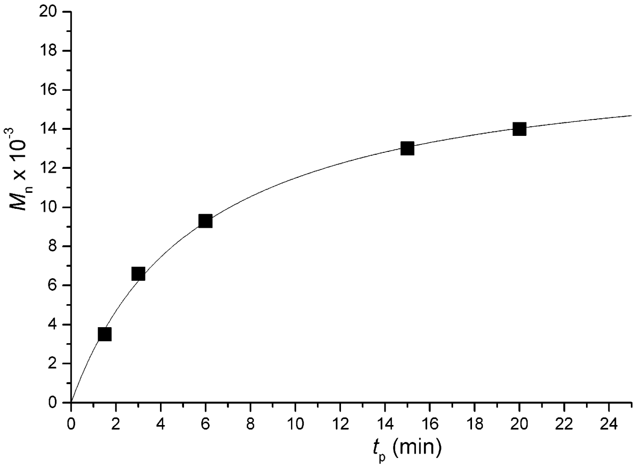

Figure 1. Number-average molecular mass (M_n) vs polymerization time (t_p) for ethene homopolymers prepared at 25 °C in the presence of **1**/[$HMe_2N(C_6H_5)$][$B(C_6F_5)_4$]/**2**.

NMR low amounts (ca. 0.4 mol %) of vinylidene chain ends, which can be traced to β-H elimination.

Compared with typical metallocene-catalyzed ethene and propene polymerizations,[12] k_p and f_t are *both* lower by 3−4 orders of magnitude—in a way, as if the polymerization occurred at slow motion. If a low k_p is obviously undesirable for practical application in homopolymerization, a low f_t is highly favorable if one has block copolymerization as a target. The above results indicate that, for the investigated catalyst system, polyethylene and polypropylene chain growth at 25 °C under the used conditions takes *on average* 6 and 30 min, respectively; this is long enough to change monomer feed and achieve a block copolymer as the main product. Relative to more active and truly living catalysts (in the first place, the recently disclosed bis(phenoxy−imine)Ti systems[1,2,6,7]), the performance of **1** is definitely less appealing, *with the notable exception of its isotactic selectivity*. In view of this, we decided to attempt the synthesis of iPP-*block*-polyolefin in the presence of **1**/[$HMe_2N(C_6H_5)$][$B(C_6F_5)_4$]/**2**, starting with iPP-*block*-PE.

Figure 2 shows the ^{13}C NMR spectrum of a sample obtained by homopolymerizing ethene and propene at 25 °C in sequence for 1.5 and 20 min, respectively, with accurate reactor purging in between and final quenching with acidified methanol (see Experimental Section). The spectrum is remarkably clean and shows all and only the resonances of a PE-*block*-iPP, with the PE block initiated at a Zr−benzyl bond and the iPP block terminated by protonolysis at a 1,2 last-inserted unit (see peak attributions[13,14] in Figure 2).

Peak integration gave a mole ratio between benzyl ends, isobutyl ends, and block junctions of 1:1:1 (within the experimental error); moreover, the spectrum gave no evidence of additional end groups indicative of the copresence of homo-PE and homo-iPP chains. From the integral ratio between the C atoms within the blocks and those at the block junction, the number-average block lengths were estimated to be $L_{PE} = 130 \pm 30$ and $L_{iPP} = 120 \pm 30$ monomeric units. These data *directly* and unambiguously identify the diblock nature of the sample.

Further characterizations provided additional and obviously consistent *indirect* evidence. In particular, the sample turned out to be completely insoluble in boiling hexane (whereas a homo-iPP one prepared with the same catalyst system under corresponding conditions was totally extracted by the same solvent). The DSC heating curve showed the melting peak of the PE block at $T_m = 120$ °C, partly overlapped with the broader one of the iPP block (cumulative $\Delta h_m = 136$ J/g); upon cooling, the two blocks gave separate crystallization exotherms ($T_c = 107$ °C and $\Delta h_c = -91$ J/g for PE; $T_c = 87$ °C and $\Delta h_c = -25$ J/g for iPP). For comparison, the melting parameters of ethene and propene homopolymers prepared under corresponding conditions are (PE) $T_m = 124$ °C, $\Delta h_m = 244$ J/g and (iPP) $T_m = 123$ °C, $\Delta h_m = 72$ J/g. Last but not least, the GPC value of M_w/M_n turned out to be as low as 1.2, and that of M_n (= 6.5×10^3 Da) is in agreement within error limits with the ^{13}C NMR one.

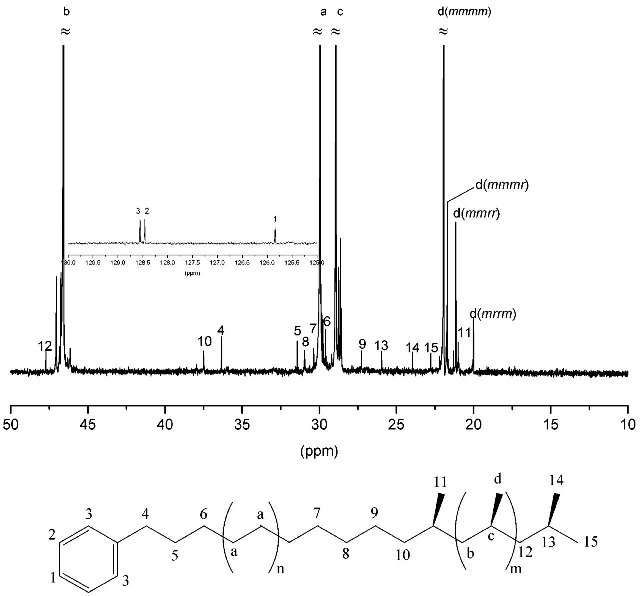

Figure 2. The 50.3 MHz ^{13}C NMR spectrum (in tetrachloroethane-1,2-d_2 solution at 125 °C; δ scale in ppm downfield of TMS) of the iPP-*block*-PE sample, with complete resonance assignment.

In conclusion, we have reported on the first synthesis of iPP-*block*-PE via "quasi-living" coordination catalysis[15] and presented the first direct ^{13}C NMR evidence of a block nature for a polyolefin-based material containing a polypropylene block of any tacticity. We are currently preparing iPP-*block*-PE and iPP-*block*-EPR (EPR = ethylene/propylene rubber) with variable block lengths and exploring their use as phase compatibilizers in iPP/PE and iPP/EPR physical blends.[3,4]

Experimental Section. Complex **1** was synthesized according to ref 8. A stock solution of **2** in dry toluene (Aldrich; 100 mL) was prepared by reacting equimolar amounts of $Al(isobutyl)_3$ (Witco GmbH; 3.0 mL) and 2,6-di(*tert*-butyl)phenol (Fluka; 2.50 g) at room temperature.

For the ethene homopolymerization runs, we used a magnetically stirred jacketted 100 mL Pyrex reactor with three necks; one was serum-capped, and the other two were connected to a Schlenk manifold, allowing to evacuate the reactor and to introduce a monomer or an inert gas in the liquid phase through a cannula. As a general procedure, the reactor was charged under nitrogen with 70 mL of dry toluene (Aldrich), 35 mg of [$HMe_2NC_6H_5$][$B(C_6F_5)_4$] (Boulder Scientific Co.), and 5 mL of stock solution of **2**, thermostated at 25 °C under stirring, evacuated with a membrane pump in order to remove nitrogen, and saturated with ethene (SON, polymerization grade) at a partial pressure of 1.5 bar. Once equilibrium was attained, the reaction was started by injecting **1** (22 mg) previously dissolved in toluene (5.0 mL). The reaction was allowed to proceed at constant monomer pressure for a convenient time (1.5−20 min), after which it was quenched with 5 mL of methanol/HCl(aq,conc) (95/5 v/v). The polymer was then coagulated with excess methanol/HCl, filtered, washed with more methanol, and vacuum-dried.

The synthesis of PE-*block*-iPP was carried out similarly in a 250 mL reactor. This was charged under argon with 140 mL of dry toluene, 110 mg of $[HMe_2NC_6H_5]$-$[B(C_6F_5)_4]$, and 10 mL of stock solution of **2**, thermostated at 25 °C, evacuated with a membrane pump in order to remove argon, and saturated with ethene at a partial pressure of 1.5 bar. The reaction was started by injecting **1** (73 mg) predissolved in toluene (5.0 mL) and allowed to proceed at constant monomer pressure for 1.5 min, after which the reactor was evacuated and flushed with argon several times in order to remove all ethene (overall purging time, 1 min). After a last evacuation, the liquid phase was saturated with propene at a partial pressure of 3.0 bar, propene polymerization left to proceed at constant pressure for 20 min, and quenched with 5 mL of methanol/HCl(aq,conc) (95/5 v/v). The polymer was then coagulated with excess methanol/HCl, filtered, washed with more methanol, and vacuum-dried (yield, 0.44 g).

All polymer samples were characterized by gel permeation chromatography (GPC), using a Polymer Laboratories GPC220 apparatus equipped with a Viscotek 220R viscosimeter, on polymer solutions in 1,2,4-trichlorobenzene at 135 °C.

Quantitative ^{13}C NMR polymer microstructural analysis was carried out with a Varian VXR 200 spectometer operating at 50.3 MHz on 100 mg/mL solutions in tetrachloroethane-1,2-d_2 at 125 °C in standard 5 mm o.d. tubes. Acquisition conditions: 76° pulse; acquisition time, 1.5 s; relaxation delay, 4.0 s; 30K transients.

DSC curves were recorded with a Perkin-Elmer DSC-7 apparatus, at the scanning rate of 10 °C/min, in the range 30−180 °C; the melting parameters refer to the second heating scan.

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