

## Controlled Ethylene Polymerization Catalyzed by $\text{Cp}_2^*\text{ZrBu}_2/[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]/\text{Bu}_4\text{Al}_2\text{O}$ above Room Temperature

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The ternary system composed of  $\text{Cp}_2^*\text{ZrBu}_2$  ( $\text{Cp}^* = \text{Me}_5\text{Cp}$ ),  $[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ , and tetraisobutylaluminumoxane (TIBAO) catalyzed the polymerization of ethylene in a controlled fashion at temperatures up to 60 °C. The consumption of ethylene remained constant during the polymerization process, the molecular weight of the polyethylene increased linearly with time, and polydispersity indexes down to 1.3 were obtained. Characterization of the polyethylene by  $^{13}\text{C}$ -NMR and FT-IR spectroscopy did not indicate any branching or C=C linkages, even for polymer produced at 40 °C or above. The linear and saturated polymer structure is due to the absence of  $\beta$ -hydride transfer,  $\beta$ -hydride elimination and chain walking during the polymerization. The absence of termination reactions is consistent with the system's demonstrated controlled polymerization.

**Introduction.** – Mechanism-based catalyst engineering seeks to design catalytic systems that give access to products with desirable properties. In a living polymerization, monomers are enchainned without chain transfer or termination, and such systems are used to produce polymers with controlled molecular weight and molecular structures [1–3]. A particularly interesting design target is a living or controlled polymerization of ethylene catalyzed with metallocene at temperatures significantly higher than room temperature. This would have the advantage that cooling of the exothermic reaction could be achieved with room-temperature water, an important consideration in the translation of laboratory results into a practical industrial process. Controlled polymerization of ethylene above room temperature was reported in a few instances as recently reviewed in [4][5].

We report herein the polymerization of ethylene catalyzed by  $\text{Cp}_2^*\text{ZrR}_2$  ( $\text{R} = \text{Me}, \text{Bu}$ ) activated with  $[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$  (TB) and an alkylaluminum species (tetraisobutylaluminumoxane (TIBAO) or triisobutylaluminum (TIBA)). The bulk polymer molecular structure is discussed on the basis of GPC, IR, and NMR spectroscopy. We demonstrate that, despite the high activity of the catalyst, controlled polymerization of ethylene is feasible, and narrow molecular-weight distributions of polymer can be obtained at temperatures up to 60 °C.

Recently, our group reported an electrospray ionization mass spectrometry (ESI-MS) technique [6][7] that allow quick quantification of  $\beta$ -hydride ( $\beta$ -H) elimination and  $\beta$ -H transfer for a given catalytic system. By this method, it was demonstrated that neither significant  $\beta$ -H elimination to metal nor  $\beta$ -H transfer to monomer occurs at temperatures up to 60 °C for polymerizations catalyzed by  $\text{Cp}_2^*\text{ZrCl}_2$  activated with methylaluminumoxane (MAO) [8]. We concluded that, under these conditions, the

remaining termination process for the MAO (trimethylaluminum (TMA) free) activated  $\text{Cp}_2^*\text{ZrCl}_2$  catalytic system is chain transfer to Al, which was furthermore found to be effectively irreversible at the low MAO concentrations employed. The low polymerization activity could be attributed to a low degree of activation, *i.e.*, few active centers. Consequently, with the goal of performing a living polymerization at temperatures significantly higher than room temperature, we activated the catalyst  $\text{Cp}_2^*\text{ZrR}_2$  with TB as a non-transfer activator, expecting higher activity with the more efficient activation mechanism.

**Results and Discussion.** – Activation of  $\text{Cp}_2^*\text{ZrMe}_2$  with boron- $\text{C}_6\text{F}_5$  compounds [9] as sole activator for ethylene polymerization has been previously reported [10–12]. In the case of using TB as activator, high concentrations of both reactants were required in order to initiate polymerization (on the order of  $1 \cdot 10^{-3}$  M). But, lower concentrations of reactant (on the order of  $1 \cdot 10^{-4}$  M) were necessary if an alkylaluminum compound (*e.g.*, TIBAO or TIBA) was added as coactivator beside TB. The Al compound did not only serve as scavenger but also acted in the formation of the active site by reacting with TB (formation of  $\text{HCPH}_3$  and isobutene) and most probably by forming an active bridged alkyl ( $\text{Zr}-\text{R}-\text{Al}$ ) species [13][14]. The important role of the Al compound was emphasized by the following experiment: a low-concentration mixture ( $1 \cdot 10^{-4}$  M) of catalyst and TB did not initiate polymerization but rather started when TIBAO or TIBA was added (after 15 min) to the pre-mixed solution. It implied that the catalyst had not been irreversibly deactivated by impurities, and that the aluminum compound acted in the formation of the active species. Similar ternary systems have been reported [15–17].

The activity of the ternary system was high, so that polymer precipitated within mixing time. Accurate estimation of the activity was, therefore, hampered by precipitation problems and by mass-transport limitations. To solve these problems, the concentration of the catalyst was decreased. However, the concentration could only be reduced to a threshold (addition of *ca.* 2  $\mu\text{mol}$  of catalyst), below which activation of the system became unreliable. Under the described reaction conditions, the catalyst activity could be estimated to be 3750 kg PE/(mol Zr h bar). Moreover, to further reduce the number of active Zr-centers, we reduced the amount of TB to 0.25 equiv. with respect to Zr. Accordingly, the number of chains decreased but not the activity (*Table, Entries 1 and 2*), clearly showing that mass-transport limitation occurred due to the high activity of the catalyst. Thus, we surmise that the activity potential of the catalytic system could exceed 10000 kg PE/(mol Zr h bar). For comparison, *Rytter* and co-workers [18] reported an activity of 19600 kg PE/(mol Zr h bar) using  $\text{Cp}_2^*\text{ZrCl}_2$ /MAO system with an Al/Zr ratio of 2200 at 42 °C.

Verification of the controlled character of an active system is possible only if precipitation of polyethylene is reduced, for example, by lowering the monomer concentration. To better control the temperature and delay the onset of precipitation, the reaction was artificially retarded by saturating the system with Ar and subsequently applying an overpressure of ethylene. The lower ethylene concentration then reduced the productivity and allowed better control over the polymerization experiment and a fair assessment of the polydispersity indexes (PDI) under various conditions.

Table. Results of Ethylene Polymerization Catalyzed by  $Cp_2^*ZrR_2/TB/TIBAO$  in Toluene at 40°C

Entry	Catalyst	TB Equiv.	TIBAO Equiv.	Time [s]	Yield [mg]	Activity <sup>a)</sup>	$\bar{M}_n$ [g mol <sup>-1</sup> ]	PDI	$N_{chains}/N_{Zr}$
1 <sup>b)</sup>	$Cp_2^*ZrMe_2$	1	2	20	99	3750	39040	3.25	1.01
2 <sup>b)</sup>	$Cp_2^*ZrMe_2$	0.25	2	20	94	3560	114650	2.03	0.33
3 <sup>c)</sup>	$Cp_2^*ZrMe_2$	1	4	180	17	134	36380	1.85	0.18
4 <sup>c)</sup>	$Cp_2^*ZrBu_2$	1	4	180	22	181	32100	1.57	0.27
5 <sup>d)</sup>	$Cp_2^*ZrBu_2$	1	1	180	17	24	2470	1.4	0.49
6 <sup>d)</sup>	$Cp_2^*ZrBu_2$	1	2	180	16	23	2800	1.3	0.41
7 <sup>d)</sup>	$Cp_2^*ZrBu_2$	1	10	180	13	19	1430	1.49	0.66
8 <sup>d)</sup>	$Cp_2^*ZrBu_2$	1	20	180	13	19	1222	1.42	0.78
9 <sup>d)</sup>	$Cp_2^*ZrBu_2$	1	100	180	19	27	1460	1.49	0.89

<sup>a)</sup> kg PE/(mol Zr h bar). <sup>b)</sup> No preactivation period; catalyst concentration:  $3.5 \cdot 10^{-4}$  mol · l<sup>-1</sup>; monomer pressure 2 bar. <sup>c)</sup> 15-min preactivation period; catalyst concentration:  $3.5 \cdot 10^{-4}$  mol · l<sup>-1</sup>; monomer pressure 1 bar. <sup>d)</sup> 15-min preactivation period; catalyst concentration:  $2 \cdot 10^{-3}$  mol · l<sup>-1</sup>; monomer pressure 1 bar.

Furthermore, premixing of the components of the catalyst formulation under Ar atmosphere 15 min before saturating the system with ethylene (method called preactivation period) was conducted in order to prevent any induction period arising from a slow activation of the catalyst leading to the cationic active species. Thus, the catalyst should be fully activated at the beginning of the reaction (Fig. 1, Trace A, shows the induction period in the rate of ethylene uptake when no preactivation period was conducted). Interestingly, polymerizations catalyzed by  $Cp_2^*ZrMe_2$  exhibited a small induction period even when a preactivation period was applied (Fig. 1, Trace B). This was interpreted as being caused by the first insertion of ethylene into Zr–Me bond, which is *ca.* 100 times slower than insertion into higher Zr–alkyl bonds [14][19]. Since

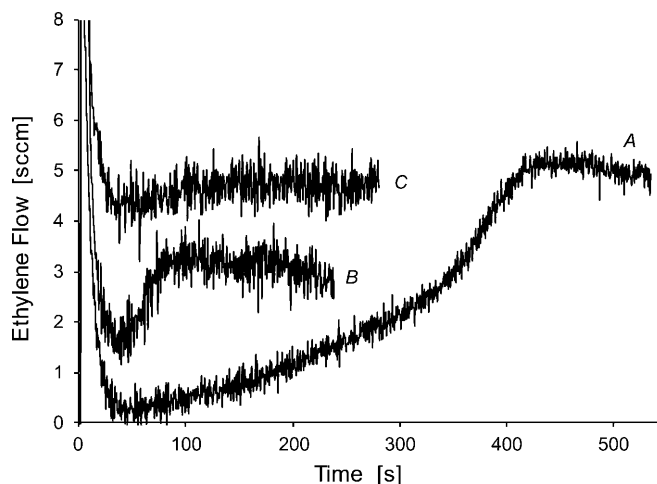


Fig. 1. Ethylene flow as a function of time for polymerization without a preactivation period (A), and for polymerizations with a preactivation period catalyzed by  $Cp_2^*ZrMe_2$  (B) and catalyzed by  $Cp_2^*ZrBu_2$  (C)

polymerization of ethylene catalyzed by  $\text{Cp}_2^*\text{ZrX}_2$  ( $X = \text{Cl}, \text{Me}$ ) does not undergo significant  $\beta$ -H elimination or  $\beta$ -H transfer (*vide supra*), the Me residues on the catalyst can be replaced by higher alkyl residues bearing  $\beta$ -H-atoms. The slower initial insertion of ethylene would then be skipped. Indeed, polymerization of ethylene with  $\text{Cp}_2^*\text{ZrBu}_2$  as catalyst exhibited no induction period (*Fig. 1, Trace C*). One should comment that metallocene precatalysts alkylated with groups bearing  $\beta$ -H-atoms are usually not employed in the literature because activation would ordinarily lead to rapid  $\beta$ -H elimination.

The behavior of the two catalytic systems ( $\text{Cp}_2^*\text{ZrMe}_2$  and  $\text{Cp}_2^*\text{ZrBu}_2$ ) was investigated in order to determine the influence of the alkyl residues on the polymer molecular weight time dependence and on the polymer molecular-weight distribution. Aliquots were taken at regular intervals from 50 ml polymerization mixtures at 40 and 60 °C using either  $\text{Cp}_2^*\text{ZrMe}_2$  or  $\text{Cp}_2^*\text{ZrBu}_2$  catalysts. For all polymerizations, the number average molecular weight ( $\bar{M}_n$ ) increased linearly with time (*Fig. 2*), which demonstrates the absence of significant transfer reaction<sup>1</sup>). The time dependences of the molecular weights obtained with both catalysts were similar. Slightly lower PDIs were obtained with the  $\text{Cp}_2^*\text{ZrBu}_2$  catalyst (lower by *ca.* 0.2; for typical comparable results, see *Table, Entries 3 and 4*). The slower rate of the initial insertion of ethylene (*vide supra*) for  $\text{Cp}_2^*\text{ZrMe}_2$  did not affect the  $\bar{M}_n$  but caused a broader molecular weight distribution. The polymerization results were reproducible within the experimental errors in spite of the high activity and sensitivity of the catalytic system.

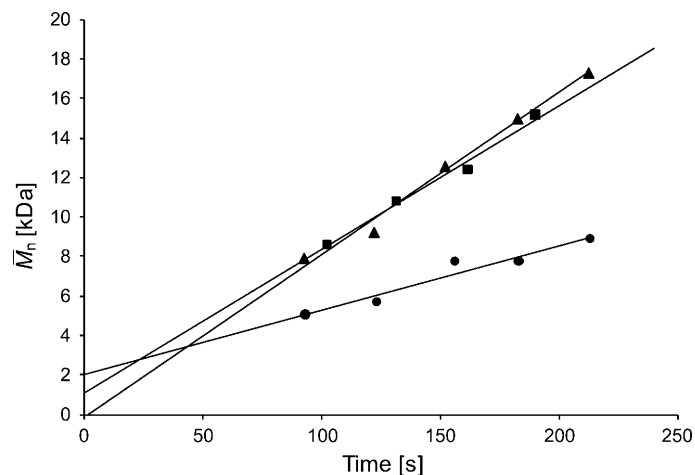


Fig. 2. Number average molecular weight ( $\bar{M}_n$ ) as a function of time for the polymers catalyzed by both  $\text{Cp}_2^*\text{ZrMe}_2$  (■) and  $\text{Cp}_2^*\text{ZrBu}_2$  (▲) at 40 °C, and linear fit of each data set (solid lines). The polymerization catalyzed with  $\text{Cp}_2^*\text{ZrBu}_2$  at 60 °C is represented with plain dots (●).

<sup>1</sup>) At 60 °C, the linear trace does not extrapolate to zero. This could be due to the lower solubility of ethylene in toluene at high temperatures. At 60 °C, the propagation rate is higher than at 40 °C, but the concentration of ethylene is lower as is the overall growth of polymer with time. Clearly, mass-transport limitations would be more prominent at 60 °C than at 40 °C, which could cause the polymer chains to grow faster in the very beginning of the reaction than later. Therefore, the linear trace would not extrapolate to zero but to a higher value of  $\bar{M}_n$ .

Results for typical polymerizations catalyzed by  $\text{Cp}_2^*\text{ZrBu}_2$  are summarized in the Table (Entries 5–9). The polymerization times were relatively short, because even the measures to slow down the reaction could not hold off precipitation indefinitely. To analyze the effect of alkylaluminum on the polymer molecular structure, (*i.e.*, its influence on activation efficiency and chain transfer), the amount of TIBAO was systematically varied. The number of polymer chains increased with the TIBAO concentration. This could be explained either by an increase in the number of active sites or, less probably, by a higher extent of chain transfer to Al occurring despite the branched alkyl residues on Al. We had earlier found for the TMA-free  $\text{Cp}_2^*\text{ZrCl}_2/\text{MAO}$  system [8] that transfer of alkyl residues between Zr and Al were slow for the sterically bulky metallocene, leading, on the one hand, to an inefficient activation, but also making chain transfer from Al to Zr kinetically non-competitive with propagation for alkyl residues larger than Me. In the present work, the alternative activation process circumvents the activation problem, but the transmetalation should remain slow. The smallest PDI (1.3) was obtained when 2 equiv. of TIBAO were used, which was interpreted as being the best compromise between a low degree of transfer and a high number of active centers. The replacement of TIBAO by TIBA gave similar polymerization results. A higher number of chains were produced for the polymerizations activated with TIBA, which may attest for a slightly higher degree of chain transfer to Al.

Additionally,  $^{13}\text{C}$ -NMR (Fig. 3) and FT-IR (Fig. 4) spectra exhibited no features corresponding to branching or C=C linkages that would arise from transfer or termination reactions. The linear and saturated molecular structure of the polyethylene indicates that chain walking, which is closely linked to  $\beta$ -H elimination or  $\beta$ -H transfer, is also disfavored.

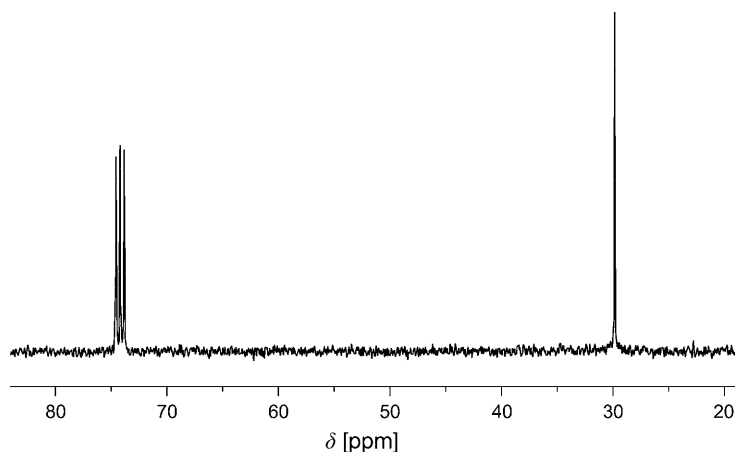


Fig. 3.  $^{13}\text{C}$ -NMR Spectrum of polyethylene prepared with  $\text{Cp}_2^*\text{ZrMe}_2/\text{TB}/\text{TIBAO}$  at  $40^\circ\text{C}$ .

**Conclusions.** – The ternary system composed of  $\text{Cp}_2^*\text{ZrBu}_2$ , TB, and TIBAO catalyzed the polymerization of ethylene in a controlled fashion up to  $60^\circ\text{C}$ . Polymerizations catalyzed by  $\text{Cp}_2^*\text{ZrMe}_2$  exhibited a small induction period in the

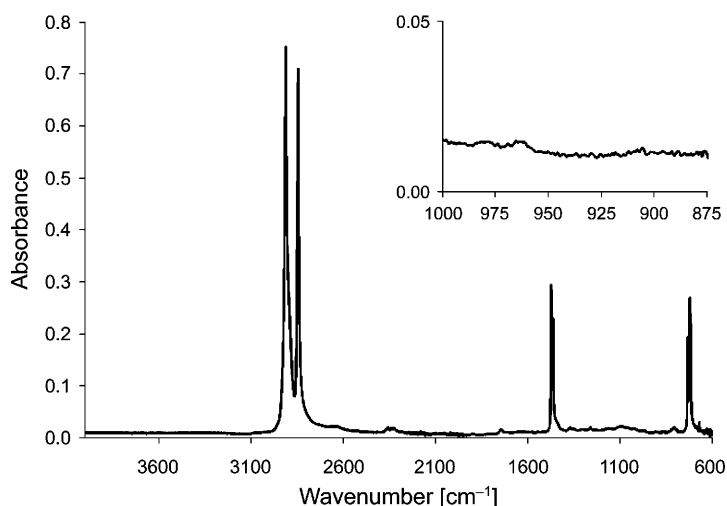


Fig. 4. FT-IR Spectrum of polyethylene prepared with  $\text{Cp}_2^*\text{ZrMe}_2/\text{TB}/\text{TIBAO}$  at  $60^\circ\text{C}$ . The inset graphic is an enhanced view of the zone where the out-of-plane vibrations of the H-atoms in the unsaturated groups should absorb.

rate of ethylene uptake due to the slower initial insertion into the Zr–Me bond, whereas polymerizations catalyzed by  $\text{Cp}_2^*\text{ZrBu}_2$  did not display any induction period. As a result,  $\text{Cp}_2^*\text{ZrBu}_2$  produced polyethylene with smaller PDI values than the one by  $\text{Cp}_2^*\text{ZrMe}_2$ . PDI values as low as 1.3 were obtained. The molecular weight of the polymer catalyzed by both catalysts increased linearly with time, implying that no significant termination or transfer reaction under the above mentioned reaction conditions occurred. Furthermore,  $^{13}\text{C}$ -NMR and FT-IR spectroscopy revealed a highly saturated and linear structure of the polyethylene, which further demonstrated the absence of chain walking,  $\beta$ -H elimination, and  $\beta$ -H transfer for the polymerization catalyzed by the ternary system. The absence of termination processes establishes the potential of the catalytic system to perform living polymerization under industrially relevant conditions. The low activity of the  $\text{Cp}_2^*\text{ZrCl}_2/\text{MAO}$  system is solved here by increasing the number of active sites through an alternative activation scheme.

#### Experimental Part

**Materials.** All operations were carried out under Ar using standard *Schlenk* techniques. Ethylene (purity 3.0, from *PanGas*), bis(pentamethylcyclopentadienyl)zirconium dichloride ( $\text{Cp}_2^*\text{ZrCl}_2$ , from *Acros Organics*, 97%), trityl tetrakis(pentafluorophenyl)borate (TB, from *Acros Organics*, 97%), tetraisobutylaluminumoxane soln. (TIBAO, 10% in toluene, from *Aldrich-Fine Chemicals*), MeLi (1.6M soln. in  $\text{Et}_2\text{O}$ , from *Acros Organics*), BuLi (1.6M soln. in hexane, from *Fluka*) were used without further purification. Research-grade toluene was dried by refluxing over Na. Bis(pentamethylcyclopentadienyl)zirconium dimethyl ( $\text{Cp}_2^*\text{ZrMe}_2$ ) was synthesized according to a literature procedure [20]. Bis(pentamethylcyclopentadienyl)zirconium dibutyl ( $\text{Cp}_2^*\text{ZrBu}_2$ ) was synthesized by modification of a literature procedure [21]. An X-ray crystal structure of the compound has been published [22].

**Synthesis of Bis(pentamethylcyclopentadienyl)zirconium Dibutyl ( $\text{Cp}_2^*\text{ZrBu}_2$ ).** Under Ar, a suspension of bis(pentamethylcyclopentadienyl)zirconium dichloride ( $\text{Cp}_2^*\text{ZrCl}_2$ ; 0.5 g, 1.16 mmol) in

Et<sub>2</sub>O (15 ml) was cooled in a CaCl<sub>2</sub>/ice bath to –15 °C. With magnetic stirring, a soln. of BuLi in hexane (1.6M; 1.45 ml, 2.32 mmol) was added dropwise over a period of 15 min. The temp. was then allowed to rise to 0 °C and then this temp. was kept for additional 2 h, during which a white crystalline solid (LiCl) formed. The soln. was filtered under Ar, and the solvent was evaporated. A faintly red, crystalline solid, Cp<sub>2</sub><sup>\*</sup>ZrBu<sub>2</sub> (415 mg, 75%) was obtained. <sup>1</sup>H-NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): –0.04–0.06 (*m*, 2 CH<sub>2</sub>Zr); 1.03 (*t*, 2 Me); 1.10–1.26 (*m*, 2 CH<sub>2</sub>); 1.35–1.48 (*m*, 2 CH<sub>2</sub>); 1.82 (*s*, 2 Me<sub>5</sub>Cp).

*Polymerization Procedure for High-Productivity Measurements* (without preactivation period). The reactor and control studies were described in [6]. In a typical experiment, at temp. between 40–60 °C, a toluene soln. of precatalyst Cp<sub>2</sub><sup>\*</sup>ZrR<sub>2</sub> (2.5 μmol in 1 ml) and an equimolar amount of TB (2.5 μmol in 1 ml) in toluene were added successively to a rapidly stirred toluene soln. of TIBAO (5 μmol in 6 ml) pressaturated with ethylene at a constant pressure of 2 bar. A flowmeter (*mks PR 4000*) was used to measure the consumption of ethylene. The polymerization reactions were quenched by injection of acidified MeOH, and the polymers were filtered, dried in vacuum, and weighed.

*Polymerization Procedure for Molecular Weight Distribution Measurements* (with preactivation period). In a 250-ml reactor under Ar and at temp. from 40 to 60 °C, toluene (45 ml) and a soln. of TIBAO in toluene (25 μmol in 1.5 ml) were introduced and magnetically stirred for 10 min. Cp<sub>2</sub><sup>\*</sup>ZrR<sub>2</sub> (25 μmol in 1.5 ml) and TB (25 μmol in 1.5 ml) in toluene were successively added, and the mixture was stirred for 15 min. The soln. was then pressurized with ethylene at a constant total pressure of 1.2 bars. Aliquots (3 ml) were taken after 90, 120, 150, and 180 s. After a total reaction time of 210 s, the polymerization was quenched by injection of acidified MeOH.

*Polymer Characterization*. The molecular weights and molecular weight distributions of the obtained polyethylenes were determined by gel permeation chromatography (*PL-GPC 220*) at 150 °C using 1,2,4-trichlorobenzene as solvent, at a flow rate of 1.0 ml/min, and with refractive-index and viscosimetry detection. Two different sets of columns were used (2 × *PLgel 5-μm MIXED-D* or 2 × *PLgel 10-μm MIXED-B*), and the instrument was calibrated with polystyrene standards using a universal calibration, and the results were compared to narrowly distributed polyethylene standards. FT-IR Spectra were recorded on a *Perkin-Elmer Spectrum-BX*. <sup>13</sup>C-NMR Spectra were recorded on a *Varian Gemini* instrument at 75 MHz and 100 °C in 1,1,2,2-tetrachloro[1,2-<sup>2</sup>H<sub>2</sub>]ethane.

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