

## SUPPORTING INFORMATION

# Improving the Behavior of bis(Phenoxy-Amine) Group 4 Metal Catalysts for Controlled Alkene Polymerization

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## 1. EXPERIMENTAL SECTION

### 1.1. Precatalyst Preparation

The known dibenzyl complexes **Zr-1**, **Zr-2** and **Zr-3** were prepared as described in the literature.<sup>7,8</sup> The novel complexes **Hf-1**, **Hf-2** and **Hf-3** were synthesized with the same procedure. Typically, 5.0 mmol of (ONNO) ligand were weighed in a Schlenk flask and dissolved in 10 mL of warm dry toluene. The resulting solution was added to another Schlenk flask containing a solution of 5.0 mmol of HfBn<sub>4</sub> (Bn = benzyl) in 10 mL of the same solvent under argon. The mixture was kept at 65°C for 2 h, then the solvent was removed under vacuum and the product obtained as an off-white powder in nearly quantitative (ca. 95%) yield.

#### NMR characterization data (all $\delta$ values are in ppm downfield of TMS)

Complex **Hf-1**: <sup>1</sup>H-NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K):  $\delta$  = 0.81 (*d*, 2H, NCH<sub>2</sub>CH<sub>2</sub>N), 1.82 (*s*, 6H, N-CH<sub>3</sub>), 1.89 (*bd*, 6H, CH<sub>2</sub>, adamantyl group), 2.10 (*bd*, 6H, CH<sub>2</sub>, adamantyl group), 2.30-2.40 (*m*, 14H, CH<sub>3</sub>, NCH<sub>2</sub>Ar, CH adamantyl group), 2.40-2.52 (*m*, 14H, CH<sub>2</sub> adamantyl group, NCH<sub>2</sub>CH<sub>2</sub>N), 2.53 (*d*, 2H, Hf-CH<sub>2</sub>), 2.74 (*d*, 2H, Hf-CH<sub>2</sub>), 3.71 (*d*, 2H, N-CH<sub>2</sub>Ar), 6.39 (*s*, 2H, Ar), 6.72 (*t*, 2H, Ar), 7.10-7.30 (*m*, 10H, Ar).

<sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K):  $\delta$  = 21.1 (CH<sub>3</sub>), 29.8 (CH, adamantyl group), 37.6 (CH<sub>2</sub>, adamantyl group), 41.5 (CH<sub>2</sub>, adamantyl group), 45.7 (N-CH<sub>3</sub>), 52.9 (NCH<sub>2</sub>CH<sub>2</sub>N), 63.6 (NCH<sub>2</sub>Ar), 76.7 (HfCH<sub>2</sub>), 121.1 (C-H), 126.0 (C<sub>ipso</sub>), 126.8 (C-H), 125.7 (C<sub>ipso</sub>), 126.7 (C-H), 128.3 (C-H), 128.5 (C<sub>ipso</sub>), 129.3 (C<sub>ipso</sub>).

Complex **Hf-2**: <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K):  $\delta$  = 0.56 (*d*, 2H, NCH<sub>2</sub>CH<sub>2</sub>N), 1.05 (*s*, 6H, NCH<sub>3</sub>), 1.63 (*s*, 12H, C(CH<sub>3</sub>)<sub>2</sub>(Ar)), 1.70 (*s*, 6H, C(CH<sub>3</sub>)<sub>2</sub>(Ar)), 1.99 (*s*, 6H, C(CH<sub>3</sub>)<sub>2</sub>(Ar)), 2.04 (*d*, 2H, ZrCH<sub>2</sub>), 2.05 (*d*, 2H, ZrCH<sub>2</sub>), 2.32 (*d*, 2H, NCH<sub>2</sub>CH<sub>2</sub>N), 2.47 (*d*, 2H, NCH<sub>2</sub>Ar), 3.33 (*d*, 2H, NCH<sub>2</sub>Ar), 6.52 (*s*, 2H, Ar), 6.77 (*t*, 2H, Ar), 6.87 (*d*, 4H, Ar), 6.97-7.08 (*m*, 6H, Ar), 7.10-7.19 (*m*, 6H, Ar), 7.25 (*d*, 4H, Ar), 7.40 (*d*, 4H, Ar), 7.51 (*s*, 2H, Ar).

$^{13}\text{C}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ , 300 K):  $\delta = 25.2$  ( $\text{C}(\text{CH}_3)_2(\text{Ar})$ ), 29.4 ( $\text{C}(\text{CH}_3)_2(\text{Ar})$ ), 31.9 ( $\text{C}(\text{CH}_3)_2(\text{Ar})$ ), 40.8 ( $\text{C}(\text{CH}_3)_2(\text{Ar})$ ), 42.2 ( $\text{NCH}_3$ ), 50.6 ( $\text{NCH}_2\text{CH}_2\text{N}$ ), 61.6 ( $\text{NCH}_2\text{Ar}$ ), 74.8 ( $\text{ZrCH}_2$ ), 118.9 ( $\text{C}_{\text{ipso}}$ ), 122.9 ( $\text{C-H}$ ), 123.5 ( $\text{C-H}$ ), 124.0 ( $\text{C-H}$ ), 124.8 ( $\text{C-H}$ ), 125.0 ( $\text{C-H}$ ), 125.2 ( $\text{C-H}$ ), 125.6 ( $\text{C-H}$ ), 126.1 ( $\text{C-H}$ ), 126.3 ( $\text{C-H}$ ), 126.4 ( $\text{C-H}$ ), 126.6 ( $\text{C-H}$ ), 135.1 ( $\text{C}_{\text{ipso}}$ ), 138.2 ( $\text{C}_{\text{ipso}}$ ), 148.1 ( $\text{C}_{\text{ipso}}$ ), 149.8 ( $\text{C}_{\text{ipso}}$ ), 150.0 ( $\text{C}_{\text{ipso}}$ ), 154.6 ( $\text{C}_{\text{ipso}}$ ).

Complex **Hf-3**:  $^1\text{H}$ -NMR ( $\text{C}_6\text{D}_6$ , 400 MHz, 300 K):  $\delta = 0.77$  (*d*, 2H,  $\text{NCH}_2\text{CH}_2\text{N}$ ), 1.35-1.42 (*m*, 2H,  $\text{CH}_2$ , cyclohexyl group), 1.51-1.63 (*m*, 2H,  $\text{CH}_2$ , cyclohexyl group), 1.69-1.74 (*m*, 4H,  $\text{CH}_2$ , cyclohexyl group), 1.77 (superimposed *s*, 6H,  $\text{NCH}_3$ ), 1.79-1.81 (*m*, 4H,  $\text{CH}_2$ , cyclohexyl group), 1.87-2.05 (*m*, 6H, cyclohexyl group), 1.94 (superimposed *d*, 2H,  $\text{HfCH}_2$ ), 2.29 (*s*, 6H,  $\text{CH}_3$ ), 2.32-2.51 (*m*, 2H,  $\text{CH}_2$ , cyclohexyl group), 2.36 (superimposed *d*, 2H,  $\text{NCH}_2\text{Ar}$ ), 2.41 (superimposed *d*, 2H,  $\text{HfCH}_2$ ), 2.57 (*d*, 2H,  $\text{NCH}_2\text{CH}_2\text{N}$ ), 3.56 (*m*, 2H,  $\text{CH}$ , cyclohexyl group), 3.76 (*d*, 2H,  $\text{NCH}_2\text{Ar}$ ), 6.41 (*d*, 2H,  $\text{Ar-H}$ ), 6.79 (*t*, 2H,  $\text{Ar-H}$ ), 7.1-7.3 (*m*, 10H,  $\text{Ar-H}$ ).

$^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , 100 MHz, 300 K):  $\delta = 21.01$  ( $\text{CH}_3$ ), 27.91 ( $\text{CH}_2$ , cyclohexyl group), 27.97 ( $\text{CH}_2$ , cyclohexyl group), 33.22 ( $\text{CH}_2$ , cyclohexyl group), 34.85 ( $\text{CH}_2$ , cyclohexyl group), 35.01 ( $\text{CH}_2$ , cyclohexyl group), 38.11 ( $\text{CH}$ , cyclohexyl group), 44.44 ( $\text{NCH}_3$ ), 52.70 ( $\text{NCH}_2\text{CH}_2\text{N}$ ), 63.26 ( $\text{NCH}_2\text{Ar}$ ), 73.18 ( $\text{HfCH}_2$ ), 121.33 ( $\text{C-H}$ ), 124.23 ( $\text{C}_{\text{ipso}}$ ), 128.02 ( $\text{C-H}$ ), 128.39 ( $\text{C}_{\text{ipso}}$ ), 128.53 ( $\text{C-H}$ ), 128.80 ( $\text{C-H}$ ), 129.30 ( $\text{C-H}$ ), 136.66 ( $\text{C}_{\text{ipso}}$ ), 149.44 ( $\text{C}_{\text{ipso}}$ ), 155.08 ( $\text{C}_{\text{ipso}}$ ).

**IMPORTANT WARNING.** Commercially available  $\text{HfBn}_4$  may contain up to 1-2 mol% of  $\text{ZrBn}_4$ , which is highly detrimental in the present case because Zr-based catalysts are much more active than the Hf homologues, and even when they are present in trace amounts their polymerization products are not negligible. Therefore, for the present work a batch of  $\text{HfBn}_4$  was synthesized from ultra-pure  $\text{HfCl}_4$  (Aldrich, 99.9%) according to: Westmoreland I., *Synthetic Pages* 211, 2003 ([www.syntheticpages.com](http://www.syntheticpages.com)).  $\text{HfCl}_4$  (7.7 g, 24.0 mmol) was weighted in a Schlenk flask, suspended in diethyl ether (200 mL, dry, distilled over sodium) and stirred for 1 h. The suspension was then cooled to  $-78^\circ\text{C}$  and benzyl magnesium chloride (100 mL, 1.0 M in diethyl ether) added dropwise over 30 min. The creamy off-

white mixture obtained was stirred overnight in the dark, covering the flask with aluminium foil. The solvent was removed under vacuum, and the residue was extracted with warm (60°C) heptane (3 x 100 mL). The combined extracts were concentrated to ca. 100 mL and cooled to -30°C. The product was obtained in the form of fine yellow needles after cooling for several hours at this temperature. Yield, 10.0 g (78%).

$^1\text{H}$  NMR (200 MHz,  $\text{C}_6\text{D}_6$ , 300 K):  $\delta$  = 1.62 (*s*, 8H,  $\text{CH}_2$ ), 6.65 (*d*, 8H, Ar), 7.07 (*t*, 4H, Ar), 7.21 (*t*, 8H, Ar).

## 1.2 Ethene and Propene Homopolymerization Runs

All ethene and propene homopolymerization runs (Table S1 and S2, respectively) were carried out in a 250 mL magnetically stirred jacketed Pyrex reactor with two necks (one of which capped with a silicone rubber septum, the other connected to a Schlenk manifold), according to the following procedure. The reactor was charged under nitrogen with 150 mL of toluene (toluene HPLC, Lab-Scan 99.8%, previously purified in an MBraun SPS unit) containing 5.0 mL of MAO (Chemtura, 10% w/w solution in toluene) and 1.7 g of 2,6-di-*tert*-butylphenol (Aldrich, 99%), and thermostated at 25°C. After 1 h, 5.0 mL of the liquid phase were syringed out, and used to dissolve the proper amount of precatalyst in a glass vial. The reactor was then evacuated to remove nitrogen, and saturated with the monomer (SON, polymerization grade) at a partial pressure of 1.6 bar for ethene, 2.0 bar for propene. The polymerization was started by syringing in the catalyst solution, left to proceed at constant monomer pressure for the appropriate time, and quenched with 5 mL of methanol/HCl(aq, conc.) (95/5 v/v). The polymer was coagulated with excess methanol/HCl, filtered, washed with more methanol and vacuum-dried.

**Table S1.** Ethene homopolymerization runs.

Precatalyst	$n(\text{M}), \mu\text{mol}$	$t_p, \text{min}$	$Y, \text{mg}$
<b>Hf-1</b>	30	30	66
		60	96
		120	150
<b>Zr-1</b>	11	1.5	76
		3	116
		5	165
		10	306
		20	505
<b>Hf-2</b>	16	40	56
	32	60	150
	32	120	230
	16	180	215
	31	240	450
<b>Zr-2</b>	5	1.5	140
		3	255
		6	390
		15	1008

**Table S2.** Propene homopolymerization runs.

Precatalyst	$n(M)$ , $\mu\text{mol}$	$t_p$ , min	$Y$ , mg
<b>Zr-1</b>	40	115	507
		240	910
		360	1100
<b>Hf-1</b>	70	210	71
		390	96
		1200	490
<b>Zr-2</b>	18	4	123
		8	245
		15	420
	9	30	435
<b>Hf-2</b>	76	180	128
		270	197
		360	286
		540	362

### 1.3. Synthesis of *iPP-block-EPR* and *iPP-block-EPR-block-iPP*

The block copolymerization experiments were carried out in a 600 mL magnetically stirred jacketed Pyrex reactor with three necks (one with a 15 mm SVL joint capped with a silicone rubber septum, another with a 30 mm SVL joint housing a pressure tight fitting for a Pyrex cannula, and the last one with a Rotaflo™ joint connected to a Schlenk manifold). A T-joint on top of the cannula enabled the connection to either the Schlenk manifold or a propene cylinder. The Rotaflo™ joint, in turn, was connected to another T-joint that could be switched to the Schlenk manifold or to an ethene cylinder. What follows is a typical procedure. The reactor was charged under nitrogen with 300 mL of dry toluene containing 8.0 mL of MAO (Chemtura, 10% w/w solution in toluene) and 2.6 g of 2,6-di-*tert*-butylphenol (TBP), and thermostated at 25°C. After 1 h (to ensure the complete reaction between TBP and “free” AlMe<sub>3</sub> in equilibrium with MAO), the reactor was evacuated to remove the nitrogen, and the liquid phase was saturated through the cannula with propene at the partial pressure of 2.0 bar, under vigorous magnetic stirring. Once equilibrium was attained, the polymerization was started by injecting through the silicone septum 173 mg of precatalyst, previously dissolved in 5 mL of the liquid phase (taken out prior to saturation). After three hours of propene homopolymerization, the unreacted propene was removed under gentle vacuum with a membrane pump, after which the reactor was saturated sequentially with propene at the partial pressure of 1.2 bar, and ethene at the partial pressure of 1.0 bar, for the copolymerization step. At this comonomer feed composition, the copolymer (EPR) produced had a molar composition of 70% ethene, 30% propene. The reaction was left to proceed at constant reactor total pressure for 1 h by continuously feeding ethene, which also ensured a constant comonomer feeding ratio in the liquid phase because propene consumption was negligible (as confirmed by GC analysis of the gas phase in equilibrium). When targeting *iPP-block-EPR*, the reaction was quenched with 5 mL of methanol/HCl(aq, conc.) (95/5 v/v). Otherwise, to prepare *iPP-block-EPR-block-iPP* the reactor was degassed under gentle vacuum as before, and saturated again with propene at the partial pressure of 2.0 bar for a further propene homopolymerization step. After 3 h, the system was quenched with 5 mL of



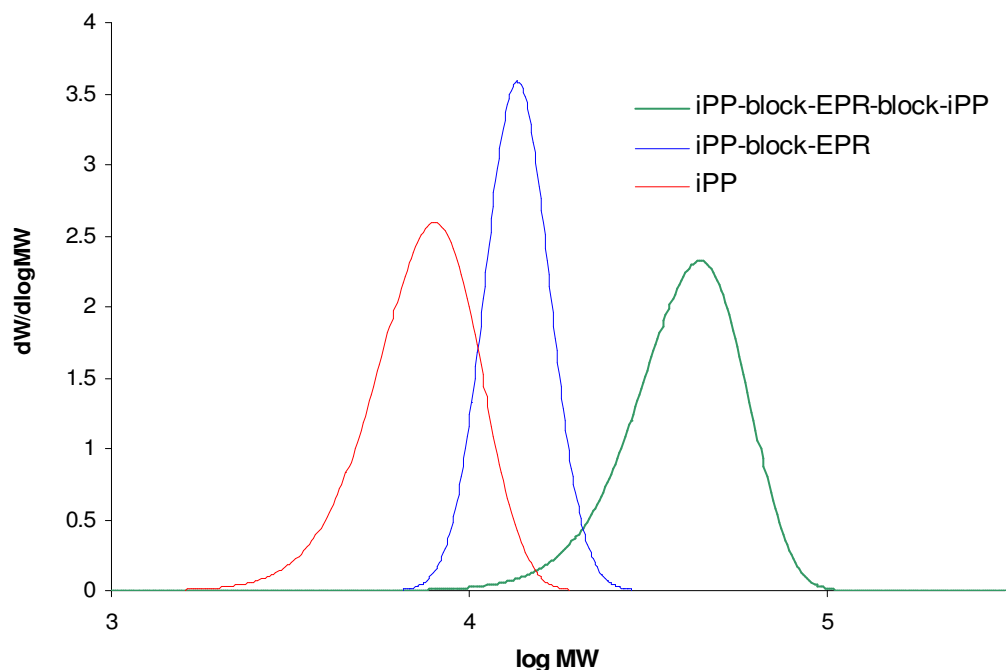
methanol/HCl(aq, conc.) (95/5 v/v). The block copolymer was coagulated with excess methanol/HCl, filtered, washed with more methanol and vacuum-dried.

Typical results for iPP-*block*-EPR and iPP-*block*-EPR-*block*-iPP are given in Table S3 and Figures S1-S4.

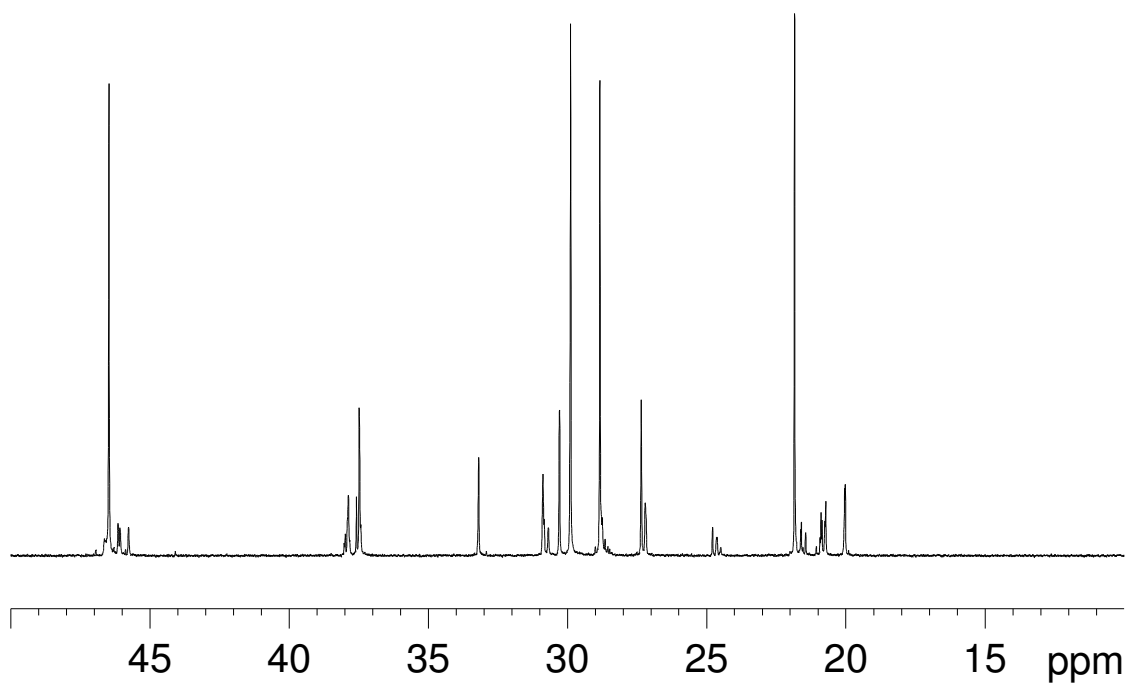
**Table S3.** Typical results of the block copolymerization experiments.

Copolymer	Yield, mg	$M_n$ , kDa <sup>(a,b)</sup>	$M_w/M_n$	$T_m$ , °C <sup>(c)</sup>	$\Delta h_m$ , J g <sup>-1</sup> <sup>(c)</sup>
iPP- <i>block</i> -EPR	718	14.0	1.1	141.5	53.3
iPP- <i>block</i> -EPR- <i>block</i> -iPP	1070	21.6	1.2	142.9	66.9

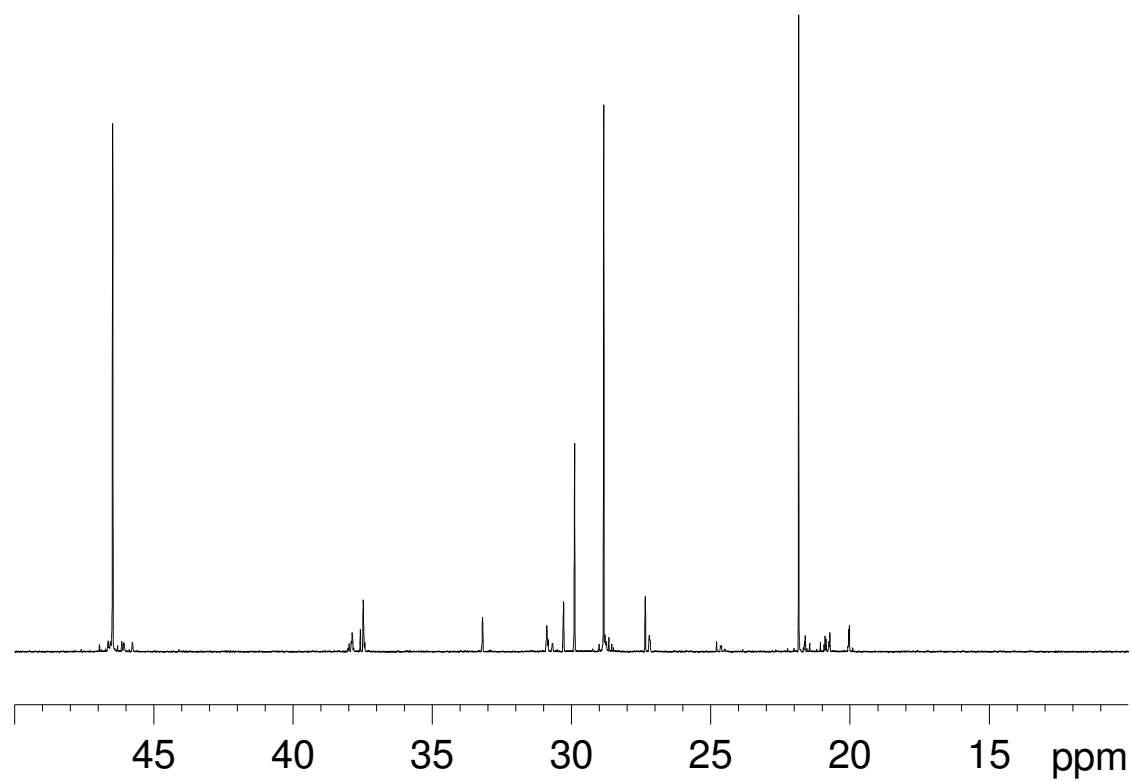
<sup>(a)</sup> Measured by <sup>1</sup>H NMR. <sup>(b)</sup> Total  $M_n$ . iPP block length: 7.6 kDa (each); EPR block length: 6.4 kDa. <sup>(c)</sup> Measured by DSC on 2<sup>nd</sup> heating scan.



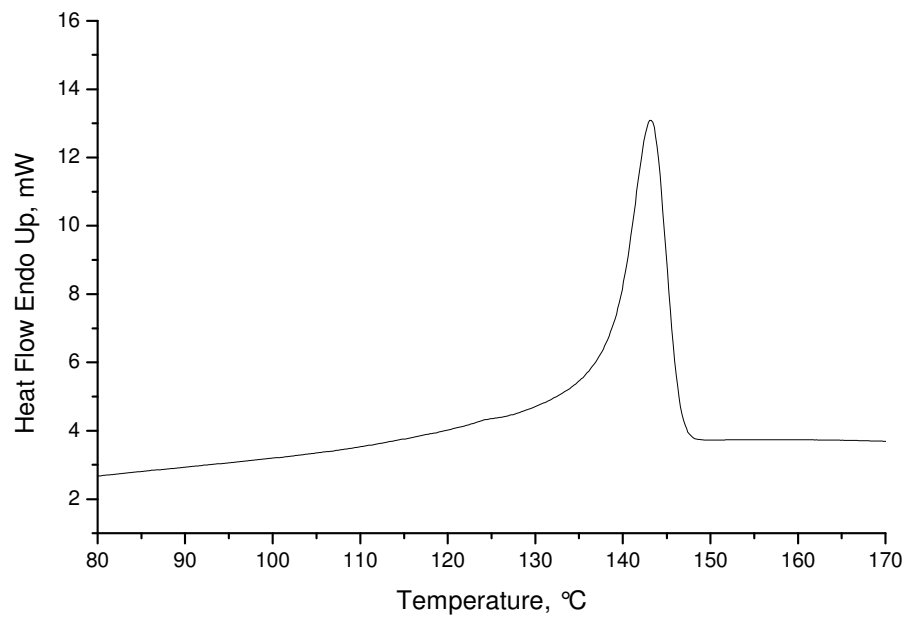
**Figure S1.** GPC traces of the products obtained after the 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> step of a block copolymerization experiment as described above (see also Table S3). The slightly broader MWD for the iPP homopolymer sample ( $M_w/M_n = 1.23$ ) is likely due to a comparatively slow initiation.



**Figure S2.** 100 MHz  $^{13}\text{C}$  NMR spectrum of *iPP-block-EPR* (Table S3).



**Figure S3.** 100 MHz  $^{13}\text{C}$  NMR spectrum of *iPP-block-EPR-block-iPP* (Table S3).

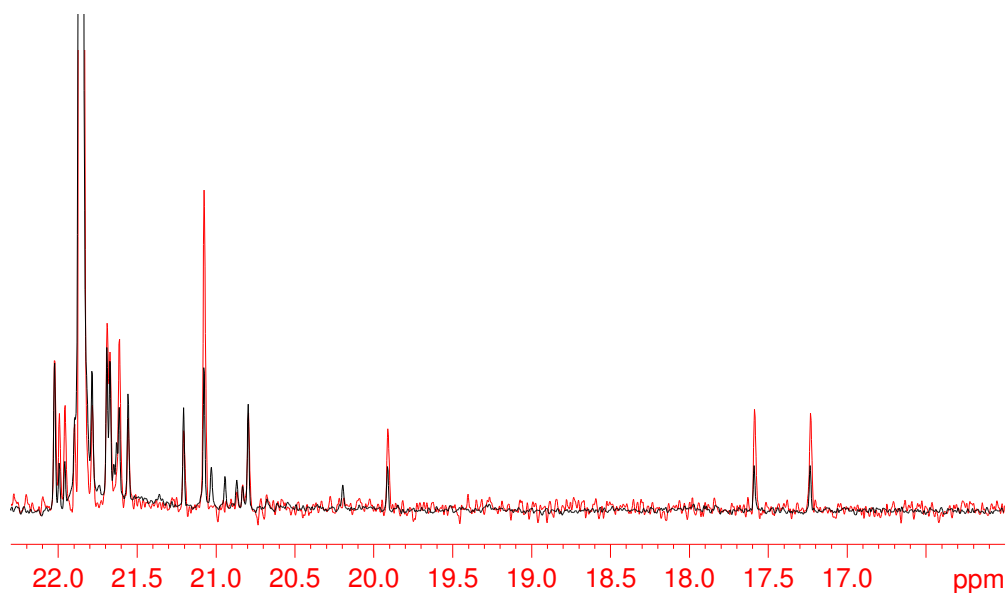


**Figure S4.** 2<sup>nd</sup> DSC heating trace of *iPP-block-EPR-block-iPP* (Table S3).

#### 1.4. NMR Polymer Characterization

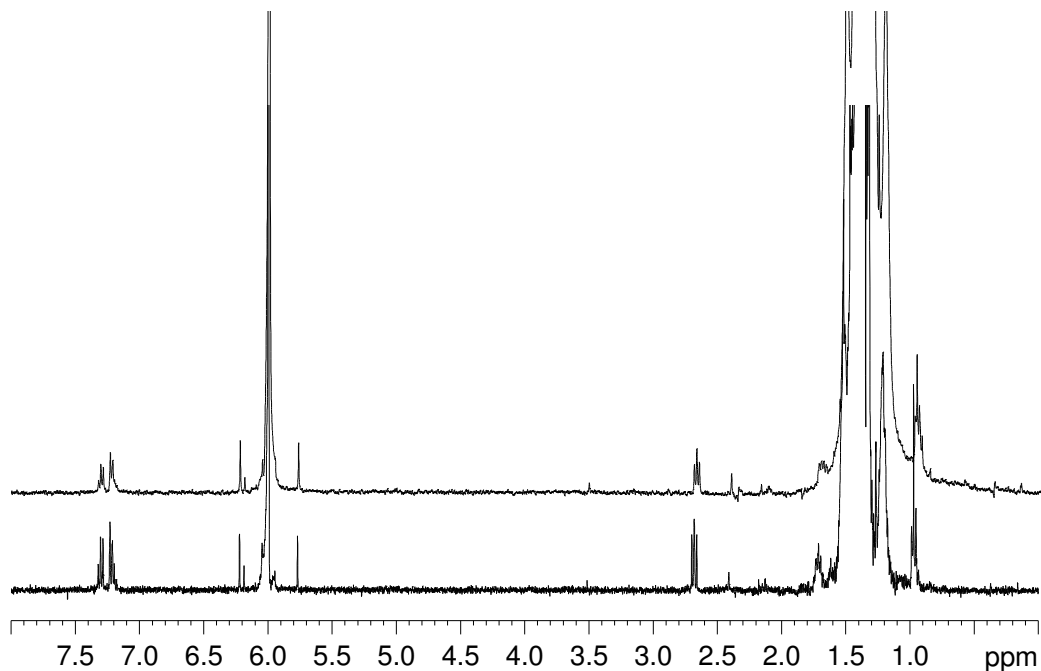
Quantitative  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded at  $120^\circ\text{C}$ , on 35 mg/mL polymer solutions in tetrachloroethane-1,2- $d_2$ , with a Bruker DRX 400 Avance spectrometer operating at 100.6 MHz with a 5 mm probe. Conditions for  $^1\text{H}$  NMR:  $90^\circ$  pulse; acquisition time, 4.0 s; relaxation delay, 2.0 s; 32 transients. Conditions for  $^{13}\text{C}$  NMR:  $80^\circ$  pulse; acquisition time, 1.6 s; relaxation delay, 3.0 s; >10K transients. Broad-band proton decoupling was achieved with a modified WALTZ16 sequence (BI\_WALTZ16\_32 by Bruker). Peak integration by full spectral simulation, and best-fit calculations of stereosequence distributions, were carried out using the SHAPE2004 and CONFSTAT (Ver. 3.1 for Windows) software packages, respectively. (Information on the software can be obtained from the Author: Prof. Michele Vacatello, Dipartimento di Chimica, Università di Napoli Federico II; e-mail: [vacatello@chemistry.unina.it](mailto:vacatello@chemistry.unina.it)). Resonance assignment was based on the literature.<sup>8,9,12,21</sup>

The methyl region of the  $^{13}\text{C}$  NMR spectra of two representative iPP samples prepared at  $25^\circ\text{C}$  with **Zr-2**/MAO/TBP and **Hf-2**/MAO/TBP, with explicit peak attributions, is shown in Figure 2 of the manuscript. A similar figure for iPP samples prepared with **Zr-1**/MAO/TBP and **Hf-1**/MAO/TBP is reported below (Figure S5).



**Figure S5.** Overlay of the methyl region of the 100 MHz  $^{13}\text{C}$  NMR spectra of two representative iPP samples prepared at  $25^\circ\text{C}$  with **Zr-1**/MAO/TBP (red trace) and **Hf-1**/MAO/TBP (black trace).

$^1\text{H}$  NMR spectra of representative PE samples prepared at  $25^\circ\text{C}$  with **Hf-2**/MAO/TBP are shown in Figure S6. Peaks due to olefinic chain ends were undetectable up to at least  $t_p = 3$  h.



**Figure S6.** 400 MHz  $^{13}\text{C}$  NMR spectra of PE samples prepared at  $25^\circ\text{C}$  with **Hf-2**/MAO/TBP. Bottom:  $t_p = 60$  min. Top:  $t_p = 180$  min. The resonances of the aromatic protons in the benzyl end groups are clearly visible in the  $\delta = 7.0$ - $7.5$  ppm range, whereas resonances attributable to olefinic chain ends, expected at around 5 ppm, are undetectable.

## 1.5. GPC Polymer Characterization

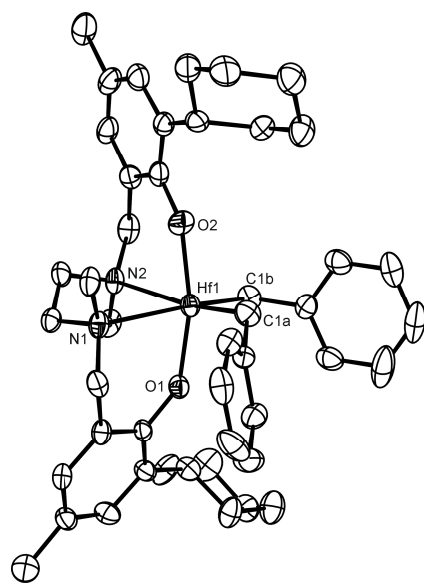
GPC curves were recorded at 135°C with a Waters Alliance GPCV2000 system with dual (differential refractometric and differential viscometric) detection, on polymer solutions in 1,2-dichlorobenzene (added with 0.25 mg mL<sup>-1</sup> of 4-methyl-2,6-di-*tert*-butylphenol as a stabilizer). A set of 4 mixed-bed Styragel HT 6E columns was used. Universal calibration was carried out with 12 samples of monodisperse polystyrene ( $M_n$  between 1.3 and 3700 KDa). In each carousel of 24 samples, 2 were of a known iPP produced with an *ansa*-zirconocene catalyst, to check for consistency.

## 1.6. DSC Polymer Characterization

The melting parameters of selected polymer samples were determined by Differential Scanning Calorimetry (DSC) with a Perkin-Elmer Pyris 1 apparatus, at the scanning rate of 10°C min<sup>-1</sup>, under nitrogen flow. The results reported in the manuscript always refer to the 2<sup>nd</sup> heating scan.

## 2. X-RAY DETERMINATION OF THE SOLID STATE STRUCTURE OF Hf-3

*Crystal data.* Crystals suitable for X-Ray diffraction were obtained from a saturated solution of the complex in toluene, at 273 K. Data collection was performed at 293 K on a Bruker-Nonius kappaCCD diffractometer (MoK $\alpha$  radiation, CCD rotation images, thick slices,  $\phi$  scans +  $\omega$  scans to fill the asymmetric unit). Cell parameters from 274 reflections are in the range  $3.95 \leq \theta \leq 21.37$ . Crystal data: C<sub>46</sub>H<sub>60</sub>N<sub>2</sub>O<sub>2</sub>Hf·C<sub>3.5</sub>,  $M = 893.48$  g/mol, monoclinic, P21/c,  $Z = 4$ , yellow crystal, 0.20 mm  $\times$  0.15 mm  $\times$  0.10 mm,  $a = 15.725(2)$  Å,  $b = 15.782(4)$  Å,  $c = 21.611(6)$  Å,  $\beta = 123.95(3)^\circ$ ,  $V = 4448.8$  Å<sup>3</sup>,  $\rho_{\text{calcd}} = 1.334$  g/cm<sup>3</sup>,  $\mu = 2.384$  mm<sup>-1</sup>. A semiempirical absorption correction (multi-scan SADABS program; Sheldrick, G.M., University of Göttingen, Germany, 1996) was applied. 42561 reflections collected ( $\pm h$ ,  $\pm k$ ,  $\pm l$ ), max.  $\theta = 27.50^\circ$ , 9979 independent reflections ( $R_{\text{int}} = 0.1529$ ). The structure was solved with the direct method (SIR97 program; Altomare, A.; Burla, M.C.; Camalli, M.; Cascarano, G.L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A.G.G.; Polidori, G.; Spagna, R. *J. Appl. Cryst.* **1999**, *32*, 115), and refined with the full matrix least-squares method (SHELX-97 program; Sheldrick, G.M., University of Göttingen, Germany 1997) on  $F^2$  against all independent measured reflections. H atoms were placed in calculated positions and refined by the riding method. 478 refined parameters,  $R_1 = 0.0593$ ;  $wR_2 = 0.1449$  (on reflections with  $I > 2\sigma(I)$ ) and  $R_1 = 0.1768$ ,  $wR_2 = 0.2155$  on all reflections. Max. and min. residual electron density (e $\cdot$  Å<sup>-3</sup>): +1.896 and -1.928.



**Figure S7.** X-ray molecular structure of **Hf-3**. Thermal ellipsoids are shown at 25% probability level. A statistic toluene solvent molecule and all the hydrogen atoms are not shown for clarity. Selected bond distances (Å) and angles ( $^\circ$ ): Hf-C1a = 2.260(1), Hf-C1b = 2.270(1), Hf-N1 = 2.450(8), Hf-N2 = 2.487(7), Hf-O1 = 1.980(7), Hf-O2 = 1.984(7), O1-Hf-O2 = 165.8(3), O1-Hf-C1b = 92.8(3), O1-Hf-C1a = 97.4(4), O1-Hf-N1 = 76.9(3), O1-Hf-N2 = 92.2(3), N1-Hf-N2 = 72.1(3), C1a-Hf-C1b = 104.6(4).

The CIF is provided as a separate file.