catalysts

MDPI

Supplementary Materials

Synthesis of Ethylene/1-Octene Copolymers with Ultrahigh Molecular Weights by Zr and Hf Complexes Bearing Bidentate NN Ligands with the Camphyl Linker

Chunyu Feng [1], Qingqiang Gou [2], Shaofeng Liu [1,*], Rong Gao [2,*] and Zhibo Li [1,3,*]

[1] Key Laboratory of Biobased Polymer Materials, College of Polymer Science and Engineering, Qingdao University of Science and Technology, Qingdao, 266042, China; ffancy7@163.com

[2] Department of Polyethylene, Sinopec Beijing Research Institute of Chemical Industry, Beijing 100013, China; gouqq.bjhy@sinopec.com

[3] College of Chemical Engineering, Qingdao University of Science and Technology, Qingdao, 266042, China

* Correspondence: shaofengliu@qust.edu.cn (S.L.), gaor.bjhy@sinopec.com (R.G.), and zbli@qust.edu.cn (Z.L.)

1. General Considerations.

All moisture/oxygen sensitive reactions/compounds were performed using standard Schlenk techniques or glovebox techniques in an atmosphere of high-purity nitrogen. Toluene, THF, and *n*-hexane were purified by first purging with dry nitrogen, followed by passing through columns of activated alumina. 1-Octene was dried by refluxing over sodium under nitrogen. C_6D_6 was stored over Na/K alloy in *vacuo* and vacuum transferred immediately prior to use. Ethylene was purified by passage through a supported MnO oxygen-removal column and an activated Davison 4A molecular sieve column. The borate $[Ph_3C][B(C_6F_5)_4]$ were purchased from Sigma Aldrich. All other chemicals were purchased from commercial suppliers and used without further purification unless otherwise noted. Reaction temperatures were controlled using an IKA temperature modulator. NMR spectra were recorded on a Bruker AVANCE NEO 400 MHz NMR spectrometer (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR). NMR experiments on air-sensitive samples were conducted in Teflon valve-sealed sample tubes (J.Young). ^{1}H and ^{13}C NMR assays of polymer microstructure were conducted in 1,1,2,2-tetrachloroethane-d_2 at 120 °C, and signals were assigned according to the literature for these polymers [1]. Elemental analyses were performed on the Flash EA 1112 microanalyzer. Gel permeation chromatography (GPC) was carried out in 1,2,4-trichlorobenzene (stabilized with 125 ppm BHT) at 150 °C on the Agilent 1260 infinity II HT GPC instrument equipped with a set of three Agilent PL gel 10 μm mixed-BLS columns with differential refractive index, viscosity, and light scattering (15 and 90°) detectors. Data reported were determined via triple detection. Molecular weights were determined through universal calibration relative to polystyrene standards. Differential scanning calorimetry (DSC) was performed using a TA differential scanning calorimeter DSC 25 that was calibrated using high purity indium at a heating rate of 10 °C/min. Melting points were determined from the second scan at a heating rate of 10 °C/min following a slow cooling rate of 10 °C/min to remove the influence of thermal history.

2. General Procedures for Ethylene/1-Octene Copolymerization.

A 1 L autoclave stainless steel reactor equipped with a mechanical stirrer and a temperature controller was used in the polymerizations. Catalyst and cocatalyst (activator) solutions were handled in the glovebox. A stirred 1 L reactor was charged with about 220 g of toluene and 120 g of 1-octene. The reactor contents were heated to the polymerization temperature of 120 °C. Once at temperature, the reactor was saturated with 3 MPa ethylene. Catalysts and cocatalysts, as dilute solutions in toluene, were mixed and transferred to a catalyst addition tank and injected into the reactor under high pressure nitrogen. The polymerization conditions were maintained for 10 min with ethylene added on demand. Heat was continuously removed from the reaction vessel through an internal cooling coil. The resulting solution was removed from the reactor and quenched with ethanol. Polymers were recovered by drying for about 12 h in a temperature-ramped vacuum oven.

3. Crystal Structure Determinations.

Single crystals of **1-Zr** and **1-Hf** were obtained by recrystallization of their *n*-hexane solutions at -30 °C. X-ray diffraction studies for **1-Zr** and **1-Hf** were carried out on a Bruker smart Apex II CCD diffractometer using graphite-monochromated Mo-Ka radiation (λ = 0.71073 Å). Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. Using Olex2, the structures were solved with the XS and refined with the ShelXL (Sheldrick, 2015) [2]. Crystal data for **1-Zr** and **1-Hf** are summarized in Table S1 in Supporting Information. CCDC reference numbers 2054386-2054387 are for complexes **1-Zr** and **1-Hf**, respectively.

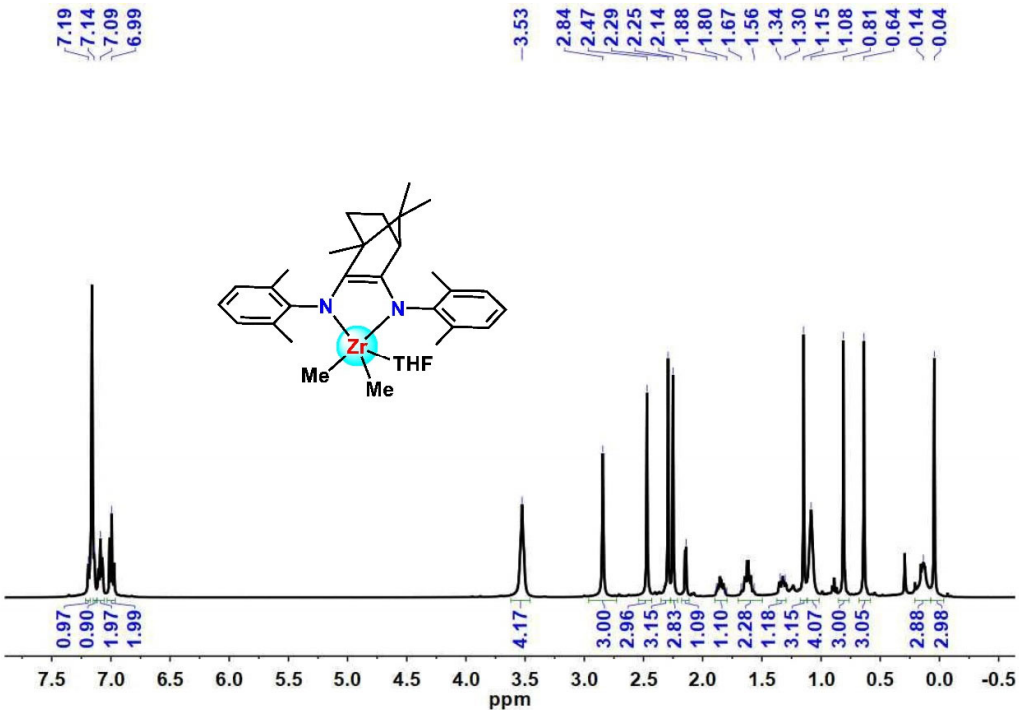

Figure S1. ^{1}H NMR spectrum of **1-Zr** in C_6D_6.

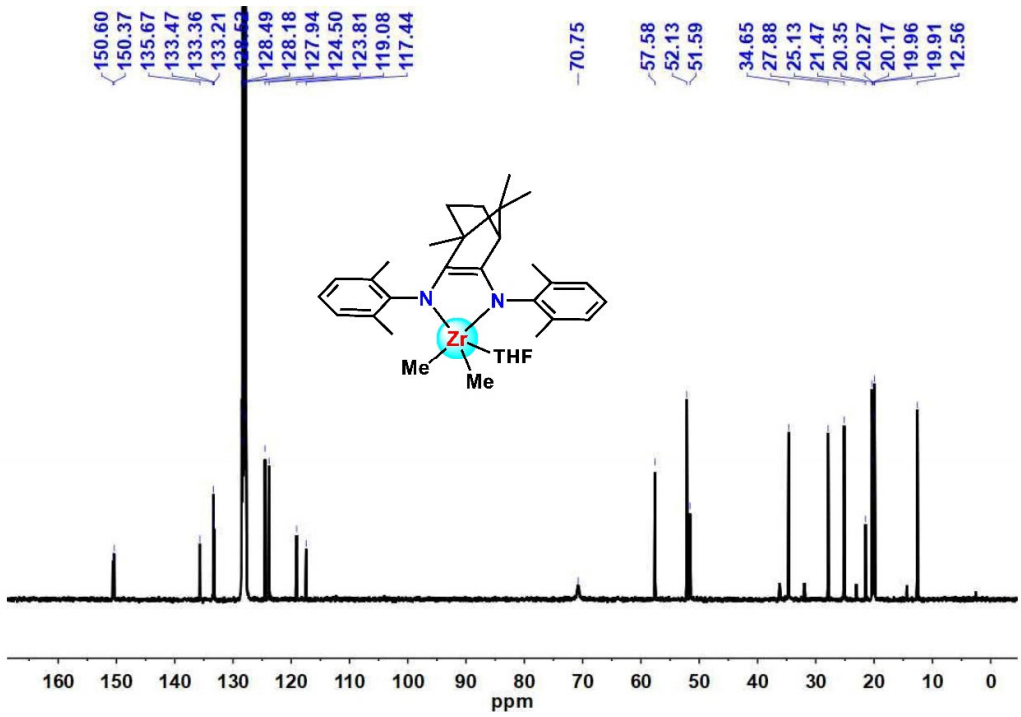

Figure S2. ^{13}C NMR spectrum of **1-Zr** in C_6D_6.

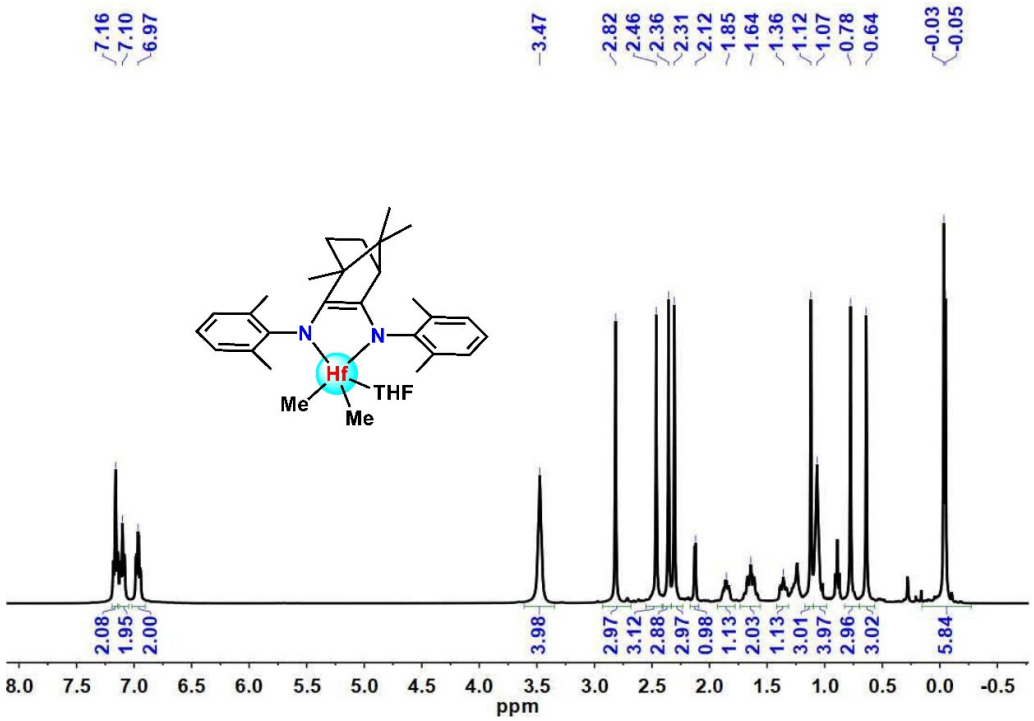

Figure S3. ^{1}H NMR spectrum of **1-Hf** in C_6D_6.

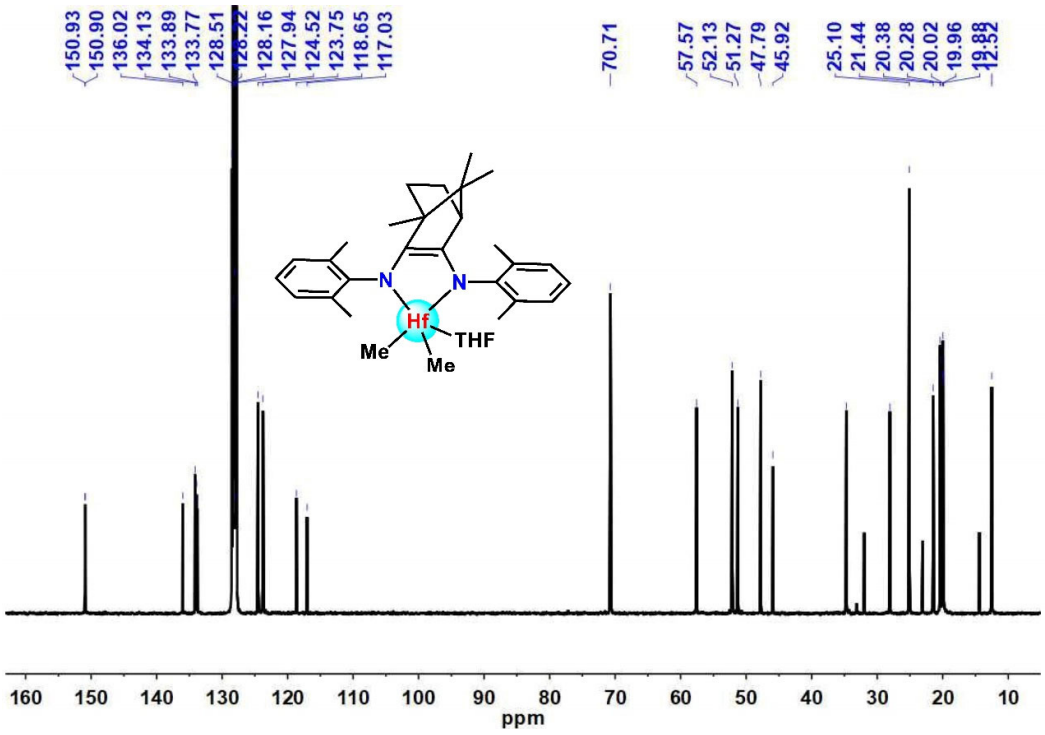

Figure S4. ^{13}C NMR spectrum of **1-Hf** in C_6D_6.

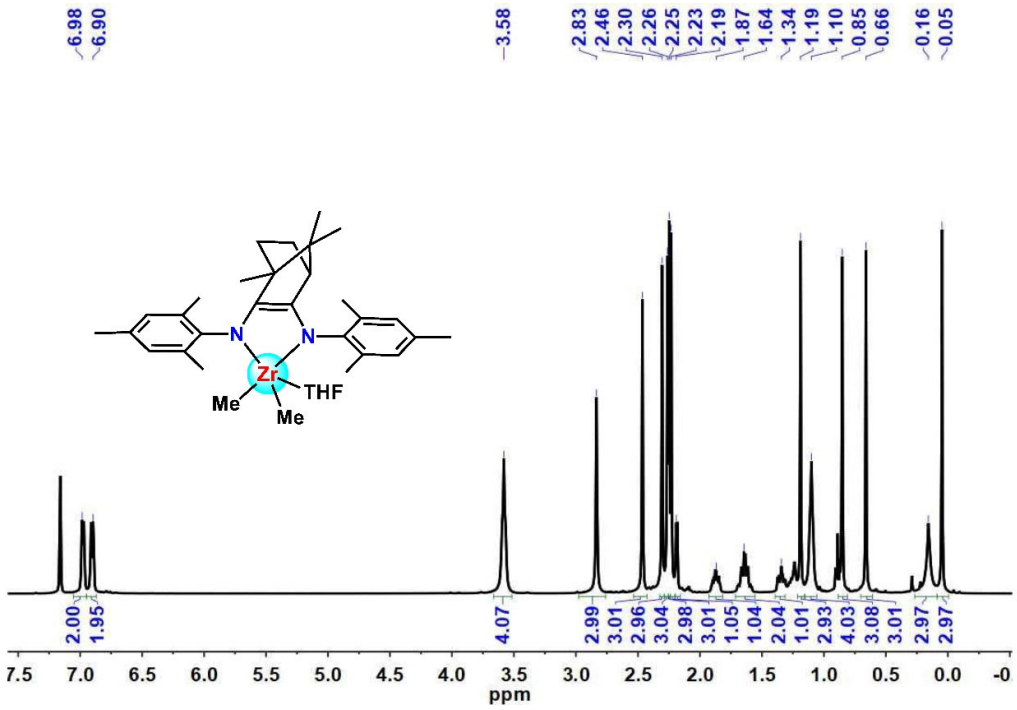

Figure S5. ^{1}H NMR spectrum of **2-Zr** in C_6D_6.

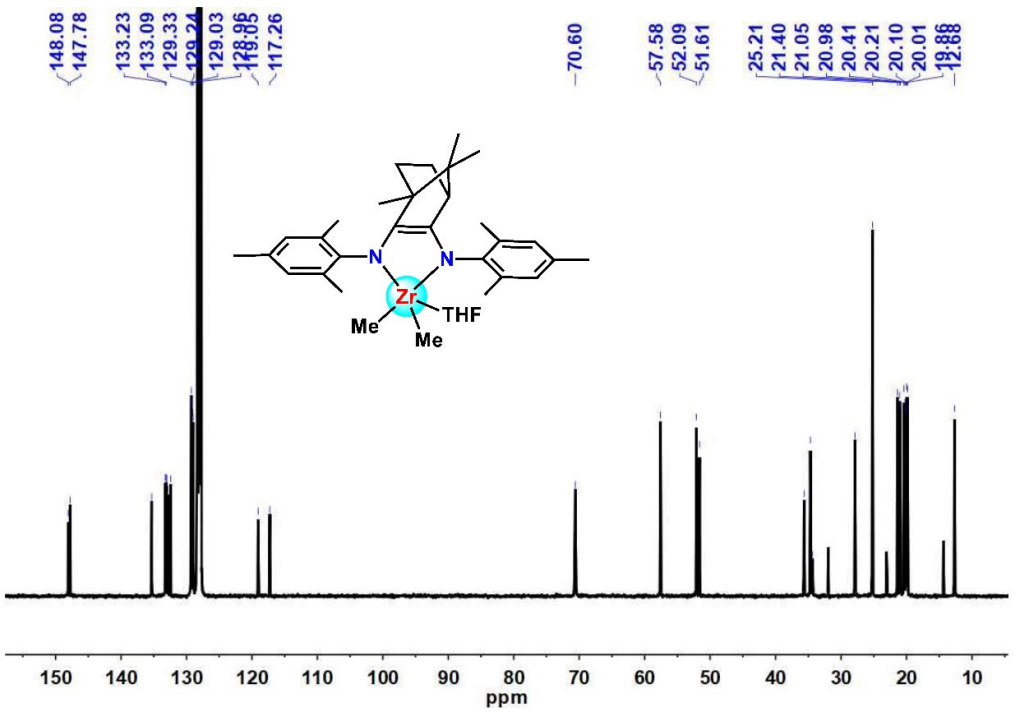

Figure S6. ^{13}C NMR spectrum of **2-Zr** in C_6D_6.

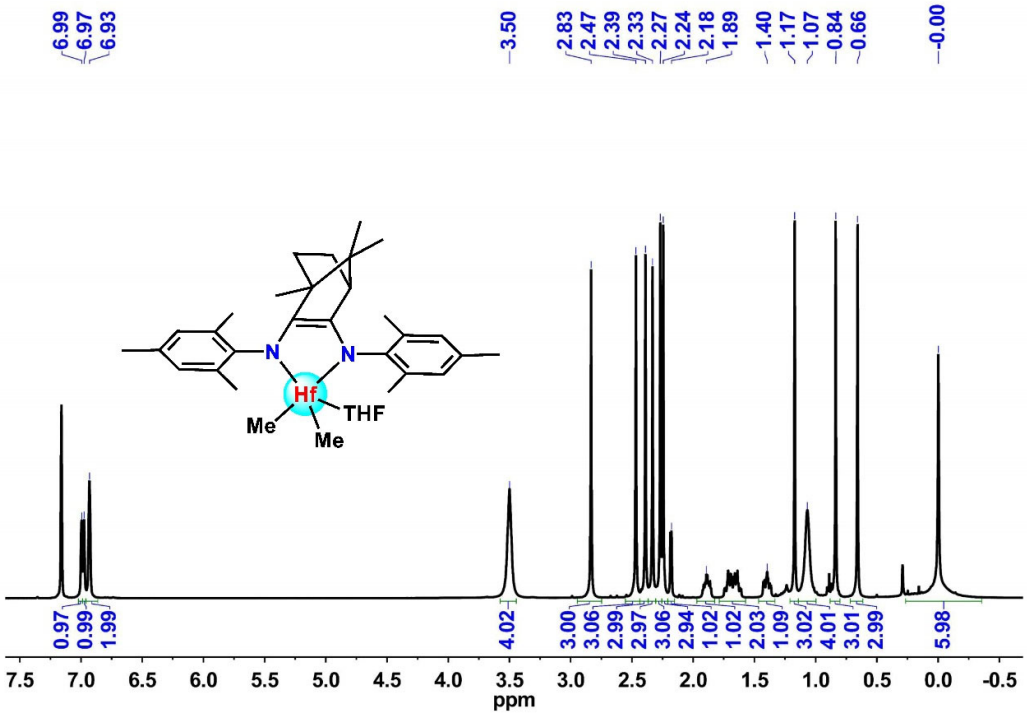

Figure S7. ^{1}H NMR spectrum of **2-Hf** in C_6D_6.

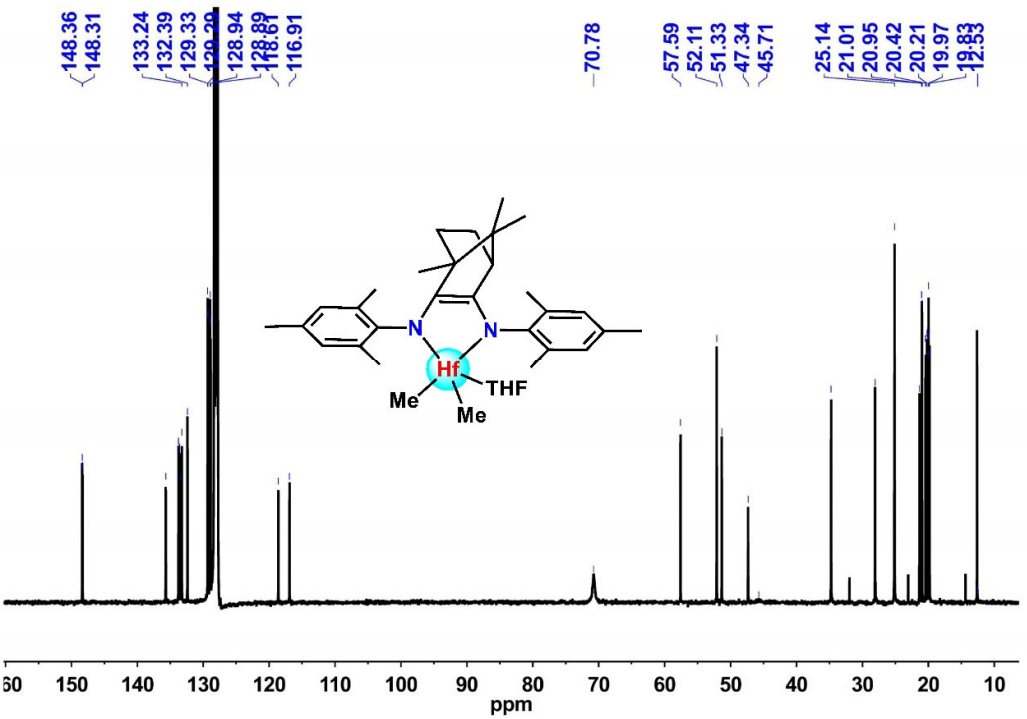

Figure S8. ^{13}C NMR spectrum of **2-Hf** in C_6D_6.

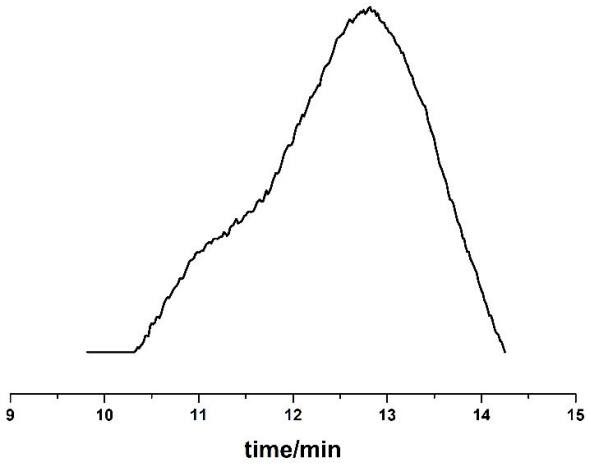

Figure S9. GPC curve of copolymer obtained in Table 1 run 2 (M_w = 337 × 10^4 g·mol^{-1}, $Đ$ = 3.3).

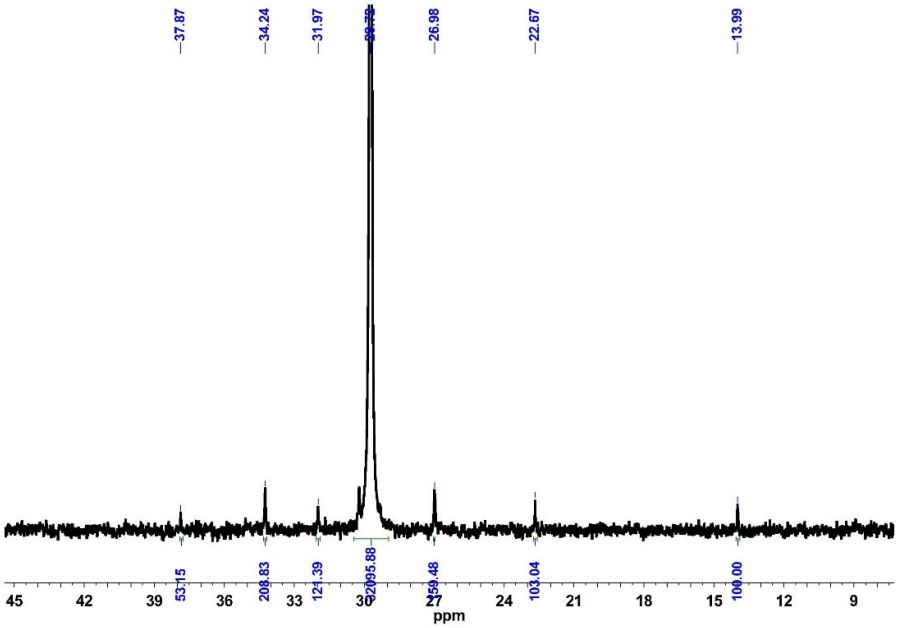

Figure S10. ^{13}C NMR spectrum of copolymer obtained in Table 1 run 1 in $C_2D_2Cl_4$ at 120 °C (0.2 mol% of 1-octene incorporation).

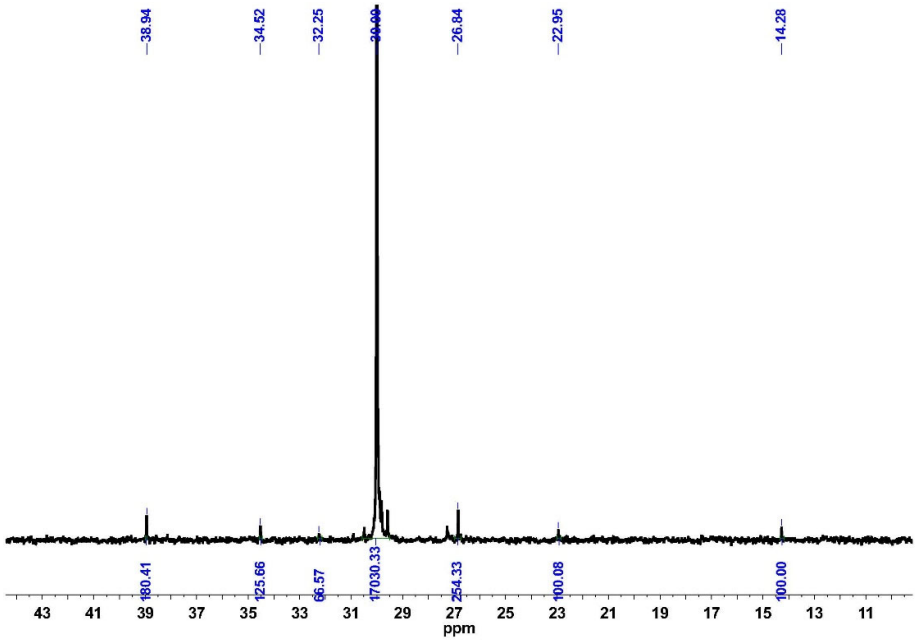

Figure S11. ^{13}C NMR spectrum of copolymer obtained in Table 1 run 2 in $C_2D_2Cl_4$ at 120 °C (1.0 mol% of 1-octene incorporation).

Table S1. Crystal data and structure refinement for metal complexes.

Complex	**1-Zr**	**1-Hf**
Empirical formula	$C_{32}H_{46}ZrN_2O$	$C_{32}H_{46}HfN_2O$
Formula weight	565.93	653.20
Temperature / K	193(2)	193(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a / Å, b / Å, c / Å	14.776(7), 11.193(5), 19.291(10)	14.7866(5), 11.1481(4), 19.2384(7)
α/°, β/°, γ/°	90, 112.176(7), 90	90, 112.2220(10), 90
Volume / Å^3	2955(2)	2935.76(18)
Z	4	4
ρ_{calc} / mg mm^{-3}	1.272	1.478
μ / mm^{-1}	0.398	3.579
F(000)	1200.0	1328.0
Crystal size / mm^3	0.280 × 0.240 × 0.230	0.120 × 0.080 × 0.070
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection	5.696 to 51.998°	4.574 to 50.018°
Index ranges	-10<=h<=18, -11<=k<=13, -23<=l<=21	-17<=h<=13, -13<=k<=13, -22<=l<=22
Reflections collected	15392	21336
Independent reflections	5649 [R(int) = 0.0532]	5132 [R(int) = 0.0405]
Data/restraints/parameters	5649/0/325	5132/0/334
Goodness-of-fit on F^2	0.957	1.078
Final R indexes [I>2σ (I)]	R_1 = 0.0449, wR_2 = 0.1188	R_1 = 0.0213, wR_2 = 0.0548
Final R indexes [all data]	R_1 = 0.0616, wR_2 = 0.1301	R_1 = 0.0230, wR_2 = 0.0558
Largest diff. peak/hole / e Å^{-3}	0.69/ -0.52	1.51/-0.78

References

1. Liu, Weixia; Rinaldi, Peter L.; McIntosh, Lester H.; Quirk, Roderic P. Poly(ethylene-co-1-octene) Characterization by High-Temperature Multidimensional NMR at 750 MHz. *Macromolecules* **2001**, *34*, 4757–4767.
2. Sheldrick, George M. Crystal Structure Refinement with SHELXL. *Acta Crystallogr., Sect. C: Struct. Chem.* **2015**, *71*, 3–8.