Supporting information belonging to the paper:

In Search for a Viable Route to High Melting Olefinic Block Copolymers

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EXPERIMENTAL SECTION

General considerations.

All manipulations were performed under an inert dry nitrogen atmosphere using glove box techniques and in an oven-dried Schlenk-type glassware. Isopar E (mainly C7-C10 isoalkanes from ExxonMobil bought at Brenntag), methylcyclohexane (MCH) and toluene (Biosolve) were employed as solvents for polymerization experiments. Isopar E, MCH, toluene, ethylene (Linde gas) and propylene (Linde gas) were dried using MBraun solvent purification system. 4-Methyl-1-pentene (TCI) and 1-octene (Sigma Aldrich) were deoxygenized via argon/vacuum and dried with 3 Å molecular sieves under an inert atmosphere (4-methyl-1-pentene was distilled over Na/K prior to this procedure). Methylaluminoxane (MAO, 30 wt.% solution in toluene) was purchased from Lanxess-Germany. Neat trimethylaluminum (TMA), triethylaluminum (TEA), triisobutylaluminum (TiBA), diethylzinc (DEZ), butylated hydroxytoluene (BHT) and dimethylanilinium tetrakis(pentafluorophenyl)borate (AB) purchased from Sigma Aldrich. Triphenylmethylium Tetrakis(pentafluorophenyl)borate (TTB) was purchased from TCI. Catalyst **1** was purchased from MCat GmbH. Catalysts **2** and **3** were purchased from Lomonosov Moscow State University (A. Z. Voskoboynikov).

Polymerization reactions.

General. The polymerizations of 4M1P and 1-octene were generally carried out in 20 mL crimp cap vials equipped with a magnetic stirring bar. The reaction conditions (temperature, concentrations, solvent, volume, time) are given in details in each table. After a set time, the polymerizations were quenched by adding a few drops of ethanol and the product mixtures of the polymerizations were poured into acidic methanol (200 mL). After stirring overnight, the resulting polymers were filtered, washed with methanol (3 × 20 mL) and diethyl ether (1 × 20 mL) and dried one day in a vacuum oven at 55 °C. The materials were then treated with Isopar E containing 2000 ppm of the antioxidant Irganox 1010 or Irganox 1076. After evaporation of the volatiles, the solids were dried one additional day in a vacuum oven at 55 °C. The monomer conversion was determined by ^{1}H NMR analysis of the raw product mixture. Irganox 1010 (2000 ppm) was then added and the volatiles were evaporated under the airflow of a fume hood and subsequently in a vacuum oven at 55 °C.

Polymerizations using MAO as scavenger/activator. In a glove box, complex **1**, **2** or **3** was activated by contacting it with 2/3 of the total amount of MAO as given in the table. The activated complex was then added to a 20 mL crimp cap vial containing a monomer/solvent mixture scavenged by the remaining 1/3 of MAO, containing DEZ as CTA, corresponding to time t_0 of the reaction. The vial was then sealed, quickly transferred out of the box and heated to the desired temperature. The polymerization was quenched after a set time. The work-up was carried out as mentioned above.

Polymerizations using $[C_6H_5N(H)Me_2]^+[B(C_6F_5)_4]^-$, $[C(C_6H_5)_3]^+[B(C_6F_5)_4]^-$, $B(C_6F_5)_3$/aluminum alkyl (or DiBAP) as activator/scavenger. Complex **1**, **2** or **3** was contacted with the borate (or borane) just prior to introduction into the solvent/monomer/aluminum alkyl(/CTA) mixture. The same protocol described above for the reactions using **1**/MAO or **2**/MAO was then applied.

Polymerizations with traces of ethylene. 1-octene and 4M1P polymerizations using **3**/TTB/TMA/DEZ were carried out in the presence of small amounts of ethylene that was added by bubbled through the reaction mixture for 1 min just after addition of the **3**/TTB mixture.

Catalyst reactivation by ethylene. After the 1-octene or 4M1P polymerization using **3**/TTB/TMA/DEZ was conducted for a 1 h (4M1P) or 2 h (1-octene), the polymerization mixture was cooled in an ice bath and ethylene was bubbled through for 1 min after which the polymerization was allowed to proceed for another 2 h (1-octene) or 3 h (4M1P).

Ethylene-propylene multi-block copolymers. The E/P di-block copolymers were prepared in a 3-neck 2L round bottom equipped with a mechanical stirred (Teflon anchor) located in a glove box under nitrogen. The vessel, connected to a vacuum pump and a propylene inlet was first charged with the solvent/scavenger mixture. Most of the nitrogen was removed via 4 vacuum (3 seconds)/propylene (1.3 bar) cycles. The vessel was then loaded with propylene during 45 min. The borane activator was then contacted to complex 2 just prior to introduction into the vessel. After a set time, 4 cycles vacuum (3 seconds)/ethylene (1.3 bar) were applied. After a desired time, the set-up was transferred out of the box and the reaction mixture poured into 2 L of acidic methanol. The purification was then carried out according to the procedure described above for P4M1P. The E/P tri- and tetra-block copolymers were obtained by extra propylene and propylene/ethylene sequential feeds, respectively.

Analytical techniques.

^{1}H NMR characterization. Selected polymer samples were analyzed by ^{1}H NMR. The analysis carried out at 130 °C using tetrachloroethane-d_2 as the solvent and recorded in 5 mm tubes on a Varian Mercury Vx spectrometer operating at a frequency of 400 MHz. Chemical shifts are reported in ppm versus tetramethylsilane and were determined by reference to the residual solvent protons. NMR spectra related to 1-octene polymerization were recorded at 25 °C in chloroform-d_1.

Size exclusion chromatography (SEC). *High temperature SEC (for P4M1P samples):* The molecular weights, reported in kDa, and polydispersity index (PDI, $Đ$) were determined by means of high temperature size exclusion chromatography, which was performed at 150 °C in a GPC-IR instrument equipped with an IR4 detector and a carbonyl sensor (PolymerChar, Valencia, Spain). Column set: three Polymer Laboratories 13 μm PLgel Olexis, 300 × 7.5 mm. 1,2-Dichlorobenzene (o-DCB) was used as eluent at a flow rate of 1 mL·min^{-1}. The molecular weights and the corresponding PDI's were calculated from HT SEC analysis with respect to narrow polystyrene standards (PSS, Mainz, Germany), using polyethylene Mark-Houwink coefficients. *Low temperature SEC (for poly(1-octene) samples):* THF-SEC was measured on a Waters Alliance system equipped with a Waters 2695 separation module, a Waters 2414 refractive index detector (40 ºC), a Waters 2487 dual absorbance detector, a PSS SDV 5 mm guard column followed by 2 PSS SDV linearXL columns in series of 5 mm (8 × 300) at 40 °C. Tetrahydrofuran (THF, Biosolve), stabilized with BHT, was used as eluent at a flow rate of 1 mL·min^{-1}. The molecular weights were calculated with respect to polystyrene standards (Polymer Laboratories, M_p = 580 Da up to M_p = 7.1·10^6 Da), using polyethylene Mark-Houwink coefficients. Before SEC analysis was performed, the samples were filtered through a 0.2 µm PTFE filter (13 mm, PP housing, Alltech).

The number of polymer chains per zinc were estimated using following equation:

$$[\mathrm{M}] = \mathrm{conversion} \cdot [1-\mathrm{octene}]_0 \cdot \frac{112.24}{\mathrm{M_n}}$$

Where M – sum of metal-polymeryl bonds; $[1\text{-octene}]_0$ – initial concentration of 1-octene; 112.24 – molar mass of 1-octene in g·mol^{-1}; M_n – the number average molecular weight in g·mol^{-1}.

Differential scanning calorimetry (DSC). Thermal analysis was carried out on a DSC Q100 from TA Instruments at a heating rate of 10 °C·min^{-1}. First and second runs were recorded after cooling down to ca. −60 °C. The melting temperatures reported correspond to second runs.

Polymerizations results for [Ph$_2$C(3-tBu-Cp)(2,7-tBu$_2$Flu)]ZrMe$_2$ (1).

Table S1. 4M1P polymerization with **1**/MAO/DEZ 30 °C.

Exp.	Zr µmol	MAO eq. Zr	DEZ eq. Zr	t min	Yield g	Conversion[a] %	M_n[b] kDa	M_w[b] kDa	$Đ_M$[b]
1[c]	0.50	1000	-	390	0.22	33	25.7	62.8	2.4
2[c]	0.50	1010	100	360	0.24	36	6.3	14.8	2.3
3[c]	0.50	500	100	340	0.32	48	5.4	13.2	2.5
4[d]	2.00	500	100	30	0.59	44	3.4	7.3	2.1
5[d]	2.00	500	100	60	0.76	57	3.5	7.5	2.2
6[d]	2.00	500	100	90	0.94	71	3.3	6.7	2.1
7[d]	2.00	500	100	120	1.06	80	3.6	7.3	2.0
8[d]	2.00	500	100	240	1.16	87	3.4	6.8	2.0
9[d]	2.00	500	100	360	1.23	92	3.1	6.9	2.2
10[d]	2.00	500	200	30	0.81	62	2.2	4.0	1.8
11[d]	2.00	500	200	60	1.03	77	2.2	4.0	1.8
12[d]	2.00	500	200	90	1.11	83	2.2	3.9	1.8
13[d]	2.00	500	200	120	1.17	88	2.1	3.8	1.9
14[d]	2.00	505	50	30	0.49	37	5.8	14.0	2.4
15[d]	2.00	505	50	60	0.59	44	6.6	15.2	2.3
16[d]	2.00	500	50	90	0.88	66	6.4	15.0	2.3
17[d]	2.00	500	50	120	0.95	71	7.2	15.8	2.2

Reaction conditions: 20 mL crimp capped vial; solvent: toluene ($V_{reaction}$ ~ 8 mL); stirring rate: 500 rpm; quenching: MeOH/HCl. (a) Determined by ^{1}H NMR; (b) Determined by SEC; (c) 4M1P: 1.0 mL (0.67 g); (d) 4M1P: 2.0 mL (1.33 g).

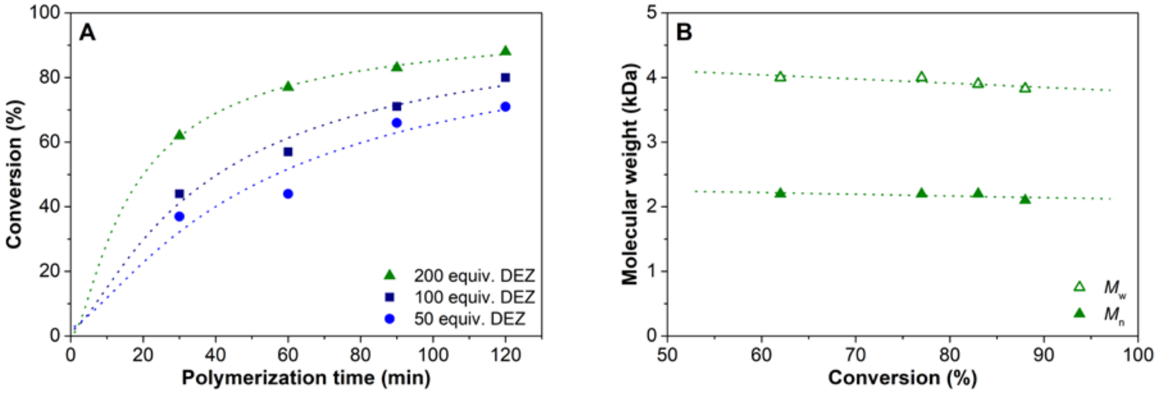

Figure S1. (A) Conversion versus polymerization time for different DEZ concentrations (Table S1) and (B) molecular weight development versus conversion for the 4M1P polymerization at 30 °C using **1**/MAO/DEZ (Table S1) using 200 equiv. of DEZ.

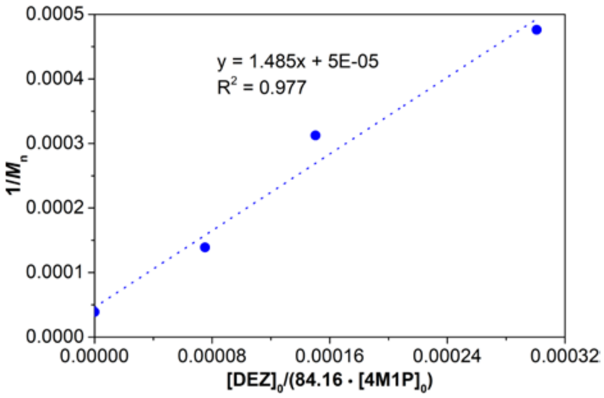

Figure S2. Approximate Mayo plot for the polymerization of 4M1P at 30 °C with **1**/MAO and various $[DEZ]_0$ (Table S1).

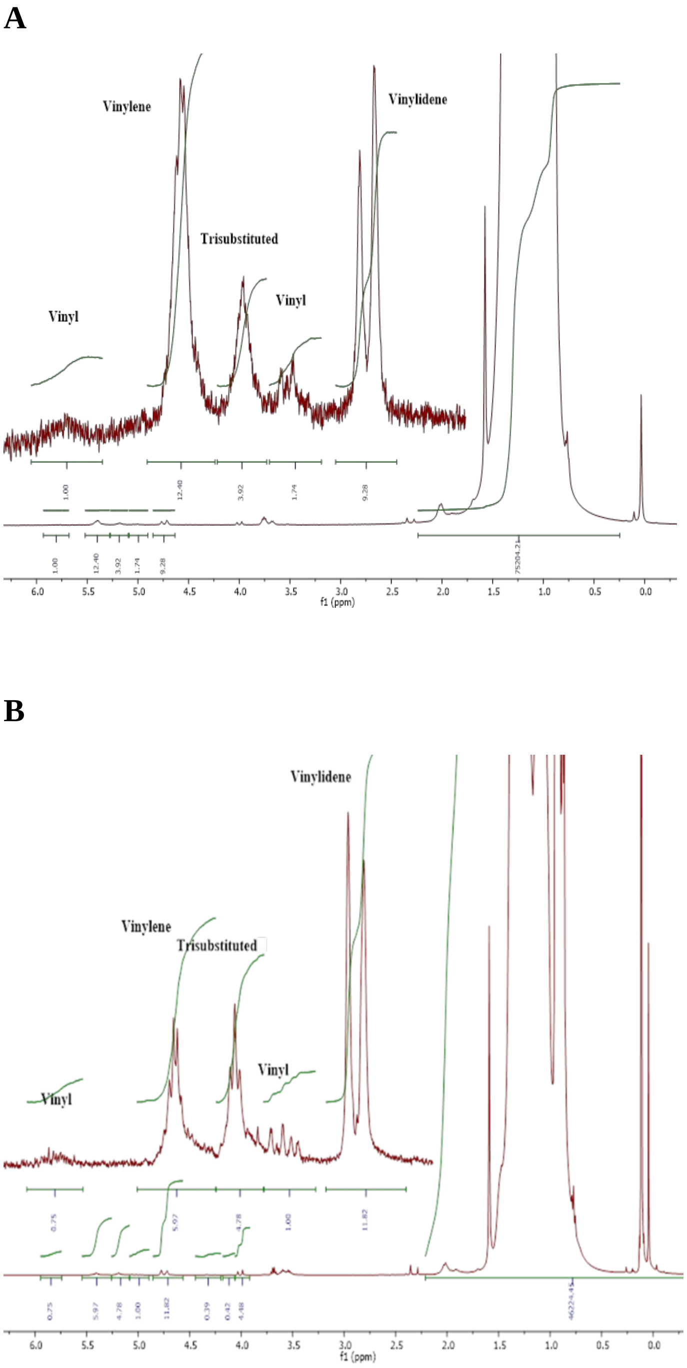

Figure S3. ^{1}H NMR spectrum of poly(1-octene)s produced at 80 °C using (A) **1**/MAO (Table 1, entry 4) and (B) **1**/MAO/DEZ (Table 1, entry 8).

Polymerization results for $[1\text{-}C_{10}H_6\text{-}5\text{-}(CMe_2\text{-}2,6\text{-}iPr_2\text{-}C_6H_3)\text{-}C_6H_3N]HfMe_2$ (2).

Table S2. Sequential ethylene/propylene copolymerization with **2**/$B(C_6F_5)_3$/DiBAP[a] at 25 °C.

Exp.	Hf µmol	Al eq. Hf	$C_3^{=\,b,c}$ min	$C_2^{=\,b,c}$ min	Yield g	$M_n^{d,e}$ kDa	$M_w^{d,e}$ kDa	$Đ_M^{e}$	$T_m^{d,f}$ °C
1	50.2	4.1	1.	2.	22.15	168.9^1	448.9^1	2.7^1	133.2^1
			30+120	30+120		225.4^2	580.7^2	2.6^2	132.0^2
2	49.9	4.1	1.	2.	24.51	40.1^1	80.7^1	2.0^1	132.2^1
			30+120	30+120		109.6^2	326.3^2	3.0^2	108.1^2
			3.						131.9^2
			60+120			147.8^3	393.0^3	2.7^3	109.4^3
									131.0^3
3	49.9	4.1	1.	2.	35.27	133.1^1	283.9^1	2.1^1	132.2^1
			20+120	20+120		158.9^2	395.4^2	2.5^2	132.1^2
			3.	4.		201.5^3	508.7^3	2.5^3	133.8^3
			40+120	40+120		189.9^4	633.5^4	3.3^4	131.4^4

Reaction conditions: 3-neck 2 L round bottom flask; solvent: toluene (800 mL); stirring rate: 200 rpm; $B(C_6F_5)_3/Hf = 1.0$. (a) DiBAP: triisobutyl aluminum/4-Me-2,6-$^tBu_2$-C_6H_2OH, 1:1; (b) $C_3^{=}$: propylene, $C_2^{=}$: ethylene; (c) x + y: $C_3^{=}$ feed stopped after x minutes and reaction let to completion for y additional minutes; (d) 1, 2, 3, 4: samples taken after feed #1, 2, 3 or 4; (e) Determined by SEC; (f) Determined by DSC.

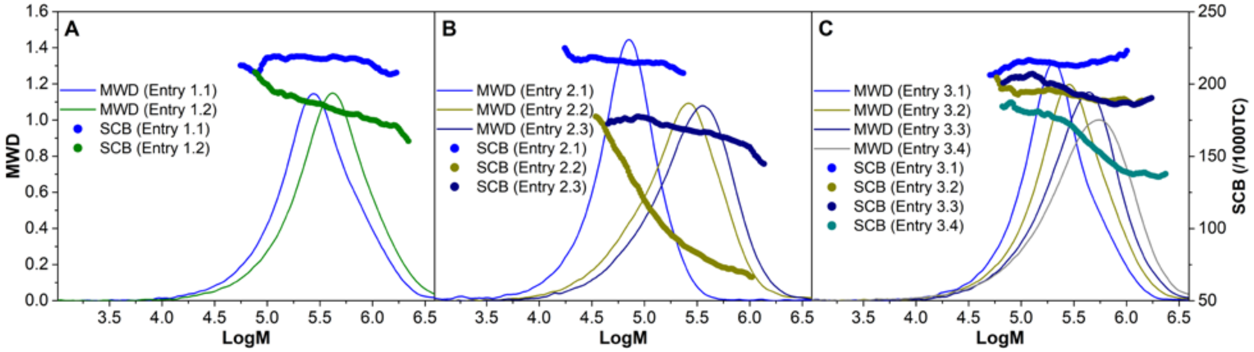

Figure S4. HT-SEC molecular weight distributions (MWD) and branching densities per 1000 total nr. of carbons (SCB/1000TC) of: (A) PP-PE di-block copolymer (Table S2, entry 1), (B) PP-PE-PP tri-block copolymer (Table S2, entry 3) and (C) PP-PE-PP-PE tetra-block copolymer (Table S2, entry 4). Samples were taken after each subsequent monomer addition (Table S2, entries: 1.1–1.2; 2.1–2.3; 3.1–3.4).

Table S3. 4M1P polymerization with **2**/AB/DiBAP at different temperatures.

Exp.	Hf µmol	DiBAP eq. Hf	T °C	t min	Yield g	Conversion[a] %	M_n[b] kDa	M_w[b] kDa	$Đ_M$[b]
1	0.15	230	25	30	0.02	2	204.2	2191.1	10.7
2	0.15	230	25	60	0.02	2	291.0	2559.4	8.8
3	0.15	230	25	90	0.12	9	250.3	2391.2	9.5
4	0.15	230	60	15	0.12	9	33.3	198.7	5.9
5	0.15	230	60	30	0.47	35	45.6	216.4	4.9
6	0.15	230	60	45	0.71	53	56.9	224.9	3.9
7	0.15	230	60	60	0.94	70	-[c]	-[c]	-[c]
8	0.20	175	100	30	0.40	30	10.9	35.1	3.2
9	0.20	175	100	60	0.42	32	-[c]	-[c]	-[c]
10	0.20	175	100	120	0.40	30	10.8	37.8	3.5
12	0.20	175	100	180	0.39	29	10.2	32.8	3.2

Reaction conditions: 20 mL crimp capped vial; 1.5 equiv. AB; 2 mL of 4M1P; solvent: MCH/toluene: 5+1 mL; $V_{reaction}$ ~ 8 mL); stirring rate: 500 rpm; quenching: MeOH/HCl. (a) Determined by ^{1}H NMR; (b) Determined by SEC; (c) Polymer not fully soluble in o-DCB.

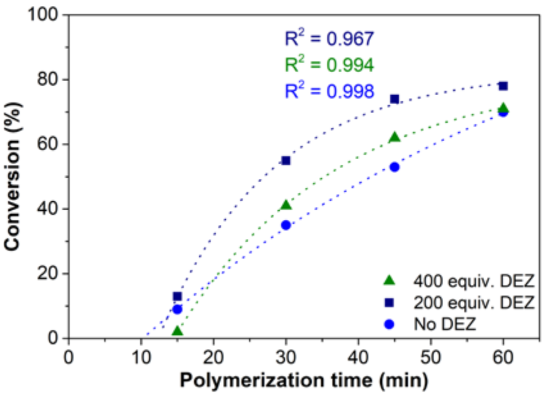

Figure S5. Conversion versus polymerization time for the 4M1P polymerization at 60 °C using **2**/AB/DiBAP as catalyst system without DEZ and with two different DEZ concentrations (Table 3).

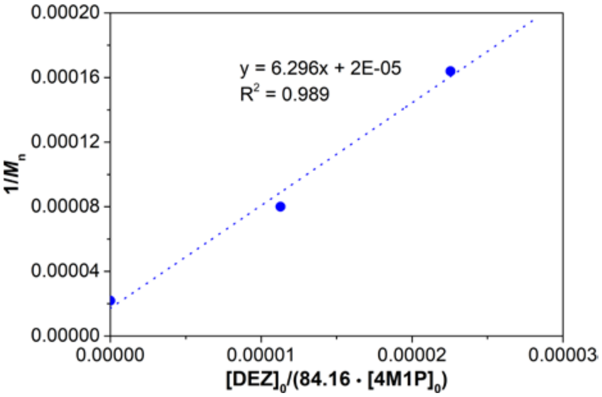

Figure S6. Approximate Mayo plot for the polymerization of 4M1P at 60 °C with **2**/AB/DiBAP(/DEZ) and various $[\mathrm{DEZ}]_0$ (Table 3).

Table S4. 4M1P polymerization with **2**/TTB/DiBAP(/DEZ).

Exp.	DEZ eq. Hf	T °C	t min.	Yield g	Conversion[a] %	M_n[b] kDa	M_w[b] kDa	$Đ_M$[b]
1	-	25	15	0.06	5	277.3	2269.1	8.2
2	-	25	30	0.11	8	303.9	2408.0	7.9
3	-	25	45	0.19	14	280.0	2197.5	7.9
4	-	25	60	0.19	14	289.0	2310.1	8.0
5	-	60	15	0.48	36	53.3	209.8	3.9
6	-	60	30	0.78	59	52.4	206.4	3.9
7	-	60	45	1.06	80	53.5	200.7	3.5
8	-	60	60	1.08	81	51.1	212.8	4.1
9	-	100	60	0.32	24	14.1	60.9	4.3
10	50	25	15	0.27	20	13.2	283.8	21.5
11	50	25	30	0.55	41	19.7	411.3	20.9
12	50	25	45	0.70	52	28.3	593.0	20.9
13	50	25	60	0.87	65	30.5	714.2	23.4
14	200	60	15	0.46	35	12.0	144.1	9.5
15	200	60	30	0.83	62	10.1	116.7	11.5
16	200	60	45	0.91	68	14.9	125.8	8.4
17	200	60	60	0.96	72	9.5	117.0	12.3

Reaction conditions: 20 mL crimp capped vial; 0.15 µmol of **2**; 1.5 equiv. of TTB; 230 equiv. of DiBAP; 2 mL of 4M1P; solvent: MCH/toluene (5 + 1 mL; $V_{reaction}$ ~ 8 mL); stirring rate: 500 rpm; quenching: MeOH/HCl. (a) Determined by ^{1}H NMR; (b) Determined by SEC.

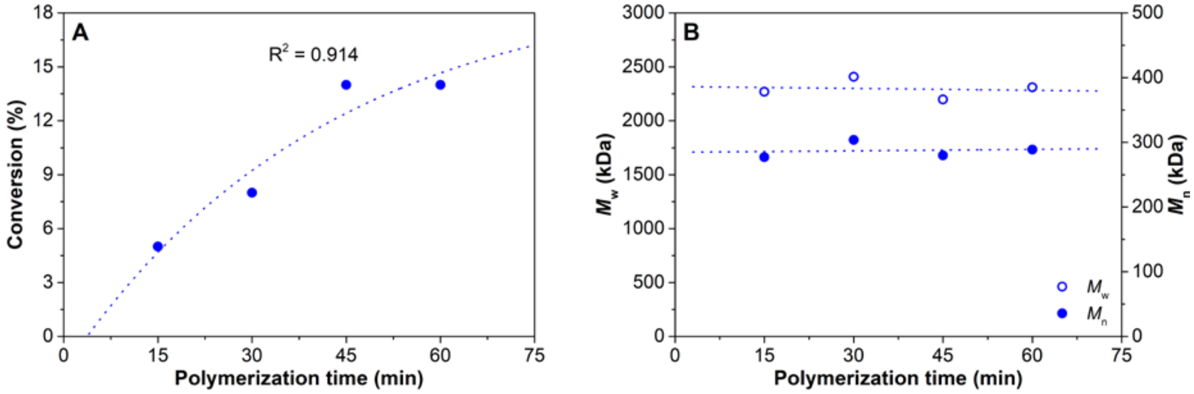

Figure S7. (A) 4M1P conversion versus polymerization time plot and (B) molecular weight development versus polymerization time plot for 4M1P polymerization using **2**/TTB/DiBAP at 25 °C (Table S4).

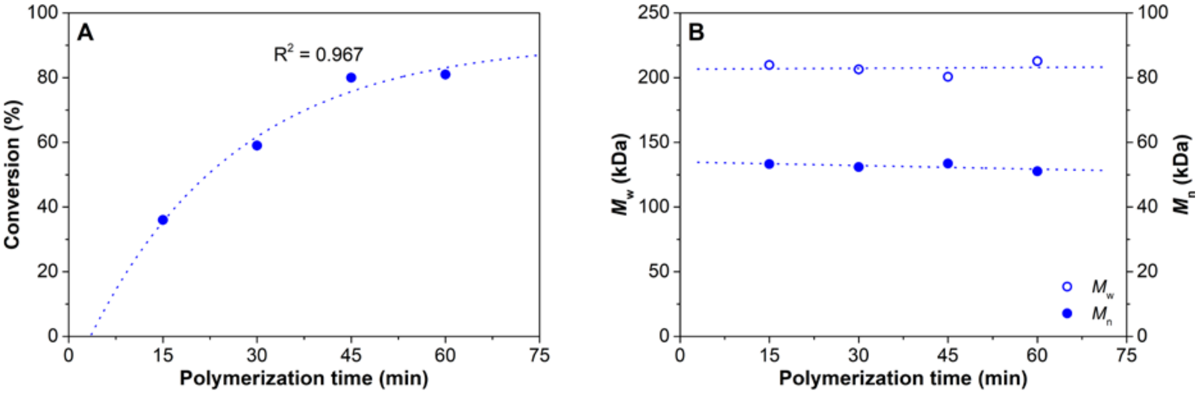

Figure S8. (A) 4M1P conversion versus polymerization time plot and (B) molecular weight development versus polymerization time plot for 4M1P polymerization using **2**/TTB/DiBAP at 60 °C (Table S4).

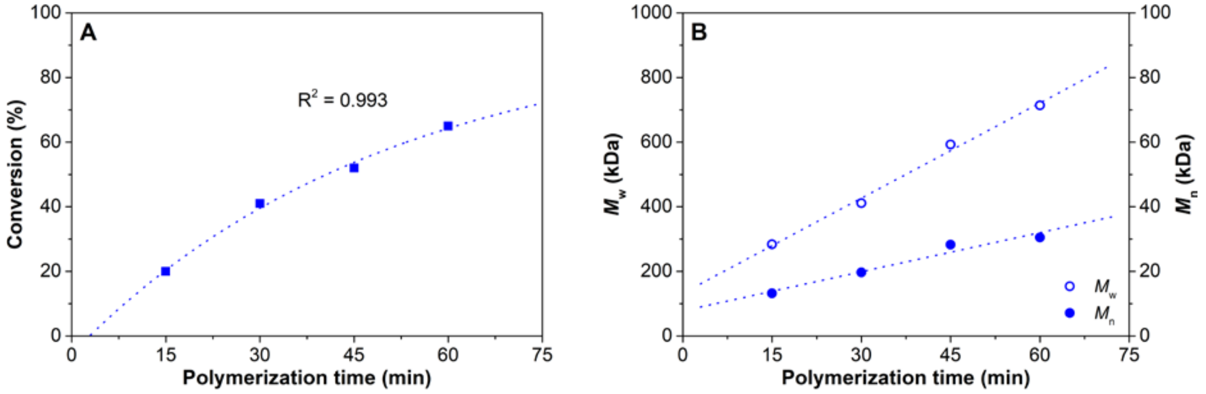

Figure S9. (A) 4M1P conversion versus polymerization time plot and (B) molecular weight development versus polymerization time plot for 4M1P polymerization using **2**/TTB/DiBAP and 50 equiv. of DEZ at 25 °C (Table S4).

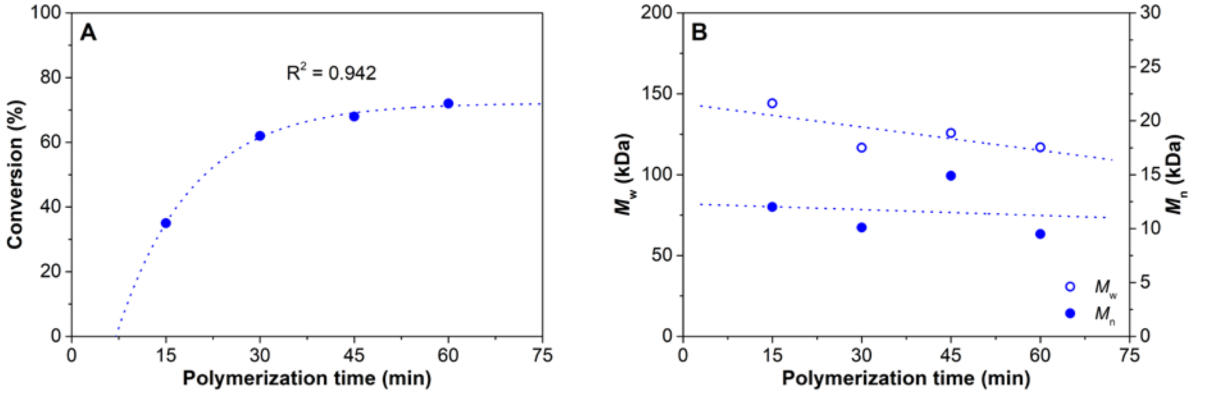

Figure S10. (A) 4M1P conversion versus polymerization time plot and (B) molecular weight development versus polymerization time plot for 4M1P polymerization using **2**/TTB/DiBAP and 200 equiv. of DEZ at 60 °C (Table S4).

Table S5. 1-Octene polymerization with **2**/AB/DiBAP(/DEZ) at 60 °C.

Exp.	DEZ eq. Hf	t min.	Yield g	Conversion^a %	M_n^b kDa	M_w^b kDa	$Đ_M^b$	Chains per Zn
1	-	15	0.10	3	91.6	408.7	4.5	-
2	-	30	0.67	19	103.9	404.8	3.9	-
3	-	45	0.88	25	103.8	409.6	3.9	-
4	-	60	1.14	32	111.7	414.5	3.7	-
5	200	15	0.19	5	n.d.	n.d.	n.d.	n.d.
6	200	30	1.02	29	13.4	203.2	15.2	2.6
7	200	45	1.86	52	19.0	256.9	13.5	3.3
8	200	60	2.43	68	21.7	280.4	12.9	3.7
9	400	60	1.65	46	14.9	248.1	16.6	1.8
10	400	120	2.11	59	16.0	171.9	17.6	2.2

Reaction conditions: 20 mL crimp capped vial; 0.15 µmol of **2**; 1.5 equiv. AB; 230 equiv. DiBAP; 5 mL of 1-octene; solvent: methylcyclohexane (2 mL) + toluene 1 mL; $v_{reaction}$ ~ 8 mL); stirring rate: 500 rpm; quenching: MeOH/HCl. (a) Determined by ^{1}H NMR; (b) Determined by SEC.

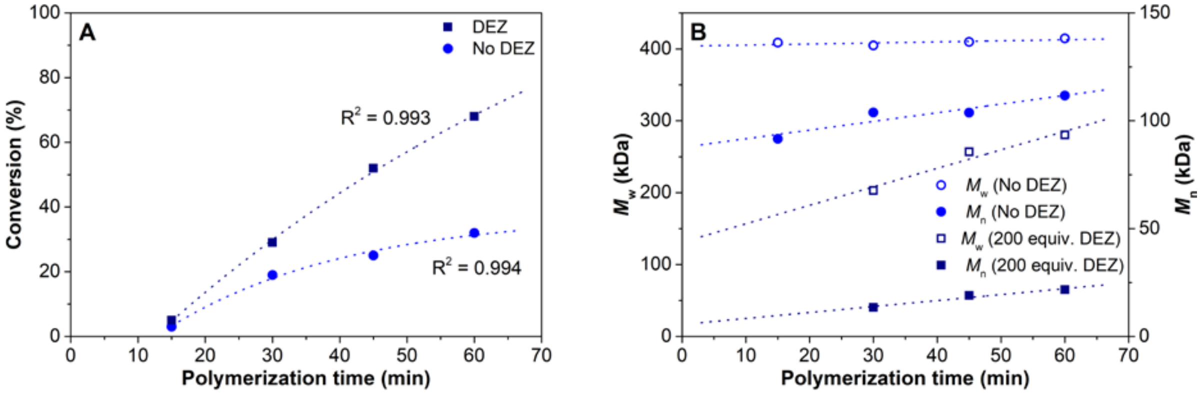

Figure S11. 1-Octene polymerization at 60 °C with a **2**/AB/DiBAP/(DEZ). (A) Poly(1-octene) production versus polymerization time. (B) Molecular weight development with polymerization time. (Table S5).

Table S6. 1-Octene polymerization with **2**/AB/DiBAP/(DEZ) at 60 °C using different amounts of 1-octene.

Exp.	DEZ eq. Hf	1-$C_8^=$ mL	t h	Yield g	Conversion^a %	M_n^{b} kDa	M_w^{b} kDa	$Đ_M$^{b}	Chains per Zn
1	-	1	24	0.62	86	45.3	130.5	2.9	-
2	-	2	24	1.12	78	81.2	256.2	3.2	-
3	-	3	24	1.79	84	105.9	349.6	3.3	-
4	-	4	24	2.63	92	103.0	355.8	3.5	-
5	-	5	24	3.17	89	134.0	472.8	3.5	-
6	200	1	72	0.62	86	10.0	59.1	5.9	2.1
7	200	2	72	1.42	99	15.9	122.4	7.7	3.0
8	200	3	72	2.09	97	20.7	173.4	8.4	3.4
9	200	4	72	2.75	96	24.8	156.0	9.4	3.7
10	200	5	72	3.16	88	40.0	314.8	7.9	2.6

Reaction conditions: 20 mL crimp capped vial; 0.15 µmol of **2**; 1.5 equiv. AB; 230 equiv. DiBAP; solvent: MCH (2-6 mL) + toluene 1 mL; $V_{reaction}$ ~ 8 mL; stirring rate: 500 rpm; quenching: MeOH/HCl. (a) Determined by ^{1}H NMR; (b) Determined by SEC.

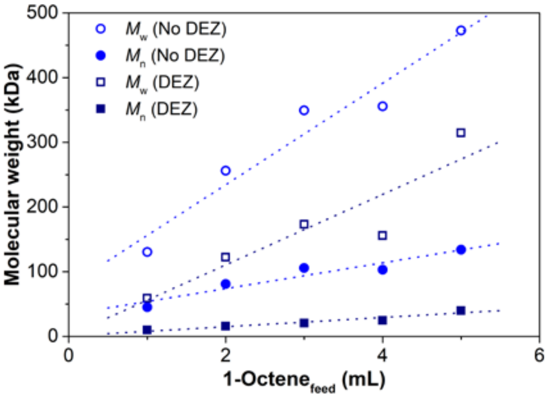

Figure S12. 1-Octene polymerization with a **2**/AB/DiBAP/(DEZ). Molecular weight dependency on initial 1-octene concentration in the absence and in the presence of DEZ (Table S6).

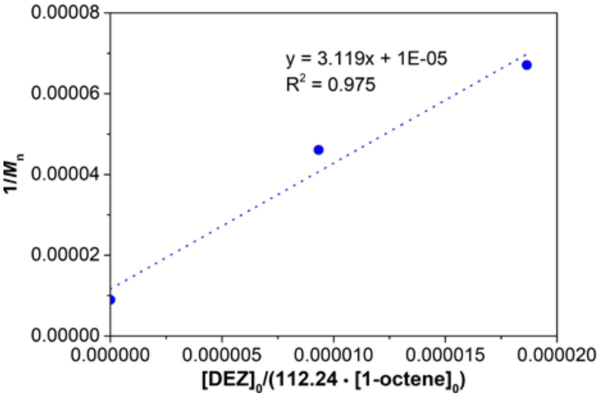

Figure S13. Approximate Mayo plot for the polymerization of 1-octene at 60 °C with **2**/AB/DiBAP(/DEZ) and various $[DEZ]_0$ (Table S5).

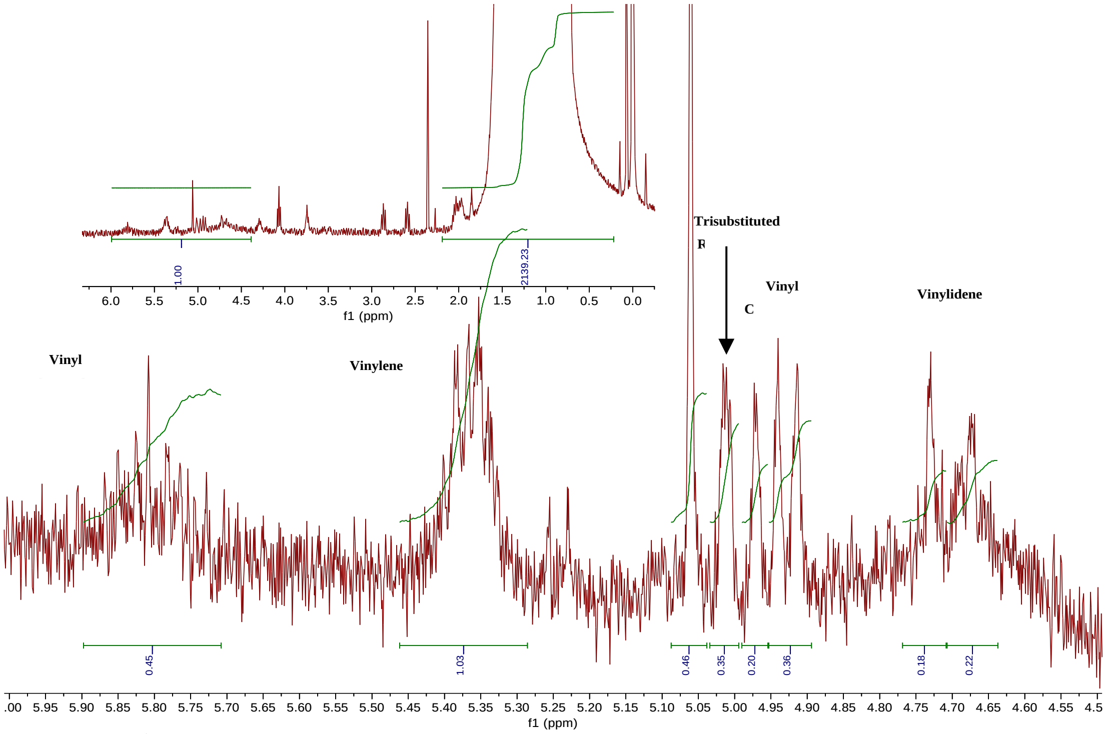

Figure S14. ^{1}H NMR spectrum of poly(1-octene) produced at 60 °C using **2**/AB/DiBAP.

Polymerization results for $\{CH_2[CH(Me)O\text{-}C_6H_4\text{-}2\text{-}(2\text{-}NC_{12}H_8)\text{-}4\text{-}Me\text{-}C_6H_2O]_2\}HfCl_2$ (3).

Table S7. 1-Octene polymerization with **3**/TTB/TMA(/DEZ) system at 100 °C.

Exp.	DEZ equiv. Hf	t min	Yield g	Conversion^a %	M_n^{b} kDa	M_w^{b} kDa	$Đ_M$^{b}	Chains per Zn
1	0	10	0.69	22	37.9	72.9	1.9	-
2	0	15	0.89	28	35.8	71.7	2.0	-
3	0	30	1.21	38	35.6	72.2	2.0	-
4	0	60	1.68	52	36.3	72.2	2.0	-
5	0	120	2.14	66	36.1	71.6	2.0	-
6	0	240	2.54	79	33.7	67.3	2.0	-
7	0	360	2.62	82	32.7	67.3	2.1	-
8	600	10	1.34	42	12.1	25.9	2.1	1.2
9	600	15	1.57	49	13.3	29.2	2.2	1.3
10	600	20	1.72	53	13.6	30.3	2.2	1.4
11	600	30	1.96	61	15.2	33.5	2.2	1.4
12	600	60	2.49	77	16.5	38.7	2.3	1.7
13	600	120	2.85	89	17.8	40.1	2.3	1.8
14	600	240	3.08	96	17.4	40.1	2.3	2.0
15	1800	15	0.36	11	5.9	11.2	1.9	0.7
16	1800	60	0.50	16	6.2	11.3	1.8	0.9

Reaction conditions: 20 mL crimp capped vial; 0.15 µmol of **3**; 1.5 equiv of TTB; 100 equiv of TMA; 4.5 mL of 1-octene; solvent: toluene (3.5 mL; $V_{reaction}$ ~ 8.0 mL); stirring rate: 500 rpm quenching: MeOH. (a) Determined by ^1H NMR; (b) Determined by THF-SEC.

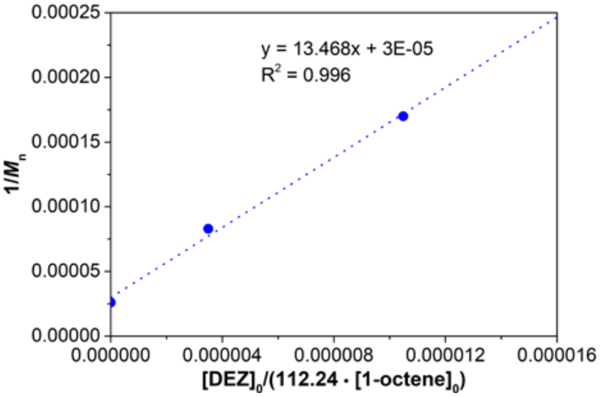

Figure S15. Approximate Mayo plot for the polymerization of 1-octene with **3**/TTB/TMA and various $[\mathrm{DEZ}]_0$ (Table S7).

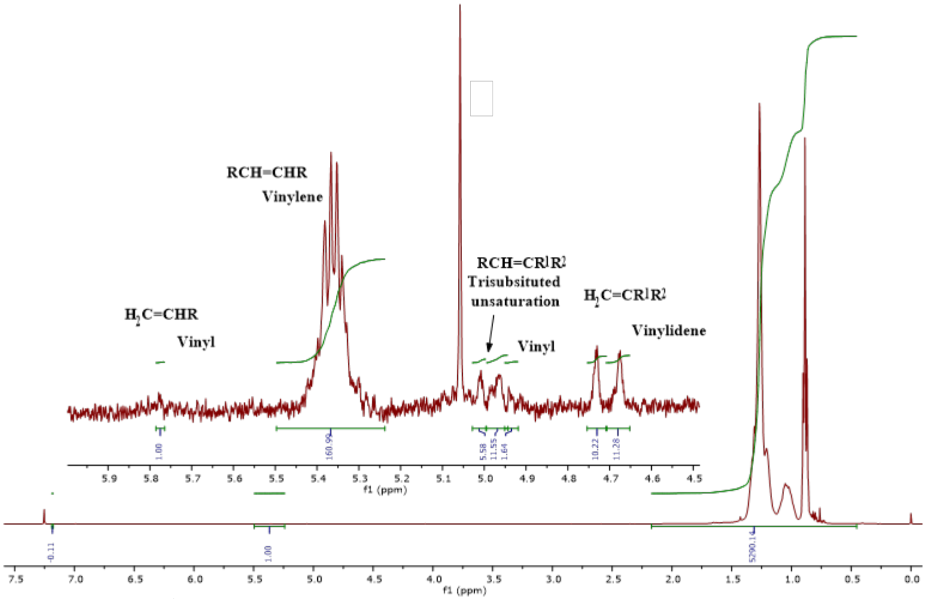

Figure S16. ^{1}H NMR of poly(1-octene), Table S7, entry 10 ($CDCl_3$).

Table S8. 1-Octene polymerization with the **3**/TTB/TMA/DEZ(/ethylene) system at 100 °C.

Exp.	t min.	Yield g	Conversion[a] %	M_n[b] kDa	M_w[b] kDa	$Đ_M$[b]	Chains per Zn
1	10	1.32	41	10.1	22.4	2.2	1.5
2	15	1.42	44	10.6	26.1	2.3	1.5
3	20	1.66	52	11.4	26.0	2.3	1.6
4	30	1.78	55	12.1	28.0	2.3	1.6
5	60	2.01	62	13.3	31.0	2.3	1.7
6	120	2.32	72	13.9	34.6	2.5	1.9
7	240	2.48	77	14.7	36.4	2.5	1.9
8[c]	120+120	3.28	92	19.2	60.3	3.1	-

Reaction conditions: 20 mL crimp capped vial; 0.15 µmol of **3**; 1.5 equiv. of TTB; 100 equiv. of. TMA; 600 equiv. of DEZ; 4.5 mL of 1-octene; solvent: toluene (3.5 mL; $v_{reaction}$ ~ 8.0 mL); stirring rate: 500 rpm; quenching: MeOH. (a) Determined by ^{1}H NMR; (b) Determined by SEC; (c) Bubbling $C_2^=$ for 2 minutes after 120 min. reaction time.

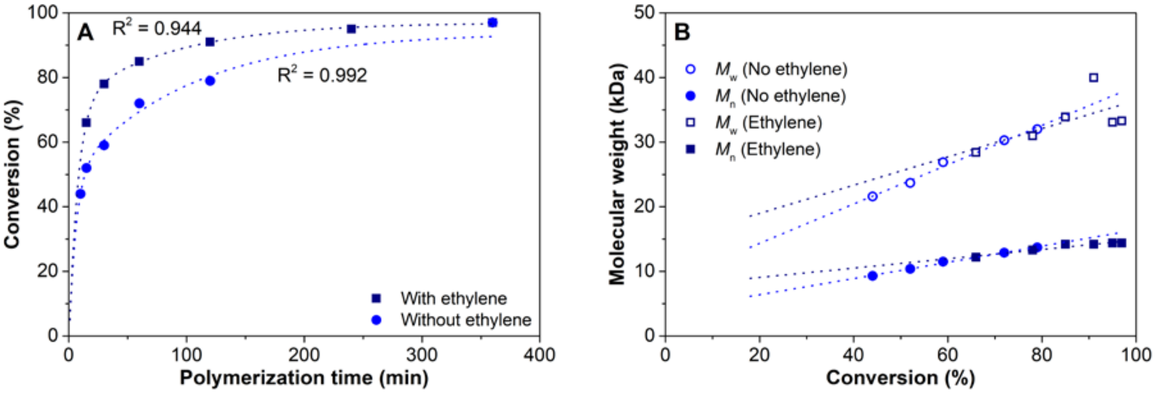

Figure S17. (A) 1-Octene conversion as a function of time and (B) molecular weight as a function of 1-octene conversion, using **3**/1.5 TTB/100 TMA/600 DEZ at 100 °C with and without the addition of ethylene prior to adding the catalyst (Table S9).

Table S9. 1-Octene polymerization with the **3**/TTB/TMA/DEZ(/ethylene) system at 100 °C.

Exp.	t min	Yield g	Conversion[a] %	M_n[b] kDa	M_w[b] kDa	Đ$_M$[b]	Chains per Zn
1	10	1.43	44	9.3	21.6	2.3	1.7
2	15	1.67	52	10.4	23.7	2.3	1.8
3	30	1.91	59	11.5	26.9	2.3	1.8
4	60	2.32	72	12.9	30.3	2.4	2.0
5	120	2.55	79	13.7	32.0	2.3	2.1
6[c]	15	2.12	66	12.2	28.4	2.3	-
7[c]	30	2.51	78	13.3	31.0	2.3	-
8[c]	60	2.74	85	14.2	33.9	2.4	-
9[c]	120	2.94	91	14.2	40.0	2.4	-
10[c]	240	3.05	95	14.4	33.1	2.3	-
11[c]	360	3.11	97	14.4	33.3	2.3	-

Reaction conditions: 20 mL crimp capped vial; 0.15 µmol 3; 1.5 equiv. of TTB; 100 equiv. of TMA; 600 equiv. of DEZ; 4.5 mL of 1-octene; solvent: toluene (3.5 mL; $v_{reaction}$ ~ 8.0 mL); stirring rate: 500 rpm; quenching: MeOH. (a) Determined by ^{1}H NMR; (b) Determined by SEC; (c) bubbling $C_2^=$ for 1 min.

Table S10. 4M1P polymerization with the **3**/TTB/TMA(/DEZ) system at 100 °C.

Exp.	DEZ	t	Yield	Conversion[a]	M_n[b]	M_w[b]	$Đ_M$[b]
	eq. Hf	min.	g	%	kDa	kDa	
1	-	15	0.14	5	3.71	7.12	1.9
2	-	120	0.36	14	3.79	7.31	1.9
3	600	15	0.65	24	2.15	3.85	1.8
4	600	30	0.87	33	1.77	3.88	2.2
5[b]	600	60	0.94	35	2.09	4.21	2.0
6	600	120	1.03	39	2.09	4.32	2.1
7	600	240	1.03	38	2.19	4.36	2.0
8	600	360	1.12	42	1.98	4.28	2.2
9	100	15	0.26	10	2.78	4.97	1.8
10	100	30	0.32	12	2.91	5.31	1.8
11	100	60	0.40	15	2.99	5.44	1.8
12	100	120	0.42	16	2.96	5.49	1.9
13	100	240	0.43	16	3.21	5.55	1.7
14	100	360	0.44	17	3.09	5.53	1.8

Reaction conditions: 20 mL crimp capped vial; 0.15 µmol **3**; 1.5 equiv. of TTB; 100 equiv. of TMA; 4.0 mL of 4M1P; solvent: toluene (4 mL; $V_{reaction}$ ~ 8.0 mL); stirring rate: 500 rpm; quenching: MeOH. (a) Determined by ^{1}H NMR; (b) Determined by SEC.

Table S11. 4M1P polymerization with **3**/MAO/DEZ(/ethylene) at 100 °C.

Exp.	t	Yield	Conversion[a]	M_n[b]	M_w[b]	$Đ_M$[b]	T_m[c]	ΔH_m[c]	Chains per Zn
	min.	g	%	kDa	kDa		°C	J/g	
1	10	0.25	20	2.1	3.6	1.7	199.8	15.7	1.8
2	15	0.50	23	1.8	3.7	2.0	203.5	29.1	3.8
3	20	0.57	27	1.7	3.4	2.1	200.7	20.9	4.7
4	30	0.62	31	1.8	3.8	2.1	205.0	31.1	5.1
5	60	0.74	43	2.0	4.4	2.3	199.9	15.9	6.4
6	120	0.79	47	2.6	6.0	2.3	204.0	14.7	5.3
7	240	0.95	52	2.5	5.9	2.4	202.5	19.9	6.2
8[d]	60+15	0.81	48	2.4	6.5	2.7	207.3	9.9	-
9[d]	60+180	1.40	73	3.2	8.3	2.6	199.5	3.0	-

Reaction conditions: 20 mL crimp capped vial; 0.15 µmol **3**; 6000 equiv. of MAO; 600 equiv. of DEZ; 4.0 mL of 4M1P; solvent: toluene (4 mL; $V_{reaction}$ ~ 8.0 mL); stirring rate: 500 rpm; quenching: MeOH. (a) Determined by ^{1}H NMR; (b) Determined by SEC; (c) Determined by DSC; (d) Bubbling $C_2^{=}$ for 1 minute after 60 min. reaction time.