Supporting Information for:

"GPC and ESI-MS Analysis of Labeled Poly(1-Hexene): Rapid Determination of Initiated Site Counts During Catalytic Alkene Polymerization Reactions"

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Contents:

I. Synthesis and Characterization of New Compounds

General Experimental Information:

All experiments were performed under air- and water-free conditions using standard Schlenk line techniques or a circulating nitrogen-filled glovebox operating at <0.5 ppm oxygen. Unless otherwise stated, all chemicals were purchased from Sigma-Aldrich and used without further purification. Toluene-*d8* and 1-hexene were dried over NaK and vacuum transferred. Chlorobenzene-*d5* was dried over P_2O_5 and vacuum transferred. Ether, hexanes, dry THF, and pentane were distilled over sodium / benzophenone. Benzene was distilled over sodium. *rac*-(Me_2(1-indenyl))$ZrCl_2$ ((SBI)$ZrCl_2$) was synthesized according to known literary methods.[1] $B(C_6F_5)_3$ was purchased from Sigma-Aldrich and repeatedly sublimated to purify or was synthesized according to known procedures.[2] 4-Trimethylsilyl-*N,N*-dimethylaniline[3] and 4-(chloromethyl)dimethylsilyl-*N,N*-dimethylbenzenamine[4] were synthesized according to published literary procedures. For a description of NMR characterization techniques, see Section III. MALDI-TOF-MS analysis of (SBI)Zr(Chrom)Me was performed on a Bruker Reflex II equipped with a 337 nm nitrogen laser, a reflectron, and delayed extraction. Samples for MALDI-MS were prepared by crushing with matrix in the glovebox. The mixture was pressed onto a plate, which was double-bagged and removed from the glovebox. The sample plate was transferred to the instrument under a steady stream of nitrogen gas.

For reaction workup, samples were dissolved in unstabilized Chromosolv THF purchased from Sigma-Aldrich.

Synthesis and Characterization of (SBI)ZrChromMe:

1.) 4-(Chloromagnesium Methyl)Dimethylsilyl-*n,n*-Dimethylbenzenamine: 7.9 g 4-(chloromethyl)dimethylsilyl-*N,N*-dimethylbenzenamine (35 mmol) in THF was added dropwise to achieve a gentle reflux to a Schlenk flask under nitrogen containing 1.07 g (44.8 mmol) magnesium turnings, THF, and a catalytic amount of 1,2-dibromoethane. Following addition, the solution was refluxed for 30 minutes, then 30 mL more dry THF was added for a total volume of 50 mL THF. The solution was refluxed for 3.5 more hours, then brought inside a glovebox where its purity was checked by NMR. The Grignard reagent is stable indefinitely in the glovebox and was used without further purification.

^{1}H NMR (300 MHz, rt): δ7.90 ppm (d, 2H, *J* = 8.7 Hz); δ6.78 ppm (d, 2H, *J* = 8.7 Hz); δ2.60 ppm (s, 6H); δ0.68 ppm (s, 6H); δ-1.00 ppm (s, 2H).

2.) (SBI)Zr(Chrom)Cl: A 100 mL tube-shaped Schlenk flask was charged with 448.5 mg (SBI)ZrCl$_2$ (1.0 mmol), 20 mL benzene, 2.2 mL (1.2 mmol) of a 0.68 M solution of 4-(chloromagnesium methyl)dimethylsilyl-*n,n*-dimethylbenzenamine in THF, and a stirbar, sealed with a rubber septem, and removed from the glovebox. The solution was stirred at 80°C for four hours, cooled to room temperature, and filtered. The filtrate was dried under reduced pressure, stirred with hexanes (10 mL), and dried to yield to a yellow solid. The solid was cracked to yield a yellow powder, then washed with hexanes (10 mL x 3), and extracted with ether (10 mL x 2). Drying under vacuum yielded the final product, (SBI)Zr(Chrom)Cl. Yield: 350 mg (55%).

^{1}H NMR (300 MHz, C_6D_6, rt): δ7.64 ppm (d, 2H, *J* = 8.6 Hz); δ7.51 ppm (d, 1H, *J* = 8.6 Hz); δ7.45 ppm (d, 1H, *J* = 8.6 Hz); δ7.31 ppm (d, 1H, *J* = 8.6 Hz); δ7.22 ppm (d, 1H, *J* = 8.0 Hz); δ7.08 ppm (d, 1H, *J* = 8.7 Hz); δ6.88 ppm (d, 1H, *J* = 3.7Hz); δ6.82 ppm (d, 3H?, *J* = 8.8 Hz); δ6.70 ppm (d, 1H, *J* = 3.5 Hz); δ5.91 ppm (d, 1H, *J* = 3.3 Hz); δ5.41 ppm (d, 1H, *J* = 3.2 Hz); δ2.59 ppm (s, 6H); δ0.57 ppm (s, 3H); δ0.56 ppm (s, 3H); δ0.46 ppm (s, 3H); δ0.40 ppm (s, 3H); δ-1.54 ppm (d, 1H, *J* = 11.9 Hz).

^{13}C NMR (125.7 MHz, C_6D_6, rt): δ150.8 ppm, δ134.7 ppm, δ132.7 ppm, δ130.8 ppm, δ129.7 ppm, δ126.3 ppm, δ126.2 ppm, δ126.0 ppm, δ125.9 ppm, δ125.5 ppm, δ125.3 ppm, δ124.9 ppm, δ123.5 ppm, δ117.7 ppm, δ116.3 ppm, δ115.2 ppm, δ112.6 ppm, δ112.2 ppm, δ88.3 ppm, δ86.2 ppm, δ54.5 ppm, δ39.8 ppm, δ0.9 ppm, δ0.4 ppm, δ-1.9 ppm, δ-2.9 ppm.

Note: (SBI)Zr(Chrom)Cl is unstable in solution, although it is stable indefinitely at room temperature in the solid state.

3.) (SBI)Zr(Chrom)Me: In the glovebox, a 50 mL tube-shaped Schlenk flask was charged with 350 mg (SBI)Zr(Chrom)Cl (0.55 mmol) and a stir bar and sealed with a rubber septem. Outside of the box, 10 mL ether was added via syringe and the solution was cooled to 0°C, where 0.55 mmol of an 0.5 M solution of MeMgBr in THF was added slowly. The solution was warmed to room temperature, stirred for six hours, then filtered. Volatiles were removed under reduced pressure and the remaining material was stirred with hexanes (10 mL), which was removed under reduced pressure to yield a yellow solid. The solid was cracked to yield a yellow powder, then washed quickly with 10 mL pentane. The resulting solid was extracted twice by a mixture of 10 mL hexanes and 5 mL ether, which yielded the final product upon drying.

^{1}H NMR (300 MHz, C_6D_6, rt): δ7.55 ppm (m, 3H); δ7.44 ppm (d, 1H, *J*=9.2 Hz); δ6.88 ppm (d, 1H, *J*=3.2 Hz); δ6.80 ppm (m, 4H); δ6.67 ppm (d, 1H, *J*=3.9 Hz); δ5.66 ppm (d, 1H, *J*=3.3 Hz); δ5.57 ppm (d, 1H, *J*=3.4 Hz); δ2.58 ppm (s, 6H); δ0.54 ppm (s, 3H);

δ0.51 ppm (s, 3H); δ0.38 ppm (s, 3H); δ0.29 ppm (s, 3H); δ-0.18 ppm (d, 1H, *J*=11.3 Hz); δ-0.98 ppm (s, 3H); δ-1.78 ppm (d, 1H, *J*=11.7 Hz).

^{13}C NMR (125.7 MHz, toluene): δ150.6 ppm; δ134.5 ppm; δ134.2 ppm; δ130.8 ppm; δ129.9 ppm; δ129.5 ppm; δ126.5 ppm; δ125.8 ppm; δ125.6 ppm; δ124.3 ppm; δ123.9 ppm; δ117.4 ppm; δ116.4 ppm; δ113.3 ppm; δ112.1 ppm; δ112.0 ppm; δ109.2 ppm; δ85.9 ppm; δ82.9 ppm; δ49.9 ppm; δ39.7 ppm; δ39.4 ppm; δ39.0 ppm; δ32.0 ppm; δ29.9 ppm; δ29.8 ppm; δ29.5 ppm; δ22.8 ppm; δ13.9 ppm; δ1.6 ppm; δ0.9 ppm; δ-1.1 ppm; δ-1.8 ppm; δ-2.9 ppm.

MALDI-MS (anthracene matrix): MALDI-MS yielded three distinct catalyst species, identified as $[(SBI)ZrChrom]^+$ (most abundant), $[(SBI)ZrMe]^+$, and $[(SBI)Zr]^+$.

$[(SBI)ZrChrom]^+$ (*m/z* (%)): 568 (100%), 569 (76), 570 (66), 571 (31), 572 (52), 573 (19), 574 (13). Calculated ($C_{31}H_{36}NSi_2Zr$): 568 (100), 569 (66), 570 (59), 571 (22), 572 (41), 573 (17), 574 (11).

$[(SBI)ZrMe]^+$ (*m/z* (%)): 391 (100%), 392 (53), 393 (53), 394 (18), 395 (42). Calculated ($C_{21}H_{21}SiZr$): 391 (100), 392 (50), 393 (46), 394 (12), 395 (36).

$[(SBI)Zr]^+$ (*m/z* (%)): 376 (100%), 377 (60), 378 (53), 380 (44). Calculated ($C_{20}H_{18}SiZr$): 376 (100), 377 (49), 378 (46), 379 (11), 380 (36).

II. Polymerization Procedures: Polymerizations were performed using a modified version of a previously published procedure.[5] In a typical reaction, in the glovebox, (SBI)ZrChromMe (4.7 mg; 8.0 μmol) dissolved in 0.5 mL toluene-*d8* was added to an NMR tube charged with 0.2 mL chlorobenzene-*d5*, 0.1 mL 1-hexene (0.8 M), and 5 μL of a 1.09 M solution of diphenylmethane in toluene-*d8* (5.45 mM) as an internal standard. Separately, $B(C_6F_5)_3$ (4.6 mg; 9.0 μmol) was dissolved in 0.2 mL toluene-*d8* and transferred into a gas-tight syringe capped with a large septem. The NMR tube was sealed with a septem and removed from the glovebox, where it was wrapped in parafilm and stored in a Dewar at -33°C. Prior to polymerization, samples were placed in a pre-cooled NMR probe (-33°C, methanol calibration) to determine the exact concentration of (SBI)ZrChromMe in solution. To initiate polymerization, a solution of $B(C_6F_5)_3$ in toluene-*d8* (4.6 mg (9.0 μmol) in 0.2 mL) was injected via gas-tight syringe into the NMR tube, followed by a bolus of nitrogen to facilitate mixing. Polymerizations lasting longer than 15 minutes were followed by NMR by placement into a pre-cooled NMR probe, but were returned to the Dewar to be quenched.

To quench samples intended for GPC analysis, a solution of 7 μL triethylamine in 43 μL methanol-*d4* was injected via gas-tight syringe at the designated time of quench. NMR tubes were then inverted to mix and returned to the NMR, where the fraction of initiated catalyst (as measured by the resonance for **4** at δ0.4 ppm) and the extent of polymerization (measured either by the remaining concentration of 1-hexene or by the growth of the polyhexene resonances) were determined. Samples were then stored in a Dewar for up to several hours at -33°C. For workup, samples were filtered through a plug of neutral alumina which had been pre-treated with a mixture of unstabilized THF and triethylamine and diluted with unstabilized THF for a total volume of 10 mL. Following workup, chromophore-labeled polymer chains are stable for up to one to two weeks without significant decomposition.

III. NMR Analysis, Kinetics, and Characterization of 3a and 4:

General NMR Information: ^{1}H NMR spectra were obtained on a Varian UNITY-500 MHz spectrometer equipped with a bbext probe, an INOVA-500 MHz spectrometer equipped with an hcx probe, or an INOVA-600 MHz spectrometer equipped with an hpx probe. Unless otherwise stated, calibrated 90^{o} pulses were employed, followed by a 1-4 second acquisition time and a 10 second relaxation delay. Typically, either 32 or 64 transients were averaged per spectrum. ^{13}C{^{1}H} NMR spectra were obtained at 125 MHz with gated decoupling using 3.5 second delays between uncalibrated 30^{o} pulses. ^{19}F NMR spectra were recorded at 470 MHz using uncalibrated 30^{o} pulses separated by 0.32 second acquisition periods and a 1 second relaxation delay. 128 transients were averaged per spectrum. Unless otherwise noted, NMR spectra were acquired on a probe pre-cooled to -33^{o}C (methanol calibration).

When applicable, species were characterized by a combination of TOCSY1D (typical pulse sequence: mix times of 0.015-0.08 seconds, acquisition times of 2-4 seconds, and relaxation delays of 3-5 seconds; 16-32 transients were acquired per spectrum) and NOESY1D (typical pulse sequence: mix times of 0.01-2 seconds, acquisition times of 2-4 seconds, and relaxation delays of 5-10 seconds; 32-64 transients were acquired per spectrum). ^{19}F NMR was assigned based upon peak integrations and known locations for *para*, *meta*, and *ortho*-fluorines attached to tris(pentafluorophenyl)borane ligands.

Low field NMR spectra were obtained on a Bruker AC-300+ instrument, using an uncalibrated 30^{o} pulse.

NMR Kinetics: Preliminary kinetic data on the **3a**-catalyzed polymerization of 1-hexene were acquired at -33°C using 8 mM **3a** (prepared *in situ* from 8 mM **1** and 9 mM **2**) and 0.8 M 1-hexene. 20 mM 1,2-dichloroethane was employed as an internal standard. NMR analysis used uncalibrated 30° pulse widths, a six second relaxation delay, and a two second acquisition time. 32 transients were averaged per spectrum.

Kinetic results were modeled via COPASI and fitted to a basic two-step polymerization mechanism involving catalyst initiation and propagation. The timecourse is shown in Figures S3-4.

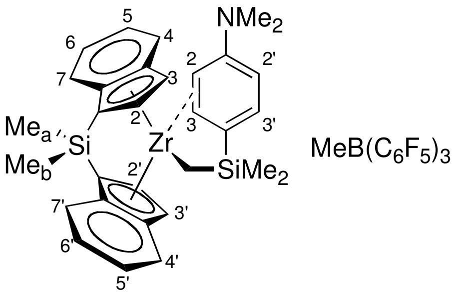
Characterization of 3a: See Figure S1 (below) for an image of the catalyst.

^{1}H NMR: δ7.29 ppm (Chromophore-3', d, 8.9 Hz); δ7.27 ppm (Indenyl-7, d, *J* = 8.9 Hz); δ7.22 ppm (Indenyl-4, d, *J* = 8.4 Hz); δ7.15 ppm (Indenyl-4', 1H, d, *J* = 6.8 Hz); δ7.12 ppm (Indenyl-5', 1H)*; δ7.05 ppm (Indenyl-5, 1H)*; δ6.84 ppm (Indenyl-6, 1H, t, *J* = 7.8 Hz); δ6.79 ppm (Indenyl-7', 1H, d, *J* = 7.8 Hz); δ6.76 ppm (Indenyl-6', 1H, t, *J* = 8.4 Hz); δ6.68 ppm (Indenyl-3, 1H, d, *J* = 2.1 Hz); δ6.43 ppm (Chromophore-2', d, *J* = 7.7 Hz); δ6.19 ppm (Chromophore-3, 1H, d, *J* = 7.7 Hz); δ5.50 ppm (Indenyl-2', d, 3.3 Hz); δ5.16 ppm (Indenyl-2, d, 2.5 Hz); δ4.63 ppm (Chromophore-2, d, *J* = 7.2 Hz); δ4.05 ppm (Indenyl-3', d, 3.2 Hz); δ2.41 ppm ($\underline{Me_2}$N-, 6H, s); δ2.11 ppm ($C\underline{H_2}SiMe_2$, 1H, d, *J* = 12.2 Hz); δ1.34 ppm ($\underline{Me}B(C_6F_5)_3$, 3H, bs); δ0.56 ppm ($SiMe_b$, 3H, s); δ0.26 ppm ($SiMe_a$, 3H, s); δ0.13 ppm (Chromophore: Si$\underline{Me}$, 3H, s); δ0.01 ppm (Chromophore: Si$\underline{Me}$, 3H, s); δ-1.47 ppm ($-SiC\underline{H_2}-$, d, *J* = 12.2 Hz).

* Could not be directly observed due to toluene resonances. Location determined by TOCSY1D.

^{19}F NMR: δ-166.2 ppm (MeB($C_6\underline{F}_5$)$_3$, *meta*-F, 3F, bs) δ-163.7 ppm (MeB($C_6\underline{F}_5$)$_3$, *para*-F, 3F, t, *J* = 19.3 Hz); δ-131.8 ppm (MeB($C_6\underline{F}_5$)$_3$, *ortho*-F, 6F, bs)

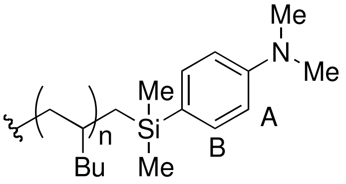
Figure S1: Image of 3a:



Characterization of 4:

^{1}H NMR (500 MHz, toluene-*d8* / chlorobenzene-*d5*, -33°C): δ7.48 ppm (B, 2H, d, *J* = 7.5 Hz), δ6.61 ppm (A, 2H, d, *J* = 6.5 Hz), δ2.56 ppm (-NMe$_2$, 3H, s), δ0.43 ppm (-Si$\underline{Me}_2$-3H, s), δ0.42 ppm (-Si$\underline{Me}_2$-, 3H, s).

Figure S2: Image of 4



IV. Sample Analysis: NMR, ESI-MS and GPC Procedures:

NMR Analysis of Quenched Samples: See above for general NMR conditions. Spectra of the quenched polyhexene samples were integrated to determine the concentration of polyhexene (typically through integration of the methyl group at δ0.9 ppm) and the concentration of **4** (through integration of the dimethylsilyl signals at δ0.4-0.45 ppm). Note that accurate integration of the resonances at δ0.4 ppm requires careful baseline fitting.

ESI-MS Analysis: All ESI-MS experiments were conducted with a Mariner orthogonal-acceleration time-of-flight (oaTOF) mass spectrometer. Several drops of quenched or warmed sample were diluted into a solution of CH_2Cl_2 doped with a small amount of acetic acid. All samples were electrosprayed from a stainless steel capillary (235 μm OD, 108 μm ID, Small Parts Inc., Miami Lakes, FL)., and then infused using a syringe pump. Spray tip potential was optimized for each sample and ranged from ~2500-3200 V. Nozzle potentials of 250-400 V and quadrupole RF voltages of 1000-2000 V were employed; detection voltage was held constant at 2200 V. Spectra were signal averaged for 15-120 seconds, depending upon spectral quality.

Caution: ESI-MS analysis of labeled poly(1-hexene) samples is **not** advised. Poly(1-hexene) is sticky and may leave a residue inside the instrument, potentially leading to a build-up of hydrocarbon-containing char and significantly reducing instrumental performance. MALDI-MS may be an alternative approach, but efforts to analyze labeled samples to date have not yielded satisfactory reproducible results.

GPC Analysis: GPC-SEC analysis (Viscotek GPCmax VE 2001) was performed on a set of two PolyPor 5 um mixed columns (300 x 7.5 mm) from Polymer Laboratories.

Polymer sample analysis used THF as the eluent at a flow rate of 1 mL/min at 40 C. The polymer was detected by a Differential Refractive Index (RI) and UV detectors (Viscotek Model 302-050 Tetra Detector Array). For absolute molecular weight detection, low-angle and right-angle light-scattering detectors were also employed. Data were analyzed using the Omnisec software (Viscotek, Inc.). Unless otherwise stated, injection volumes of 100 μL were employed.

Molecular weight calibrations on the VE 2001 were performed daily using a ten-point polystyrene (PS) calibration (EasiCal PS-2 from Polymer Laboratories (Varian)). An absolute molecular weight calibration was created for an isotactic poly(1-hexene) sample using the Omnisec software. PS-equivalent molecular weights were then converted into isotactic poly(1-hexene) molecular weights using a third-order polynomial curve constructed based upon a molecular weight calibration performed using a multi-detector (LALS, RALS) calibration curve constructed with a broad poly(1-hexene) standard. This calibration, performed empirically, uses the following equation:

decompressor
are needed to see this picture.

where:

a = **0.072338628**
b = **-1.14026412**
c = **7.076718034**
d = **-10.95937204**

This method has been employed previously.[6]

Sample data was processed in two steps using the Omnisec software and a homemade Excel spreadsheet program. Baseline-adjusted RI and UV traces, together with the PS-equivalent molecular weight distributions, were exported to an Excel spreadsheet and integrated manually. Peak areas were converted into concentrations of polyhexene and **4** using the following equations:

$$Conc_{PH} = \frac{\sum RI\_Area}{RI\_Cal \bullet dn / dc \bullet n_0}$$

$$Conc_{Chrom} = \frac{\sum UV\_Area}{UV\_Cal \bullet dA / dc}$$

where $Conc_{PH}$ and $Conc_{Chrom}$ represent, respectively, the concentrations of polyhexene and **4**, RI_Area and UV_Area represent the peak areas of the RI and UV traces, RI_Cal and UV_Cal are calibration factors established daily by analysis of a narrow PS standard (Varian: 71k, PDI = 1.03), n_0 is the refractive index of THF at 40°C (1.3975),[7] and dA / dc and dn / dc represent, respectively, the change in intensity of the UV peak and the RI peak as a function of concentration.

dA / dc and dn / dc were determined on the VE-2001 using calibration curves prepared using stock solutions of either the free chromophore (*p*-trimethylsilyl-*N,N*-dimethylaniline) or isotactic poly(1-hexene) previously synthesized under bulk conditions.[8] The final computed values of each used in calculation are: dA / dc = 1.44e+4, and dn / dc = 0.0626.

A model crude GPC trace is shown in Figure S11.

GPC Sensitivity Analysis: To test the limits of GPC sensitivity towards CPol, the injection volumes of two CPol samples were reduced from 100 μL to as low as 1 μL. Integration of peak areas yielded concentrations of **4** similar to those measured at higher injection volumes (±25%); however, baseline drift at lower injection volumes becomes an increasing concern. It is recommended that attempts to analyze low concentrations of **4** or other chromophore-labeled polymers allow sufficient time for all low molecular weight species to elute from the column prior to subsequent sample analysis, as baseline stability is crucial for accurate results.

CPol concentrations measured using lower injection volumes of sample are reported in Table S4; a sample GPC trace, showing detection of 2 μL of sample, is reported in Figure S12.

V. Supplemental Data:

Complete GPC Data: Tables shown here include (1) reaction conditions and molecular weights established by GPC; and (2) crude results obtained directly from GPC and NMR analysis and the measured percent conversion and percent initiation. **Numbered** entries are those presented in Table 1 in the Communication; supplemental entries are indicated.

Table S1: Reaction conditions and quantified molecular weights via GPC.

		Reaction conditions				**GPC Data:**	
Table #	**Name**	**[Zr] (mM)**	**[B(C_6F_5)$_3$] (mM)**	**[Hexene] (M)**	**Time (min)**	**M_w**	**PDI**
1	42361	5.1	9	0.8	5	17,800	2.0
2	42363	5.8	9	0.8	30	34,600	2.2
S1	42434	6.3	9	0.8	30	28,400	2.2
3	43432	5.9	9	0.8	60	31,200	2.3
S2	42433	5.2	9	0.8	60	36,900	2.2
4	42431	4.8	9	0.8	180	34,400	2.3
S3	42364	5.0	9	0.8	180	36,900	2.2
5	42284	5.5	9	0.4	60	34,500	2.2
6	42402	1.4	2.5	0.8	60	38,000	2.3
S4	42401	1.6	2.5	0.8	60	37,600	2.4
7	42403	3.0	4.5	0.8	60	40,500	2.2
S5	42404	3.3	4.5	0.8	60	35,600	2.3

Table S2: Quantified concentrations and percentage initiation / hexene consumption as measured by GPC and NMR.

	GPC:		**NMR:**		**GPC:**		**NMR:**	
Table #	**mg Polyhexene**	**µmol 4**	**Polyhexene (M)**	**4 (mM)**	**% Polyhexene**	**% 4**	**% Polyhexene**	**% 4**
1	1.2	0.098	0.03^a	^{b}	1.8	1.9	3.6^a	^{b}
2	46.1	0.72	0.57	0.82	68.5	12.5	71.1	14.1
S1	51.6	0.97	0.60	1.01	76.7	15.5	75.0	16.0
3	70.3	0.98	0.76	1.07	104	16.6	94.6	18.2
S2	72.1	0.97	0.76	1.06	107	18.7	95.1	20.4
4	75.3	0.98	0.80	1.05	112	20.5	100	22.0
S3	75.6	0.89	0.88	0.83	112	17.6	110	16.5
5	30.2	0.64	0.35	0.69	89.7	11.9	88.6	12.6

6	33.2	0.31	0.42	0.34	49.4	21.3	52.4	23.5
S4	27.3	0.29	0.36	0.36	40.6	18.5	45.6	23.0
7	48.9	0.54	0.61	0.62	72.6	17.9	76.7	20.5
S5	53.3	0.61	0.67	0.71	79.3	18.6	83.3	21.7

Footnotes:

a: Due to the low integration, this value has a high margin of error.

b: The resonance for **4** could not be detected.

Table S4: Results from GPC Sensitivity Analysis

Sample bmg42433:

Name:	**Inj. Vol. (μL)**	**UV Area**	**Amt. Inj. (mol)**	**Calc'd Conc. (M)**
bmg4254b	100	409.83	1.30E-08	0.000129815
bmg4254c	1	4.12	1.31E-10	0.000130503
bmg4254d	2	10.53	3.34E-10	0.000166771
bmg4254e	3	9.77	3.09E-10	0.000103156
bmg4254f	4	13.01	4.12E-10	0.000103024
bmg4254g	5	21.68	6.87E-10	0.000137345
bmg4254h	10	37.71	1.19E-09	0.000119448

Sample bmg42434:

Name:	**Inj. Vol. (μL)**	**UV Area**	**Amt. Inj. (mol)**	**Calc'd Conc. (M)**
bmg4254i	100	412.06	1.31E-08	0.000130522
bmg4254j	1	3.15	9.98E-11	9.97776E-05
bmg4254k	2	8.39	2.66E-10	0.000132878
bmg4254l	3	10.96	3.47E-10	0.000115721
bmg4254m	4	16.04	5.08E-10	0.000127019
bmg4254n	5	18.14	5.75E-10	0.000114919
bmg4254o	10	38.11	1.21E-09	0.000120715
bmg4254p	25	98.67	3.13E-09	0.000125017

VI. Supplemental Figures:

Kinetic Data: The timecourse used to establish the preliminary kinetics for **3a**-catalyzed 1-hexene polymerization is shown below, together with fits from COPASI. Due to batch-to-batch variations in catalyst rates and slight sample warming during the quench procedure, this timecourse may not agree exactly with the results of reactions presented in Table 1.

Figure S3: Plot of 1-hexene consumption during **3a**-catalyzed 1-hexene polymerization.

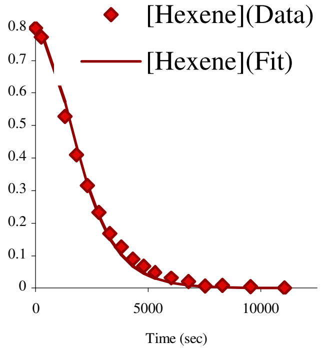
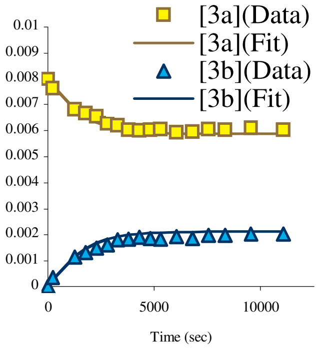


Figure S4: Catalyst speciation during **3a**-catalyzed 1-hexene polymerizations.



NMR Spectra:

Figure S5: ^{1}H NMR spectrum of (SBI)Zr(Chrom)Cl.

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Figure S6: ^{1}H NMR spectrum of (SBI)Zr(Chrom)Me.

Figure S7: ^{1}H NMR spectrum of **3a**.

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decompressor
are needed to see this picture.

Figure S8: ^{1}H NMR stackplot of typical **3a**-catalyzed 1-hexene polymerization reaction.

Each spectrum lasts 4 minutes 12 seconds.

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Figure S9: ^{1}H NMR spectrum of a quenched **3a**-catalyzed 1-hexene polymerization.

Conditions are described in Table S1, Entry 3.

QuickTime™ and a
decompressor
are needed to see this picture.

Figure S10: ^{19}F NMR of **3a**. The extra species visible are residual $B(C_6F_5)_3$ (**2**) and trace amounts of a $B(C_6F_5)_3$-THF adduct.

QuickTime™ and a
decompressor
are needed to see this picture.

Example GPC Trace:

Figure S11: Crude RI and UV-vis trace of GPC analysis of sample bmg42432 (entry 3 in Table 1 and Table S1). Plot is of intensity vs. elution volume. The RI trace is red and the UV-vis trace is purple.

Figure S12: UV-vis trace from GPC analysis of a 2 μL sample. Plot is of intensity (arbitrary units) vs. retention volume.

QuickTime™ and a
decompressor
are needed to see this picture.

1. Christopher, J. N.; Diamond, G. M.; Jordan, R. F. *Organometallics* **1996,** *15* (19), 4038-4044.
2. Lambert, J. B.; Zhang, S.; Ciro, S. M. *Organometallics* **1994,** *13* (6), 2430-2443.
3. Gilman, H.; Marshall, F. J. *J. Am. Chem. Soc.* **1949,** *71* (6), 2066-2069.
4. Ankianiec, B. C.; Young, G. B. *Polyhedron* **1995,** *14* (2), 249-265.
5. Landis, C. R.; Rosaaen, K. A.; Sillars, D. R. *J. Am. Chem. Soc.* **2003,** *125* (7), 1710-1711.
6. Mourey, T. H.; Balke, S. T. *J. Appl. Polym. Sci.* **1994,** *54*, 1455-1461.
7. Openhaim, G.; Grushka, E. *J. Chromatogr. A* **2002,** *942*, 63-71.
8. Liu, Z.; Somsook, E.; White, C. B.; Rosaaen, K. A.; Landis, C. R. *J. Am. Chem. Soc.* **2001,** *123* (45), 11193-11207.