Acknowledgements:

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Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation.

We also thank Dow Chemical for performing GPC analysis of polyethylene samples.

General Information:

Unless otherwise stated, all chemicals were purchased from Sigma-Aldrich and used without further purification. The following solvents were dried using the indicated method and stored under nitrogen: toluene (Na / benzophenone), THF (Na / benzophenone), toluene-\( \text{d}_8 \) (NaK), and methylene chloride-\( \text{d}_2 \) (P\(_2\)O\(_5\) or CaH\(_2\)). \( N,N' \)-dicyclohexylcarbodiimide (DCC) was purchased from Fluka, dried with MgSO\(_4\), and vacuum distilled prior to storage under inert gas, in accordance with standard procedure.\(^1\) Polymerization-grade ethylene (99.5\%) was purchased from Linde gas and purified through activated alumina, supported copper catalyst and an Alltech Big Oxygen trap. \( \text{B(}C_6\text{F}_5)_3 \)\(^2\) and \( \text{Cp}_2\text{ZrMe}_2 \)\(^3\) were prepared using standard literary procedures.

Unless otherwise stated, all reactions involving air-sensitive materials were performed using oven-dried glassware and standard Schlink techniques.

All quantified data are averages of 1-3 samples. Spectra, such as those in Figure 1 and 3, are representative of all acquired data.

Synthesis of \( N,N' \)-Dicyclohexyloctadecanimidamide: 3.0 mL of 0.6M octadecyl magnesium bromide (\( n \)-C\(_{18}\)H\(_{37}\)MgBr) in THF (1.6 mmol) was added to a solution of 0.33 g DCC (1.8 mmol) in 10 mL THF. The resulting solution was stirred at room
temperature for two hours, quenched with acid, then basicified prior to filtration. The crude product was recrystallized in hexanes, yielding 67.1 mg of a waxy white solid (9% unoptimized yield). \( ^1H \) NMR: \( \delta 3.28, m, 2H; \delta 2.36, m, 2H; \delta 2-1, m, 45H; \delta 0.88, t, 3H. \) ESI-MS: 461.5 ([MH]+).

**Ethylene Polymerization with Cp₂ZrCl₂:**

Ethylene polymerizations were performed at 0°C under constant ethylene pressures of either two or three atmospheres in homemade pressure reactors. The following procedure is representative. In a glovebox, a reactor was equipped with a stirbar, charged with a solution of 4.7 mg Cp₂ZrCl₂ (16.1 \( \mu \)mol) in 6 mL toluene, and sealed. Outside the glovebox, the reactor was suspended in an ice-water bath, allowed to equilibrate, then flushed repeatedly with ethylene prior to final pressurization to 15 psig (2 atmospheres). Polymerization was initiated through injection of 165 \( \mu \)mol MAO (Aldrich; 10% w/w solution in toluene, 110 \( \mu \)L), and the ensuing solution was stirred rapidly to facilitate ethylene diffusion.

To generate amidinium-terminated polyethylene samples (Am-PE), the reaction was quenched through injection of 104 mg DCC in 0.7 mL toluene after 300 seconds reaction time. Following depressurization, 100 \( \mu \)L of a 3.41 mM solution of \( N,N' \)-dicyclohexyloctadecanimidamide in toluene was injected into each reactor, and 2-5 drops of the solution was diluted in 20 mL CH₂Cl₂ for ESI-MS analysis. The remaining solution was dried to determine polymer yield. For MALDI analysis, select samples were filtered through 0.2 \( \mu \)m Whatman TF filters prior to solvent removal.

Alternately, reactions were terminated through the addition of 25 \( \mu \)L methanol-\( d \), yielding deuterated polyethylene (D-PE). Samples were dried to constant mass and analyzed by GPC. Samples intended for \( ^{13}C \) NMR analysis were quenched with methanol-\( d4 \) (99.98%) to ensure quantitative deuteration.
**Polymer Characterization:**

*ESI-MS Analysis of Am-PE Samples:* All ESI-MS experiments were conducted with a Mariner orthogonal-acceleration time-of-flight (oaTOF) mass spectrometer (Applied Biosystems, Foster City, CA). All samples were electrosprayed from a stainless steel capillary (235 μm OD, 108 μm ID, Small Parts Inc., Miami Lakes, FL). Samples in CH₂Cl₂ were filtered through a 0.2 μm Teflon Whatman filter immediately prior to use, and then infused at a rate of 6 μL min⁻¹ using a syringe pump. (Filtration was shown in control experiments to have no influence upon ESI-MS spectra, but it did significantly reduce the risk of clogging.) Spray tip potential was optimized for each sample and ranged from ~2500-3200 V. A nozzle potential of 250 V and a quadrupole RF voltage of 1000 V were employed for all samples; detection voltage was held constant at 2200 V. Spectra were signal averaged for 15-60 seconds.

Spectra were analyzed using the Data Explorer software (Applied Biosystems, Version 4.0) to determine peak heights of all methyl-terminated amidinium species. In Microsoft Excel, these peak heights were corrected for isotopic abundance and then converted to concentrations through calibration relative to the internal standard. Values for Mₙ, Mₚ, polydispersity, and the number of chains per zirconium (N/Zr) were computed using standard methods. Catalyst “activity” was computed from quantified data using the following equation:

\[
\text{Activity} = \frac{M_n \times N / Zr}{1000 \times \text{time(hr)} \times \text{pressure(atm)}}
\]

*MALDI-MS Analysis of Am-PE Samples:* All MALDI-MS spectra were acquired on a Voyager DE STR mass spectrometer (Applied Biosystems, Foster City, CA). In accordance with previous studies of solid-phase samples,⁴ crude Am-PE was crushed with an approximately equal volume of matrix (all-trans retinoic acid), then pressed onto the sample plate with a metal spatula. Large particles were then dislodged with a stream of inert gas; the residual sample remaining on the plate was found to give satisfactory ionization.
A pulsed nitrogen laser (337 nm) was used for desorption / ionization and positive ion mass spectra were acquired in linear mode. An acceleration voltage of 25 kV, a grid voltage of 99%, and a delay time of 300 ns were employed. Spectra were acquired over a mass range of 500-5000 Da, and employed a low mass gate of 500 Da. External mass calibration employed substance P (1348.7 Da) and bovine insulin (5733.49 Da) as standards. Spectra were obtained by accumulating data from a total of 50 laser shots.

MALDI-MS spectra were analyzed using Data Explorer (Applied Biosystems, Version 4.0). Spectra were baseline corrected and Gaussian smoothed prior to transference to Excel and plotting.

**GPC Analysis of D-PE:**

D-PE samples were analyzed by Dow Chemical Company in Freeport, TX. and calibrated using polystyrene standards. The gel permeation chromatographic system consists of either a Polymer Laboratories Model PL-210 or a Polymer Laboratories Model PL-220 instrument. The column and carousel compartments are operated at 140 °C. Three Polymer Laboratories 10-micron Mixed-B columns are used. The solvent is 1,2,4-trichlorobenzene. The samples are prepared at a concentration of 0.1 g of polymer in 50 mL of solvent containing 200 ppm of butylated hydroxytoluene (BHT). Samples are prepared by agitating lightly for 2 hours at 160 °C. The injection volume used is 100 μL and the flow rate is 1.0 mL/min.

Calibration of the GPC column set is performed with 21 narrow molecular weight distribution polystyrene standards with molecular weights ranging from 580 to 8,400,000, arranged in 6 “cocktail” mixtures with at least a decade of separation between individual molecular weights. The standards are purchased from Polymer Laboratories (Shropshire, UK). The polystyrene standards are prepared at 0.025 g in 50 mL of solvent for molecular weights equal to or greater than 1,000,000, and 0.05 g in 50 mL of solvent for molecular weights less than 1,000,000. The polystyrene standards are dissolved at 80 °C with gentle agitation for 30 minutes. The narrow standards mixtures are run first and in order of decreasing highest molecular weight component to minimize degradation. The polystyrene standard peak molecular weights are converted to polyethylene molecular weights using the following equation:

\[ M_{\text{polyethylene}} = 0.431 \times M_{\text{polystyrene}} \]
Polyethylene equivalent molecular weight calculations are performed using Viscotek TriSEC software Version 3.0.

*Quantitative $^{13}C\{^1H\}$ NMR Analysis of Select D-PE Samples:* All NMR analysis of D-PE samples was performed at 125 MHz on a Varian UNITY-500 instrument equipped with a bbext probe preheated to 120°C (ethylene glycol standard). For all studies, crude D-PE was suspended in 0.6 mL tetrachloroethane-$d_2$ and heated in a 120°C oil bath for several hours prior to placement in the preheated probe.

Quantitative $^{13}C$ NMR studies employed inverse gated decoupling and calibrated 90° pulses separated by 50 second relaxation delays. 4.0 Hz line broadening was applied to all $^{13}C$ NMR FIDs prior to Fourier Transformation.

*In Situ Quench-Label Experiments:*

Quench-label reactions were performed at room temperature (24°C) on a Varian UNITY-500 equipped with a bbext probe. $^1H$ NMR experiments employed 15 second delays, 2.5 second acquisition times, and calibrated 90° pulse widths. Kinetic studies employed two transients; spectra were collected every 35 seconds over a 9 minute period. Select species were characterized by 1D TOCSY (typical experiment: 10 second relaxation delay, mix time varied from 0-0.08 seconds, 16 transients) and/or 1D NOESY experiments (typical experiment: 16 second delay, 0.3 second mix time, 64 transients). Intermediate concentrations are relative and not referenced to an absolute internal standard.

Toluene-$d_8$ solutions of all model compounds were prepared in an inert atmosphere and loaded into septem-capped NMR tubes. Solutions of DCC in toluene-$d_8$ were injected as quenches, followed by 0.3 mL CD$_2$Cl$_2$ to enhance product solubility.

*DCC Quench of Cp$_2$ZrMe(Me(B(C$_6$F$_5$)$_3$)$_3$) (1):* Injection of 60 mg DCC (291 μmol) into a pale yellow 17.5 mM solution of Cp$_2$ZrMe(MeB(C$_6$F$_5$)$_3$)$_3$ (0.6 mL; 10.5 μmol) formed a pink oil insoluble in pure toluene.
Insertion rates were computed by determination of the instantaneous concentrations of Cp₂ZrMe(DCC)⁺ (2) and Cp₂Zr((cyN)₂CMe) (3) at 5.83 ppm and 6.0 pnm respectively. Insertion rates were computed from - ∂[2]/∂t and [2] and were fitted using Excel.

In separate experiments, coupling between resonances for 3 were confirmed through NOESY-1D and TOCSY-1D. Only visible resonances are listed:

Cp₂ZrMe(DCC)⁺ (2): δ5.83 (s, 10 H, Cp), δ0.25 (s, 3H, Me)
Cp₂Zr((cyN)₂CMe) (3): δ6.05 (s, 10 H, Cp), δ0.51 (5H?, qd, J = 12.1, 3.1 Hz, cy?)

AlMe₃: Injection of 106.8 mg DCC (518 μmol) into a 86.8 mM solution of AlMe₃ (52.1 μmol) was slightly exothermic but yielded no visible color change. After 10 minutes, ¹H NMR analysis revealed the presence of Me₂Al((cyN)₂CMe) and unreacted AlMe₃.

Supplemental Data:

Response of ESI-MS Spectra to Instrument Settings: Two instrument settings – nozzle potential and RF quadrupole voltage – were systematically varied to evaluate their influence upon detected amidinium ion distributions for a sample synthesized under the conditions listed in Run 2, Table 1. These results are displayed in Figure S.1 and quantified in Table S.1. Consistent with prior reports, increases in nozzle potential and RF quadrupole voltage enhanced heavier oligomers at the expense of lighter ones.

Figure S.1: Influence of Instrument Settings Upon ESI-MS Spectra: (a) nozzle potential of 250 V, RF quadrupole of 1000 V; (b) nozzle potential of 250 V, RF quadrupole of 2000 V; (c) nozzle potential of 400 V, RF quadrupole of 1000 V; (d) nozzle potential of 400 V, RF quadrupole of 2000 V.
Table S.1: Influence of Instrument Settings Upon Quantified ESI-MS Data:

<table>
<thead>
<tr>
<th>Nozzle Potential</th>
<th>RF Quadrupole</th>
<th>$N / \text{Zr}^{a}$</th>
<th>$M_{n}^{b}$</th>
<th>PDI$^{c}$</th>
<th>Activity$^{d}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>1000</td>
<td>0.49</td>
<td>290</td>
<td>1.35</td>
<td>0.85</td>
</tr>
<tr>
<td>250</td>
<td>2000</td>
<td>0.46</td>
<td>300</td>
<td>1.32</td>
<td>0.83</td>
</tr>
<tr>
<td>400</td>
<td>1000</td>
<td>0.39</td>
<td>350</td>
<td>1.17</td>
<td>0.81</td>
</tr>
<tr>
<td>400</td>
<td>2000</td>
<td>0.40</td>
<td>350</td>
<td>1.17</td>
<td>0.86</td>
</tr>
</tbody>
</table>

(a): Number of chains per zirconocene.
(b): Number-average molecular weight (g mol$^{-1}$).
(c): Polydispersity index: $M_{w} / M_{n}$.
(d): Catalyst activity, calculated from the estimated mass of all PE chains detected by ESI-MS. Units: g mmol$^{-1}$ atm$^{-1}$ hr$^{-1}$.
**Total GPC and ESI-MS Data:** Figures S.2 and S.3 display, respectively, representative GPC and ESI-MS spectra obtained under all conditions.

**Figure S.2: Representative GPC Traces for All Sample Conditions:** (a) 2 atm, 90 seconds, 10 eq. Al; (b) 2 atm, 300 seconds, 10 eq. Al; (c) 2 atm, 900 seconds, 10 eq. Al; (d) 2 atm, 90 seconds, 20 eq. Al; (e) 2 atm, 300 seconds, 20 eq. Al; (f) 3 atm, 90 seconds, 20 eq. Al; (g) 3 atm, 300 seconds, 20 eq. Al.
Figure S.3: Quantified ESI-MS Spectra for All Sample Conditions: (a) 2 atm, 90 seconds, 10 eq. Al; (b) 2 atm, 300 seconds, 10 eq. Al; (c) 2 atm, 900 seconds, 10 eq. Al; (d) 2 atm, 90 seconds, 20 eq. Al; (e) 2 atm, 300 seconds, 20 eq. Al; (f) 3 atm, 90 seconds, 20 eq. Al; (g) 3 atm, 300 seconds, 20 eq. Al.

All plots represent concentration (normalized relative to [Zr]) vs. m/z.
**Quench-Label Reaction of** \( \text{Cp}_2\text{ZrMe(MeB(C}_6\text{F}_5)_3} \) **with DCC:** Analysis of the room-temperature reaction of \( \text{Cp}_2\text{ZrMe(MeB(C}_6\text{F}_5)_3} \) with DCC revealed an intermittent species, \( \text{Cp}_2\text{ZrMe(DCC)}^+ \) (2), which converted to the final product, \( \text{Cp}_2\text{Zr((CyN)_2CMe)}^+ \) (3), over approximately a ten-minute period. All data is in accordance with the rate law: 

\[
-\frac{\partial [2]}{\partial t} = \frac{\partial [3]}{\partial t} = k_1[2],
\]

where \( k_1 = 0.0058 \text{ sec}^{-1} \), for \( t_{1/2} = 199.5 \text{ sec} \). A plot of quantified rate data is shown in Figure S.4.

**Figure S.4: Quantified Rate Data for Quench-Label Reaction of** \( \text{Cp}_2\text{ZrMe(MeB(C}_6\text{F}_5)_3} \):
Figure S.5: Sample ESI-MS Spectra (300 sec, 10 eq. MAO, 2 atm ethylene):
   164.
4. S. Lin-Gibson, L. Brunner, D. L. Vanderhart, B. J. Bauer, B. M. Fanconi, C. M.
   399-408.
   1812-1822.
   223-238.
    128, 273-280.