

## Direct Observation of Insertion Events at *rac*-(C<sub>2</sub>H<sub>4</sub>(1-indenyl)<sub>2</sub>)Zr(MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>)–Polymeryl Intermediates: Distinction between Continuous and Intermittent Propagation Modes

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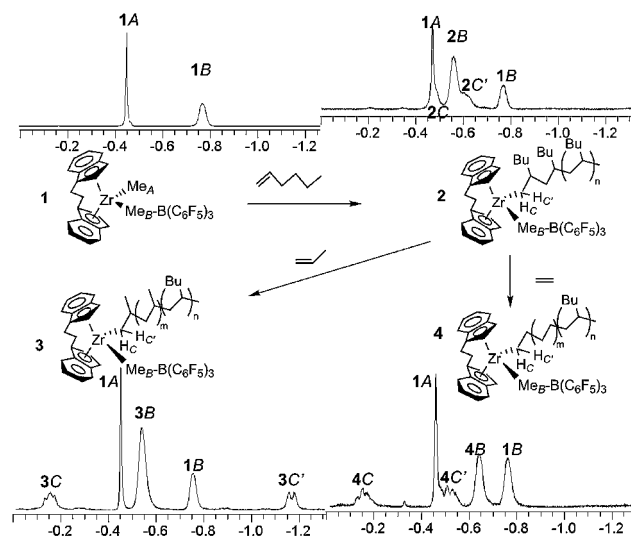
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Metallocene-catalyzed alkene polymerization reactions are technologically important but exhibit complex behavior that hinders reconciliation of observed macroscopic behavior (such as reaction kinetics) with elementary steps at catalyst centers.<sup>1</sup> Direct observation of catalyst speciation, kinetics, and stereodynamics could facilitate resolution of mechanistic issues such as the origins of stereoerrors in isotactic, syndiotactic, and elastomeric polypropene synthesis, the nature of the catalyst resting state, and the extent of ion-pairing during polymerization.<sup>1b–d</sup> Herein we report direct in situ observation of Zr–polymeryl species, characterization of their initiation, propagation, and termination kinetics, growth of copolymers, and definitive distinction between intermittent and continuous propagation behavior.<sup>2</sup>

Reaction of excess 1-hexene (0.8 M) and *rac*-(C<sub>2</sub>H<sub>4</sub>(1-indenyl)<sub>2</sub>)Zr(Me)(MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>) (**1**, 8.2 × 10<sup>−3</sup> M) in toluene-*d*<sub>8</sub> solution at −40 °C leads to quantitative consumption of 1-hexene in approximately 45 min; at −40 °C the <sup>1</sup>H, <sup>11</sup>B, and <sup>19</sup>F NMR spectra of the resulting solution remain unchanged for at least 12 h. All NMR data<sup>3</sup> are consistent with the presence of a single diastereomer of *rac*-(C<sub>2</sub>H<sub>4</sub>(1-indenyl)<sub>2</sub>)Zr(polymeryl)(MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>) (**2**) and unreacted **1**, only, in the approximate ratio 1.8:1 (**2**:**1**) (Figure 1). Subsequent addition of ca. 10 equiv of propene or ethene to such a solution at −40 °C results in quantitative conversion of **2** to **3** or **4**, respectively. Compounds **2–4** have been characterized by extensive application of 1- and 2-D NMR methods and isotopic labels.<sup>3</sup> <sup>1</sup>H NMR spectra of **2–4** in the 0 to −2 ppm region (Figure 1) demonstrate clear resonances for the diastereotopic Zr–CH<sub>2</sub>–POL protons and the Zr–Me–B groups. For **2** and **3** produced with 1-<sup>13</sup>C-labeled 1-hexene and propene, respectively, diagnostic <sup>13</sup>C NMR resonances for the Zr–CH<sub>2</sub>–polymer are observed with chemical shifts (88.5 and 84.1, respectively) that are consistent with previously reported Zr–alkyl<sup>4</sup> and Zr–polymeryl<sup>5</sup> chemical shifts. Observed <sup>1</sup>H and <sup>19</sup>F NMR chemical shifts<sup>3,6</sup> and NOE data indicate coordination of MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub><sup>−</sup> to Zr; the <sup>1</sup>H chemical shifts order as **2** > **3** > **4** > **1** suggesting diminished anion coordination with increasing Zr–alkyl steric bulk. During polymerization at −40 °C, only resonances for **1**, **2** (or **3** or **4**), and free alkene are observed, indicating that no other intermediates (such as alkene complexes, secondary alkyls, diastereomers of **2** or **3**, or termination products) accumulate to detectable levels.

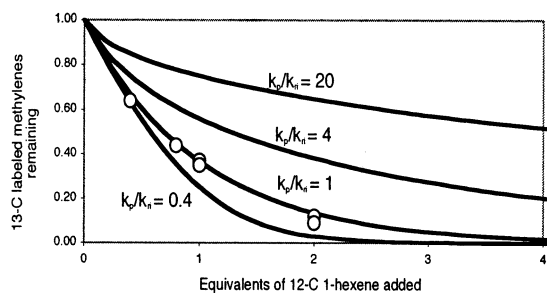
Interception of well-characterized Zr–polymeryl species enables direct monitoring of initiation, propagation, and termination processes. Simultaneous monitoring of the conversion of **1** to **2** and the consumption of 1-hexene at −40 °C yields rate laws and rate constants for initiation and propagation<sup>7a</sup> that are consistent with previous measurements over the temperature range of −10 to 50 °C.<sup>8</sup> Warming a solution of **2** to −20 °C effects clean and



**Figure 1.** <sup>1</sup>H NMR spectra in the 0 to −1.3 ppm region resulting from the indicated reactions at −40 °C in toluene-*d*<sub>8</sub>.

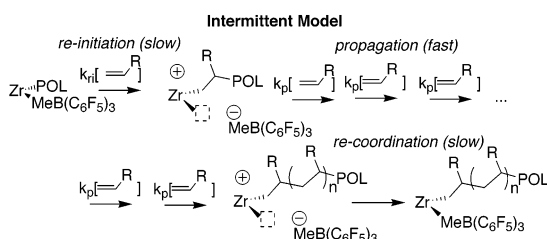
conveniently monitored elimination to a vinylidene-terminated polymer and a single metallocene (tentatively identified as *rac*-(C<sub>2</sub>H<sub>4</sub>(1-indenyl)<sub>2</sub>)Zr(Me)(HB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>)) at a rate<sup>7b</sup> consistent with less direct, prior measurements.<sup>8</sup> Notable features of in situ kinetic measurements include: (1) At −40° the first insertion of 1-hexene into a Zr–Me bond is ca. 400 times slower than subsequent insertions, emphasizing that Zr–Me species are poor kinetic models for Zr–polymeryl species. (2) Although slow to initiate, species such as **2**, **3**, and **4** are living polymerization catalysts at low temperatures with significant propagation rates (e.g., at −40 °C and [1-hexene] = 2.0 M, propagation at **2** proceeds at ca. 1 insertion/s and exceeds the termination rate by a factor of 40000). Extension of these kinetic measurements to propene and ethene homo- and copolymers are in progress.

A common model for propagation in metallocenium-catalyzed alkene polymerization invokes displacement of a weakly bound anion (e.g., MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub><sup>−</sup>, B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>−</sup>, or MAO-derived anions) by weakly coordinating alkene to form an outer-sphere ion pair prior to alkene insertion.<sup>9</sup> However, the recent finding of “unexpectedly slow” rates for displacement of MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub><sup>−</sup> by Lewis bases at various *ansa* and non-*ansa* Zr–Me<sup>+</sup> cations by Schaper, Geyer, and Brintzinger<sup>10a</sup> (SGB) led these authors to propose an intermittent<sup>10b</sup> model of propagation activity. In this model, displacement of the counterion by alkene monomer is an infrequent reinitiation event that is followed by a burst of propagations before anion re-coordination occurs. In contrast, if anion coordination



**Figure 2.** Observed (open circles) and computed fractions (solid lines) of Zr- $^{13}\text{C}_2$ -POL remaining after reaction with unlabeled 1-hexene as a function of the  $k_p/k_{ri}$  ratio.

occurs after each alkene insertion, monomers would incorporate at a continuous rate at the metal center.



Does **2** undergo infrequent reinitiation to produce highly reactive species which consume a number of monomers before relaxing back to **2**? Let  $k_{ri}$  denote the reinitiation rate constant and  $k_p$  the propagation rate constant. The condition  $k_{ri} \ll k_p$  prescribes intermittent propagation activity, whereas  $k_{ri} = k_p$  prescribes a continuous mode. Differentiation between these propagation modes is provided by monitoring the  $^1\text{H}$  or  $^{13}\text{C}$  NMR spectra of Zr- $^{13}\text{C}_2$ -POL labeled **2** (formed from 1- $^{13}\text{C}$ -1-hexene and **1**) upon addition of small amounts (0.4–2 equiv) of unlabeled 1-hexene. For a continuous propagation mode (see Figure 2) addition of 1 equiv of unlabeled 1-hexene would lead to  $1/e = 37\%$  retention of label in the Zr- $\text{CH}_2$ -POL resonance.<sup>11</sup> The method is sensitive; even  $k_p/k_{ri}$  ratios as small as 4:1 readily are distinguished from 1:1 ratios upon addition of 2 equiv of unlabeled 1-hexene. The experimental results are unambiguous: the propagation mode is continuous.

Catalytic polymerization kinetics,<sup>8</sup> kinetic isotope effects,<sup>12</sup> and spectroscopic and kinetic characterization of Zr-polymeryl intermediates (this work) provide a working model for 1-alkene polymerization with **1**. Propagation begins with reversible, endergonic (in free energy) coordination of alkene and displacement of the anion from the inner coordination sphere. Irreversible insertion of coordinated alkene is rate-determining and is followed by rapid re-coordination of the anion. Catalyst pools as primary Zr-polymeryls with no observable accumulation of dormant species. Rate constants for dibutyl ether association measured by SGB in related complexes at 298 K are similar to *initiation* rates for **1** and 1-hexene, most likely reflecting tighter ion-pairing in Zr-Me vs Zr-polymeryl species and the small steric profile of a terminal alkene vs dibutyl ether.

Significantly, this work demonstrates the most efficient and detailed characterization of metallocene active sites and kinetics to date. Direct observation of insertion events enables unique

mechanistic insight, such as the distinction between continuous and intermittent propagation modes. Ongoing studies focus on extending kinetic measurements to a wider variety of alkenes and counterions and to catalyst systems for which competition between catalyst stereodynamics and insertion events are critical.<sup>1</sup>

**Acknowledgment.** We thank the Department of Energy and the Dow Chemical Company for support of this work. We acknowledge Dr. Charlie Fry's assistance with NMR experiments and Dr. Zhixian Liu and Curtis White's synthesis of *rac*-(C<sub>2</sub>H<sub>4</sub>(1-indenyl)<sub>2</sub>)Zr(CD<sub>3</sub>)<sub>2</sub>. NMR instrumentation was supported by NSF CHE-9629688, NSF CHE-8813550, and NIH 1 S10 RR04981-01.

**Supporting Information Available:** Full experimental details,  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$ , and  $^{11}\text{B}$  NMR spectra and assignments, and kinetic data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (2) Preliminary characterization of **2** is reported in: Landis, C. R.; Rosaaen, K. A. *Poly. Mater. Sci. Eng.* **2002**, *87*, 41–43.
- (3) Representative NMR data ( $5 \times 10^{-3}$  M, toluene- $d_6$ ,  $-40^\circ\text{C}$ ): **1**  $^1\text{H}$  Zr- $\text{CH}_3$   $-0.45$ , Zr- $\text{CH}_3$ -B  $-0.80$ ;  $^{19}\text{F}$  *o*-F  $-133.72(\text{d})$   $^3J_{\text{F-F}} = 27$  Hz, *m*-F  $-164.02(\text{dd})$   $^3J_{\text{F-F}} = 26$  Hz, *p*-F  $-158.78(\text{t})$   $^3J_{\text{F-F}} = 23$  Hz;  $^{11}\text{B}$   $-14.1$ . **2**  $^1\text{H}$  Zr- $\text{CHH}$ -POL  $-0.48$ , Zr- $\text{CHH}'$ -POL  $-0.60$ , Zr- $\text{CH}_2$ -B  $-0.56$ ;  $^{13}\text{C}$  Zr- $\text{CH}_2$ -POL  $88.5$ ,  $^1J_{\text{C-H}} = 117$  Hz;  $^{19}\text{F}$  *o*-F  $-132.83(\text{d})$   $^3J_{\text{F-F}} = 27$  Hz, *m*-F  $-164.07(\text{m})$ , *p*-F  $-158.89(\text{t})$   $^3J_{\text{F-F}} = 22$  Hz;  $^{11}\text{B}$   $-14.1$ . **3**  $^1\text{H}$  Zr- $\text{CHH}'$ -POL  $-0.15$  (dd)  $^2J_{\text{HH}} = 12.5$  Hz  $^3J_{\text{HH}} = 8.5$  Hz, Zr- $\text{CHH}'$ -POL  $-1.23$   $^2J_{\text{HH}} = 12.5$ , Zr- $\text{CH}_3$ -B  $-0.57$ ;  $^{13}\text{C}$  Zr- $\text{CH}_2$ -POL  $84.1$ ,  $^1J_{\text{C-H}} = 117$  Hz;  $^{19}\text{F}$  *o*-F  $-132.55(\text{d})$   $^3J_{\text{F-F}} = 28$  Hz, *m*-F  $-164.20(\text{m})$ , *p*-F  $-158.90(\text{t})$   $^3J_{\text{F-F}} = 21$  Hz;  $^{11}\text{B}$   $-14.1$ . **4**  $^1\text{H}$  Zr- $\text{CHH}'$ -POL  $-0.15(\text{dd})$   $^2J_{\text{HH}} = 9.8$  Hz, Zr- $\text{CHH}'$ -POL  $-0.57$  (m), Zr- $\text{CH}_3$ -B  $-0.66$ ;  $^{19}\text{F}$  *o*-F  $-133.37(\text{d})$   $^3J_{\text{F-F}} = 28$  Hz, *m*-F  $-164.17(\text{m})$ , *p*-F  $-159.09(\text{t})$   $^3J_{\text{F-F}} = 21$  Hz;  $^{11}\text{B}$   $-14.1$ . (b) See Supporting Information for a full listing of spectroscopic data and complete assignments.
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JA0280700