

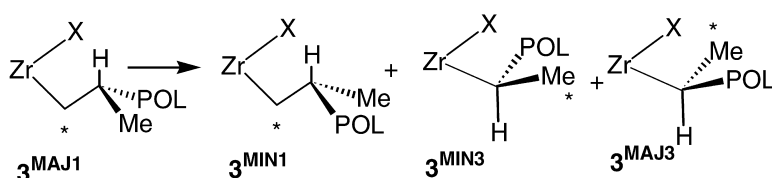
Communication

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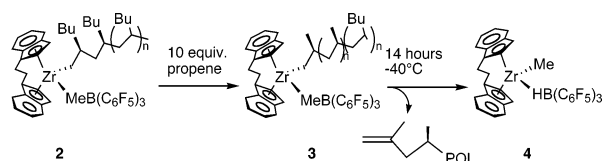
Catalytic Propene Polymerization: Determination of Propagation, Termination, and Epimerization Kinetics by Direct NMR Observation of the (EBI)Zr(MeB(C₆F₅)₃)propenyl Catalyst Species

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Metallocene-catalyzed polymerization of propene is an important industrial process that exhibits mechanistically intriguing features. Such features include complex kinetic behavior (especially for MAO-activated catalysts) and stereoerror frequencies that depend on the propene concentration.¹ It has been hypothesized that complex kinetics result from the catalyst accumulating in the form of dormant secondary alkyls and that stereoerrors result not from the insertion of the incorrect alkene enantioface, but from epimerization of the chain end following correct insertion.² Recently, we have reported³ detailed kinetic studies of the initiation, propagation, and termination rate for 1-hexene polymerization with (EBI)Zr(Me)(MeB(C₆F₅)₃) (**1**) as determined by quenched-flow kinetics with active site counting and by direct observation of polymerization events by NMR. In this contribution, we report (1) quantitation of catalyst speciation, (2) determination of propagation and termination kinetics, and (3) identification of chain-end isomerization events⁴ based on direct observation of Zr–polymeryl intermediates formed with propene.



As previously reported,^{3c} addition of 100 equiv of 1-hexene to 8 mM **1** in toluene-*d*₈ at $-40\text{ }^{\circ}\text{C}$ leads to partial conversion of **1** to **2** (i.e., 4.8 mM **2** is formed). Addition of 10 equiv of propene to this mixture of **1** and **2** effects complete consumption of the propene and conversion of **2** into **3** in less than 10 min; the concentration of **1** is unchanged by the addition of propene. Use of isotopic labels (1-¹³C-propene and 1,1'-D-2,3-¹³C-propene) and ¹H, ¹³C, ¹⁹F, ¹¹B, and gHSQC NMR spectroscopy provide definitive characterization of **3** (see Supporting Information). Subsequent addition of 60–100 equiv of propene to **3** leads to rapid consumption of all monomer. Simultaneous monitoring of [propene], [**1**], and [**3**] by ¹H NMR over the temperature range from -30 to $-60\text{ }^{\circ}\text{C}$ enables direct determination of catalyst speciation and propene disappearance kinetics. We find that propene polymerization is first order in [propene] and is 3 times faster than 1-hexene polymerization at $-40\text{ }^{\circ}\text{C}$ ^{2d} (Figure 1). Rate constants extrapolated from low temperatures are consistent with quenched-flow rate data obtained at $20\text{ }^{\circ}\text{C}$ (Figure 1 and Supporting Information). No evidence of 2,1 propene misinsertions or catalyst species other than **1** and **3** were observed during low-temperature propene polymerizations. Quenched-flow labeling with MeOD at $20\text{ }^{\circ}\text{C}$ yields polypropene with D labels at primary alkyls only. Our results imply that secondary Zr–alkyls do not accumulate under the conditions studied.

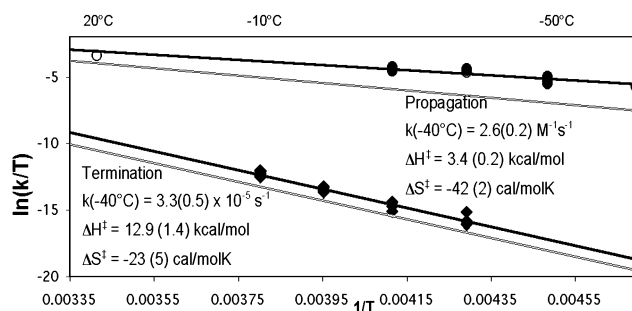


Figure 1. Eyring plots for propene propagation and termination rate constants for **3** as determined by direct (closed symbol) and quenched-flow (open circle) methods. Gray lines correspond to previously determined 1-hexene rate constants.

At temperatures above $-40\text{ }^{\circ}\text{C}$ in the absence of free propene, **3** undergoes termination, forming (EBI)Zr(Me)(HB(C₆F₅)₃) (**4**) and vinylidene-terminated polymer. Compound **4** is formulated as a hydridoborate ion pair rather than a methylborate, as is evidenced by a new doublet ($J_{\text{B-H}} = 65\text{ Hz}$) at -17 ppm in the ¹¹B NMR that sharpens to a singlet upon ¹H decoupling, as well as the appearance of a new Zr–Me peak at -0.36 in ¹H NMR that shows no ¹¹B coupling (see Supporting Information). Addition of propene to **4** results in the regeneration of **3**.

The net transformation of **3** to **4** between -40 and $-10\text{ }^{\circ}\text{C}$ is a first-order kinetic process that is slightly faster than termination with 1-hexene (Figure 1). Termination in the presence of excess 2-methylpentene results in the formation of (EBI)Zr(2-methylpentyl)(MeB(C₆F₅)₃) (**5**) at the same rate as **4** appears in the absence of 2-methylpentene; this result indicates that termination is effectively irreversible. Insertion of 2-methylpentene into the Zr–H bond exhibits low stereoselectivity; two diastereomers of **5** are formed in the ratio of approximately 1:1.

Substantial indirect data support the occurrence of chain-end epimerization through initial β -H transfer and subsequent isomerization steps.² In a pair of classic papers,^{2b,c} Brintzinger and Leclerc reported, inter alii, use of D labels to demonstrate 1,3-isomerization (migration of the metal from the 1 to 3 position of the last inserted propene) of the growing chain. More recently, Yoder and Bercaw^{2d} used double-labeled propene to show that 1,3-isomerization does not involve Zr–allyl intermediates. Because termination, also, likely proceeds through initial β -H transfer, we reasoned that chain-end epimerization should be observed under conditions where termination occurs. ¹H and ¹³C NMR spectra of **3** generated with 1-¹³C-propene at $-40\text{ }^{\circ}\text{C}$ reveal that **3**^{MAJ1} (superscripts MAJ and 1 represent the kinetically favored stereochemistry and position of the ¹³C label, respectively) slowly converts to the Zr–alkyl species **3**^{MIN3}, **3**^{MAJ3}, and **3**^{MIN1}, and the termination products **T**¹ and **T**³ (Figures 2 and 3). As is shown in Figure 3, the ¹H and ¹³C NMR spectra of **3**^{MAJ1} generated from **1**-(CD₃)₂ demonstrate both 1,3-

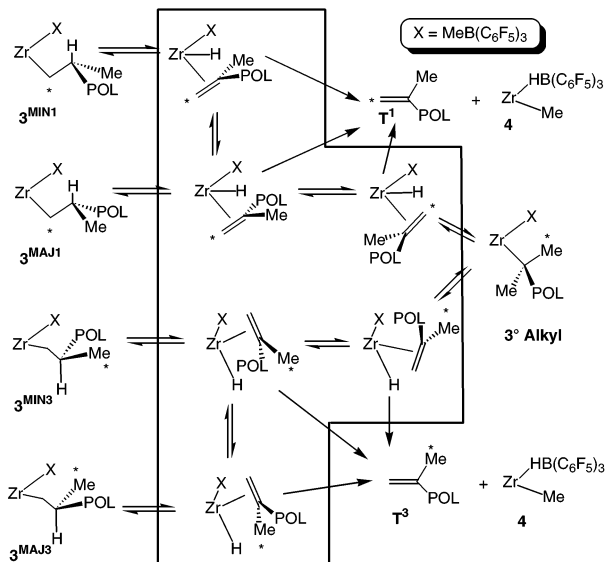


Figure 2. Labeling and proposed pathways for isomerization, epimerization, and termination events at **3**. Species outside the boxed area have been characterized by NMR methods.

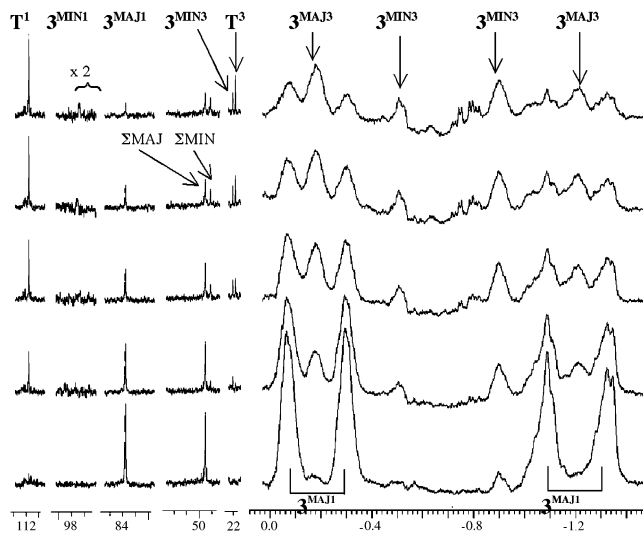


Figure 3. ^{13}C (left) and ^1H (right) NMR spectra of **3** (ca. 5 mM) formed from **1**-(CD_3) $_2$ and $1\text{-}^{13}\text{C}$ -propene in toluene- d_8 at -40°C . Spectra are presented at 3 h intervals starting from $t = 0$ (bottom spectrum).

isomerization (e.g., converting 3^{MAJ1} to 3^{MAJ3}) and chain-end epimerization (creating, e.g., 3^{MIN} isotopomers). For example, decreased intensity of the ^{13}C NMR resonance for $\text{Zr}-\text{CH}_2$ (3^{MAJ1} , 84 ppm) with concomitant appearance of a new ^{13}C Me resonance (3^{MAJ3} , 23.1 ppm) signifies 1,3-isomerization. Simultaneous loss of ^{13}C satellites for the diastereotopic $\text{Zr}-\text{CH}_2$ ^1H NMR resonances corroborates this interpretation. Epimerization yields diastereomers that exhibit ^{13}C NMR resonances at 97 and 49 ppm (vs 84 and 50 ppm for 3^{MAJ} isotopomers) for the chain-end and penultimate $\text{Zr}-\text{CH}_2$ resonances, respectively, as well as new diastereomeric $\text{Zr}-\text{CH}_2$ ^1H NMR resonances. Correlated NMR (gHSQC) data confirm assignments of the ^{13}C and ^1H NMR resonances.

Qualitatively, the time profile of isomerization/termination is as follows: termination product T^1 grows in most rapidly, followed by the near simultaneous growth of 3^{MIN3} , 3^{MAJ3} , and T^3 in comparable amounts, which is followed by slow formation of minor amounts of 3^{MIN1} . Ultimately, all of **3** terminates to T^1 and T^3 in a 2:1 ratio. Addition of excess 2-methyl-1-pentene has no influence on the isomerization rates. Significantly, these data directly demonstrate that epimerization, 1,3-isomerization, and termination occur at similar rates. A natural interpretation² is that β -H transfer to yield a $\text{ZrH}(\text{alkene})$ complex is a relatively slow event that is followed by at least three relatively rapid and competitive reaction paths: termination via alkene dissociation, rotation of the alkene and reinsertion to generate a tertiary alkyl which can further isomerize, and nondissociative exchange of the alkene enantioface followed by reinsertion to generate the opposite diastereomer. Unexpectedly, the epimerization product (3^{MIN1}) formed most directly from 3^{MAJ1} appears only in minor amounts, whereas 1,3-isomerization via a putative tertiary alkyl yields both diastereomers (3^{MAJ3} and 3^{MIN3}) in similar amounts. Several scenarios could account for the low accumulation of 3^{MIN1} . One possibility that stems from the work of Kraft and Jones⁵ is that β -H transfer from the diastereotopic Me groups of the tertiary alkyl generates two geometric isomers with different arrangements of H relative to the coordinated alkene and methylborate counterion (see Figure 2).

In summary, catalytic propene and 1-hexene polymerizations with **1** proceed with similar propagation and termination rates, but differ in their isomerization proclivities. Direct observation of epimerization/isomerization of Zr -polymeryl intermediates is reported for the first time, thus clarifying the origin of stereoerrors in propene polymerization. Future publications will report details of propene polymerization and epimerization kinetics as determined by direct NMR observation and by polymer microstructure analysis.

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Supporting Information Available: Full experimental details, NMR characterization of **3**, **4**, and **5**, time profiles for epimerization/isomerization, and quenched-flow data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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