

## A $^2\text{H}$ -Labeling Scheme for Active-Site Counts in Metallocene-Catalyzed Alkene Polymerization

Zhixian Liu, Ekasith Somsook, and Clark R. Landis\*

Department of Chemistry  
University of Wisconsin-Madison  
1101 University Avenue, Madison, Wisconsin 53705

Received September 8, 2000

Detailed kinetics of metallocene-catalyzed alkene polymerization reactions are elusive but essential to understanding the mechanism of these important industrial processes.<sup>1</sup> As noted by Busico et al.,<sup>2</sup> evaluation of the “deceptively simple” propagation rate law (eq 1) is obscured

$$R_p = -\partial[M]/\partial t = k_p[C^*][M]^\alpha$$

where M = monomer, C\* = active sites (1)

by (1) heterogeneity in the number of active sites which may lead to widely varying exponents,  $\alpha$ , (2) a lack of reliable methods for determining the concentration of active sites,<sup>3</sup> [C\*], and (3) poor reproducibility of both [C\*] and  $R_p$ . Indeed, the issue of active-site counting pervades all catalytic processes. We report reproducible, time-resolved active-site counts for the polymerization of 1-hexene as catalyzed by the “single-site” contact ion-pair, [(*rac*-C<sub>2</sub>H<sub>4</sub>(1-indenyl)<sub>2</sub>ZrMe][MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>4,5</sup> (**1**), through the use of quenched-flow kinetics and a  $^2\text{H}$ -labeling scheme.

Scheme 1 illustrates our general method for counting active sites. In a typical experiment, 5 mL of a toluene solution of **1** ( $4 \times 10^{-4}\text{M}$ ) is rapidly mixed with an equal volume of 1-hexene (0.15–3.0 M) in toluene using a quenched-flow apparatus developed in our laboratory.<sup>6</sup> After a prescribed reaction time (0.01–1000 s), the reaction is quenched by rapid addition of 5 mL of MeO<sup>2</sup>H in toluene (5 M, >99%  $^2\text{H}$ ). After removal of all volatiles, the polymer is purified by passage through a short column of alumina, weighed, and analyzed by  $^2\text{H}$  NMR. This method quantifies Zr–alkyls which can be methanolized at the time of quench. A typical  $^2\text{H}$  NMR of quenched polymer is shown in Figure 1; note that we find label at terminal methyl positions only.

An alternative to quenching with MeO<sup>2</sup>H is to use the labeled catalyst, [(*rac*-C<sub>2</sub>H<sub>4</sub>(1-indenyl)<sub>2</sub>ZrC<sup>2</sup>H<sub>3</sub>][C<sup>2</sup>H<sub>3</sub>B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] (**1-d<sub>6</sub>**), and quench with unlabeled methanol. Whereas the former method provides the number of active sites at the time of quench, the latter yields the number of sites that were active at any point before the quench.

(1) For recent reviews of metallocene-catalyzed alkene polymerization see Gladysz, J. A., Ed. *Chem. Rev.* **2000**, *100*, 1167–1682 and references therein.

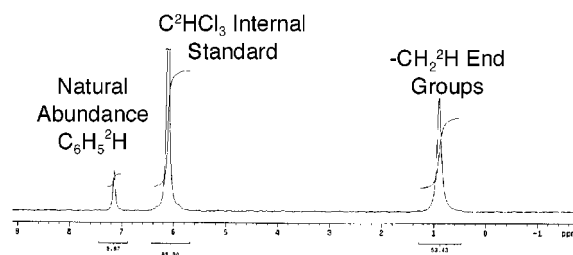
(2) Busico, V.; Cipullo, R.; Esposito, V. *Macromol. Rapid Commun.* **1999**, *20*, 116–121.

(3) (a) Marques, M. M.; Tait, P. J. T.; Mejzlik, J.; Dias, A. R. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 573–585. (b) Mejzlik, J.; Lesná, M.; Kratochvíla, A. *Polym. Sci.* **1987**, *81*, 83–120. (c) Han, T. K.; Ko, Y. S.; Park, J. W.; Woo, S. I. *Macromolecules* **1996**, *29*, 7305–7309. (d) Chien, J. C. W.; Tsai, W.-M. *Makromol. Chem., Macromol. Symp.* **1993**, *66*, 141–156. (e) Natta, G. *J. Polym. Sci.* **1959**, *34*, 21–48. (f) Chien, J. C. W.; Sugimoto, R. *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 459–470. (g) Busico, V.; Guardasole, M.; Margonelli, A.; Segre, A. L. *J. Am. Chem. Soc.* **2000**, *122*, 5226–5227.

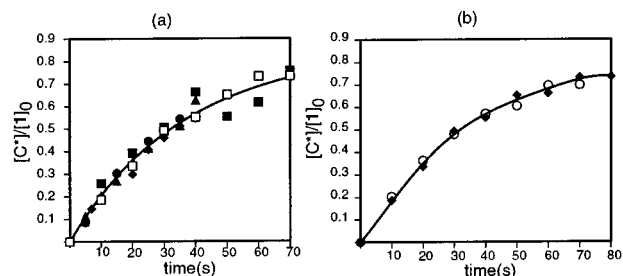
(4) Kaminsky, W.; Külper, K.; Brintzinger, H. H.; Wild, F. R. W. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 507–508.

(5) Synthesized from (*rac*-C<sub>2</sub>H<sub>4</sub>(1-indenyl)<sub>2</sub>ZrMe<sub>2</sub>: (a) Bochmann, M.; Lancaster, S. J. *Organometallics* **1993**, *12*, 633–640. (b) Chien, J. C. W.; Tsai, W. M.; Rausch, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 8570–8571. (c) Diamond, G. M.; Jordan, R. F.; Petersen, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 8024–8033.

(6) (a) Landis, C. R.; White, C.; Rosaaen, K., manuscript in preparation. (b) Mori, H.; Terano, M. *Trends in Polym. Sci.* **1997**, *5*, 314–321.

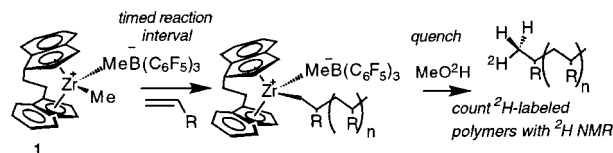


**Figure 1.**  $^2\text{H}$  NMR spectrum of  $^2\text{H}$ -labeled polymer obtained according to Scheme 1 (48 mg of poly-1-hexene in 0.65 mL of C<sub>6</sub>H<sub>6</sub>).



**Figure 2.** (a) Fractional active-site counts as a function of time for five independent polymerizations ([I]<sub>0</sub> =  $8 \times 10^{-4}\text{M}$ , [1-hexene] = 1.0 M, 0 °C, toluene solvent). (b) Comparison of fractional active-site counts using MeO<sup>2</sup>H (○) quench or MeOH quench (◆) of **1-d<sub>6</sub>** ([I]<sub>0</sub> =  $8 \times 10^{-4}\text{M}$ , [1-hexene] = 1.0 M, 0 °C, toluene solvent). In both (a) and (b) the solid line represents the best fit of the data to a single-exponential growth function.

### Scheme 1

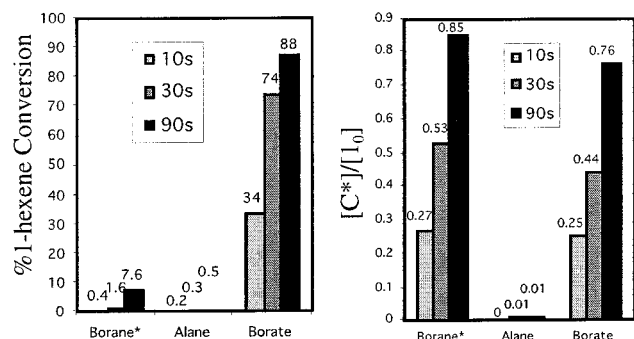


To be useful, labeling schemes for active-site counting must be quantitative and reproducible. Separate experiments establish that reaction of **1** with MeO<sup>2</sup>H yields 0.95(5) equiv of CH<sub>3</sub><sup>2</sup>H per Zr. For polymerization experiments maximum active-site counts commonly lie in the range of 85–95% of the Zr added. Inevitably some labeled polymer is lost in workup (either due to handling or the volatility of short oligomers), and it is probable that some of the catalyst is deactivated by impurities. As shown in Figure 2, the active-site counts obtained by the MeO<sup>2</sup>H quench method are reproducible (Figure 2a) and nearly identical with those obtained by quenching **1-d<sub>6</sub>** with MeOH (Figure 2b). Because the two labeling methods yield similar active-site counts, we conclude that the catalyst does not deactivate<sup>7</sup> (i.e., convert to a species incapable of catalyzing polymerization) during the time scale of the experiments. Additionally, exchange of Zr–Pol with Me–B bonds (i.e., chain transfer) does not occur because this would lead to > 1 C<sup>2</sup>H<sub>3</sub>-labeled polymer per Zr when **1-d<sub>6</sub>** is methanolized.

One application of the  $^2\text{H}$ -tagging scheme is to evaluate the number of active sites obtained with different catalyst activators. We have examined three different reagents for activating<sup>8</sup> the catalyst precursor, (*rac*-C<sub>2</sub>H<sub>4</sub>(1-indenyl)<sub>2</sub>ZrMe<sub>2</sub>: B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>,<sup>9</sup>

(7) This statement presumes that  $^2\text{H}$ -labeled polymers resulting from nonpropagating species (such as C<sup>2</sup>H<sub>2</sub>-vinyl end groups from quenching of Zr–alkyls) have chemical shifts that are different from those produced by quenching of propagating species.

(8) For a review of activators in alkene polymerization see Chen, E. Y.-X.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391–1434.



**Figure 3.** Percent conversion of monomer (left) and fraction of active sites (right) for  $(rac-C_2H_4(1-indenyl)_2)ZrMe_2$ -catalyzed polymerizations of 1-hexene in the presence of various activators at reaction times of 10, 30, and 90 s ( $0^\circ C$  in toluene solution,  $[Zr] = 8 \times 10^{-4} M$ ,  $[activator] = 8 \times 10^{-4} M$ , borane =  $B(C_6F_5)_3$ , alane =  $Al(C_6F_5)_3$ , borate =  $[PhNMe_2H][B(C_6F_5)_4]$ ,  $[1-hexene]_0 = 1.5 M$ ; \*for these runs  $[1-hexene]_0 = 1.0 M$ , reaction times = 10, 30, and 70 s).

$Al(C_6F_5)_3$ ,<sup>10</sup> and  $[PhNMe_2][B(C_6F_5)_4]$ .<sup>11</sup> The fractional conversion of monomer into polymer and the active-site counts for the three activators at each quench time are shown in Figure 3. Under these conditions,  $B(C_6F_5)_3$  is a superior activator to  $Al(C_6F_5)_3$  despite the expectation that the stronger Lewis acid,  $Al(C_6F_5)_3$ , might better promote ion-pair separation and, hence, catalyst activity.<sup>8</sup> A plausible explanation lies in the crystallographic structures of the  $Al(C_6F_5)_3$  and  $B(C_6F_5)_3$  adducts of  $(Me_4Cp)_2ZrMe_2$  (Figure 4): the Al-adduct makes a tighter ion-pair because the longer Al–C bonds relieve congestion between the “anion” and “cation”. Relative to activation with  $B(C_6F_5)_3$ , the  $[PhNMe_2][B(C_6F_5)_4]$  cocatalyst yields similar concentrations of active sites but significantly more polymer. These results suggest that  $[PhNMe_2][B(C_6F_5)_4]$ -activated catalyst propagates at a significantly faster rate.<sup>8</sup>

A second application of active-site counting is measurement of initiation kinetics.<sup>12</sup> For polymerization of 1-hexene as catalyzed by **1**, the number of active sites grows with time according to a simple exponential function (Figure 2). The empirical rate law (eq 2) determined from the active-site growth kinetics is strictly first-order in **1** and  $[1-hexene]$  and independent of excess  $B(C_6F_5)_3$  ( $k_i(0^\circ C) = 0.026(3)M^{-1} s^{-1}$ ).

$$\frac{d[C^*]}{dt} = k_i[1][1-hexene] \quad (2)$$

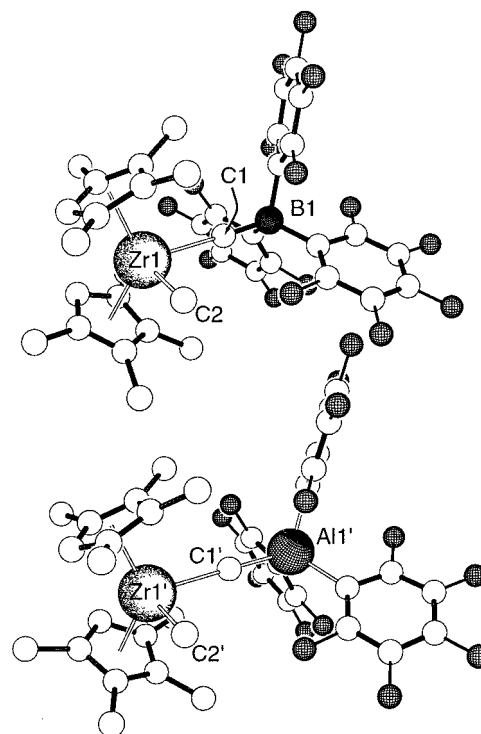
The  $CH_3O^2H$ -quench strategy complements previous active-site counting methods.<sup>3,6b</sup> The  $^2H$  NMR resonances of the labeled

(9) (a) Ewen, J. A.; Elder, M. J. *Eur. Patent Appl.* 0,427,697, 1991. (b) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1991**, *113*, 3623–3625. (c) Yang, X. M.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10015–10031. (d) Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1964**, *2*, 245–250.

(10) (a) Bochmann, M.; Sarsfield, M. J. *Organometallics* **1998**, *17*, 5908–5912. (b) Biagini, P.; Lugli, G.; Abis, L. (Enichem Elastomeri, S.P.I.). U.S. Pat. 5,602,269, 1997. (c) Chen, E. Y.-X.; Kruper, W. J.; Root, G.; Schwartz, D. J.; Storer, J. W. *PCT Int. Appl. WO*, 2000. (d) Chen, E. Y.-X.; Kruper, W. J.; Root, G. *PCT Int. Appl. WO*, 2000. (e) Cowley, A. H.; Hair, G. S.; McBurnett, B. G.; Jones, R. A. *Chem. Commun.* **1999**, 437–438.

(11) (a) Turner, H. W. (Exxon Chemical Co.). *Eur. Pat. Appl.* EP 0 277 004 A1, 1988. (b) Hlatky, G. G.; Upton, D. J.; Turner, H. (Exxon Chemical Co.). *W. PCT Int. Appl.* WO 91/09882, 1991.

(12) For recent kinetic modeling of initiation, see: Wester, T. S.; Johnsen, H.; Kittilsen, P.; Rytter, E. *Macromol. Chem. Phys.* **1998**, *199*, 1989–2004.



**Figure 4.** Crystallographic structures of  $[(Me_4Cp)_2Zr(CH_3)][(CH_3B(C_6F_5)_3)]$  (upper) and  $[(Me_4Cp)_2Zr(CH_3)][(CH_3Al(C_6F_5)_3)]$  (lower). Relevant structural parameters: Zr1–C2 2.24 Å, Zr1–C1 2.60 Å, B1–C1 1.69 Å; Zr1'–C2' 2.26 Å, Zr1'–C1' 2.51 Å, Al1'–C1' 2.06 Å.

polymer enable distinction among different types of Zr–alkyls (primary, secondary, tertiary, vinylic, allylic, etc.). For example, our results for 1-hexene polymerization as catalyzed by **1** demonstrate that the catalyst comprises primary Zr–alkyls almost exclusively; we find no evidence for dormant secondary Zr–alkyls or Zr–allyls. However, relative to radiolabeling methods,<sup>3</sup> the  $^2H$ -labeling scheme exhibits lower sensitivity. Due to the 0.015% natural abundance of  $^2H$  in the polymer and the introduction of only one  $^2H$  into each methyl end group, we estimate a maximum limit of  $\sim 5000$  insertions/active center for accurate quantitation of active sites. We are pursuing labels containing higher sensitivity nuclei to mitigate this issue. For comparison, Mori’s “stopped-flow” approach<sup>6b,2</sup> to active-site counting is not as sensitivity-limited but requires more measurements, relies on accurate molecular weight determinations, and can be complicated by induction periods.

The significance of this work is that it provides a reliable method for time-resolved active-site counting in metallocene-catalyzed alkene polymerization. In turn, these methods enable further elucidation of the kinetics of metallocene-catalyzed alkene polymerization which will be reported soon.

**Acknowledgment.** We thank the DOE Office of Basic Energy Sciences and Dow Chemical Company for support of this work.

**Supporting Information Available:** Crystallographic Data for  $[(Me_4Cp)_2Zr(CH_3)][CH_3(Al(C_6F_5)_3)]$ ,  $[(Me_4Cp)_2Zr(CH_3)][CH_3(B(C_6F_5)_3)]$  and experimental procedures (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA0055918