

Additions and Corrections

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Abdulaziz Al-Humydi, Jered C. Garrison, Wiley J. Youngs, and Scott Collins*: Propene Polymerization Using *ansa*-Metallocenium Ions: Excess Activator Effects on Polymerization Activity and Polymer Microstructure

Pages 194–195. In this article we argued that the equilibrium depicted in eq 1 on p 194 was irreversible, on the basis of the value of $K \approx 10^4 \text{ M}^{-1}$ estimated from the fit of the data to the equation depicted in Figure 1. This conclusion is true only if the active species on the right-hand side remains in this state following every insertion. If the active species reverts to the dormant state following each insertion, then the equilibrium depicted in eq 1 is coupled to an irreversible reaction and the expression used to fit the data in Figure 1 is not valid.

Under the latter conditions, and if the steady-state approximation holds for the active species, it can be shown that

$$\frac{R_p}{R_p^{\max}} = \frac{[\text{Zr}^*]}{[\text{Zr}]_0} = \frac{k_1([\text{Zr}]_0 - [\text{Zr}^*])([\text{BR}_3]_0 - [\text{Zr}^*])}{(k_{-1} + k_p[\text{M}])[\text{Zr}]_0}$$

where $[\text{Zr}]_0$ is the initial ion-pair concentration and $[\text{BR}_3]_0$ is the initial *excess* borane concentration. This equation may be solved for the quantity $[\text{Zr}^*]/[\text{Zr}]_0$ to provide the expression

$$\frac{[\text{Zr}^*]}{[\text{Zr}]_0} = \frac{[(1+r)a + (1+n)] - \sqrt{[(1+r)a + (1+n)]^2 - 4ra^2}}{2a}$$

where $r = [\text{BR}_3]_0/[\text{Zr}]_0$, $a = K[\text{Zr}]_0$, and $n = k_p[\text{M}]/k_{-1}$

with $K = k_1/k_{-1}$ and k_p being the propagation rate constant for monomer coordination and insertion involving the activated species. It can be appreciated from this expression that without independent knowledge of K or n it is not possible to unambiguously estimate either quantity from the data. Also, this expression reduces to the equation depicted in Figure 1 in the limit $n \rightarrow 0$.

On p 195 we report that $K = 6 \text{ M}^{-1}$ at $-60 \text{ }^\circ\text{C}$ for the equilibrium depicted in eq 2 involving pairs **3** and intermediate **4** and from the Supporting Information (Figure S-2) one can estimate that $K \approx 0.02 \text{ M}^{-1}$ at $30 \text{ }^\circ\text{C}$ from the T dependence of K over the range -60 to $-30 \text{ }^\circ\text{C}$ (i.e., there is very little of intermediate **4** present above $-20 \text{ }^\circ\text{C}$).

If the value of K for the equilibrium depicted in eq 1 has this same magnitude, one can easily show that, in the above expression, the term $(1+r)a \ll 1+n$ for *all values of* n with $r \leq 1000$ at $[\text{Zr}]_0 = 5 \times 10^{-6} \text{ M}$. The expression shown above would then simplify to

$$\frac{[\text{Zr}^*]}{[\text{Zr}]_0} = \frac{(1+n) - \sqrt{(1+n)^2 - 4ra^2}}{2a} \approx 0$$

thus indicating that little or no enhancement of R_p should be observed if double activation analogous to that shown in eq 2 is involved during propagation. Thus, either double activation of the propagating intermediate is somehow much more favorable than suggested by the results using model ion pairs or an alternate explanation is needed to account for the kinetic behavior at steady state.

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