Communication

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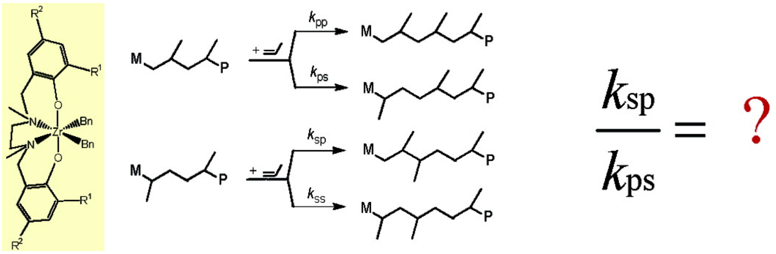

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Reactivity of Secondary Metal−Alkyls in Catalytic Propene Polymerization: How Dormant Are “Dormant Chains”?

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With only few exceptions, transition-metal-mediated propene polymerizations are highly regioselective (typically >99%) in favor of 1,2 (primary) monomer insertion.[1,2] It is often observed, though, that the addition of trace amounts of ethene or H_2 to a reaction system results in the preferential formation of $M{-}CH_2{-}CH_2{-}CH(CH_3){-}CH_2{-}P$ over $M{-}CH_2{-}CH_2{-}CH_2{-}CH(CH_3){-}P$ fragments (P = polymeryl; Scheme 1a,b) or of ^{n}butyl over ^{i}butyl chain ends (Scheme 1c,d), respectively.[3−5] The fact that this is usually associated with a strong catalyst activation led us[3,4] and others[5,6] to propose that the insertion of a substituted olefin like propene into a sterically hindered secondary M−polymeryl bond (Scheme 1g) is much slower than into a primary one (Scheme 1e), and that therefore in homopolymerization, an accumulation of secondary M−polymeryl bonds can occur (“dormant” chains).

Under steady-state conditions, and provided that chain transfer and isomerization processes are negligible, the mole fraction of dormant chains is given by[3,4a]

$$x_s^* = (1 + k_{sp}/k_{ps})^{-1} \tag{1}$$

where the specific rates, k_{sp} and k_{ps}, are as defined in Scheme 1g−f.

Unfortunately, measuring x_s^* is complicated. The very low average chain growth time (typically <1 s) for most catalysts of practical interest[7] has precluded until now the use of direct methods, such as reaction quenching with a suitable reagent and NMR analysis of the resulting chain ends. This prompted us to develop indirect approaches based on the microstructural characterization of propene/ethene copolymers[3] or of propene hydrooligomers.[4a] We have shown, in particular, that the mole ratio, Q_{pE}/Q_{sE}, of ethene units found by ^{13}C NMR following a 1,2 or a 2,1 propene unit in propene/ethene copolymers as a function of the $[C_2H_4]/[C_3H_6]$ feeding ratio extrapolates, in the limit of $[C_2H_4] = 0$, to the product $(k_{sp}/k_{ps})(k_{pE}/k_{sE})$. Similarly, the mole ratio Q_{pH}/Q_{sH} between ^{i}butyl and ^{n}butyl chain ends in propene hydrooligomers obtained at variable $p(H_2)/[C_3H_6]$ extrapolates, for $p(H_2) \rightarrow 0$, to the product $(k_{sp}/k_{ps})(k_{pH}/k_{sH})$. Experimental values of the two products for typical C_2-symmetric *ansa*-zirconocenes, documenting a large variability even within the same catalyst class, are summarized in Table 1 (entries 1−3).

The problem of such methods is that, in general, the ratios k_{pE}/k_{sE} and k_{pH}/k_{sH} are unknown quantities. On the other hand, if one makes the assumption that the relative reactivities of Scheme 1 are mainly governed by steric effects and considers the small size of the molecules of ethene and H_2, one can plausibly propose that k_{pE}/k_{sE} and k_{pH}/k_{sH} are not far from unity, and that therefore the products $(k_{sp}/k_{ps})(k_{pE}/k_{sE})$ and $(k_{sp}/k_{ps})(k_{pH}/k_{sH})$ can be approximated to k_{sp}/k_{ps}. On inspection of Table 1, it can be seen that for all three metallocenes, k_{pH}/k_{sH} is actually lower by a factor 3−6 than k_{pE}/k_{sE}; however, the two estimates of x_s^* based on the assumption that $k_{pE}/k_{sE} = 1$ ($x_s^*[C_3/C_2]$) or, alternatively, that $k_{pH}/k_{sH} = 1$ ($x_s^*[H_2]$) define a reasonably narrow range.

Very recently, the reactivity of Zr−^{n}butyl and Zr−^{s}butyl bonds for active species $[rac\text{-}C_2H_4(1\text{-indenyl})_2Zr{-}butyl][MeB(C_6F_5)_3]$ at −80 °C has been measured with elegant in situ NMR experiments by Landis and co-workers.[8] Quite unexpectedly, Zr−^{n}butyl and Zr−^{s}butyl were found to undergo 1,2 propene insertion at similar rates ($k_{(^nBu)p}/k_{(^sBu)p} \sim 1.4$). On the other hand, the reactivity of H_2 with Zr−^{s}butyl turned out to be at least 100 times higher than that with $Zr{-}CH_2{-}CH(CH_3){-}P$ ($k_{pH}/k_{(^sBu)H} \leq 0.01$). Even at −80 °C, ethene insertion rates into the same two model Zr−alkyl bonds were too high for absolute measurements; their ratio ($k_{(^nBu)E}/k_{(^sBu)E}$), though, was estimated to be ∼1. Such a large difference in relative reactivity of primary and secondary alkyls toward H_2 and ethene is definitely not in line with the results of Table 1; however, the authors suggested that β-substituted primary Zr−alkyls should be 5−100 times less reactive toward ethene than linear ones, and therefore in propene/ethene copolymerization, the ratio k_{pE}/k_{sE} should be very low as well (∼0.1−0.01).

At this point, different scenarios can be envisaged. If the findings of ref 8 can be generalized and the suggestion on k_{pE}/k_{sE} is correct, then all previous estimates of catalyst dormancy (like those of Table 1) are gross exaggerations, and the very concept of secondary M−polymeryls as dormant chains must be questioned; this would also require finding another explanation for the activating effect of H_2 and ethene in trace amounts. On the other hand, it is possible

Scheme 1

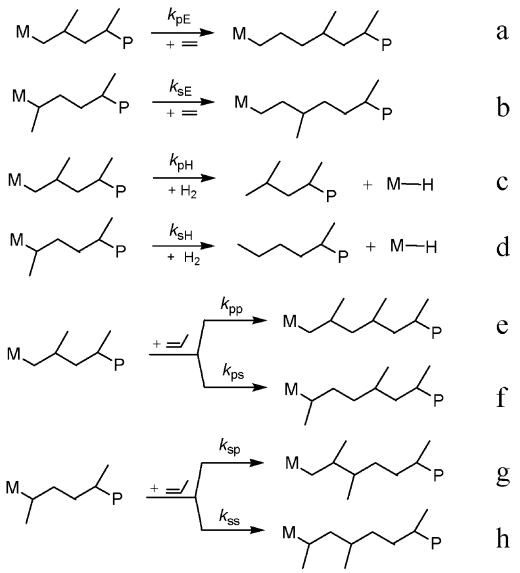

Table 1. Estimates of Catalyst Dormancy in Propene Polymerization for Different Systems (see text)

system[a]	$(k_{sp}/k_{ps})(k_{pE}/k_{sE})$	$(k_{sp}/k_{ps})(k_{pH}/k_{sH})$	x_s^*	$x_s^*[C_3/C_2]$	$x_s^*[H_2]$
1	0.35[b]	0.1[c,d]	n.a.[e]	0.74	0.9
2	1.44 ± 0.08[f]	0.35[c,f]	n.a.[e]	0.41	0.74
3	4.4 ± 0.2[f]	0.8[f]	n.a.[e]	0.19	0.5
4	2.0	0.2	0.2	0.33	0.8

[a] Legend: **1** = *rac*-$C_2H_4(1\text{-indenyl})_2ZrCl_2$/MAO. **2** = *rac*-$Me_2Si(1\text{-indenyl})_2ZrCl_2$/MAO. **3** = *rac*-$Me_2Si(2\text{-methyl-4-phenyl-1-indenyl})_2ZrCl_2$/MAO. **4** = $[ONNO]ZrBn_2$ (Chart 1; R^1 = cumyl, R^2 = methyl)/MAO/2,6-di-^{t}butylphenol. [b] Unpublished results from our laboratory (at 50 °C). [c] From ref 4b [d] From ref 4c. [e] n.a. = not available. [f] From ref 3.

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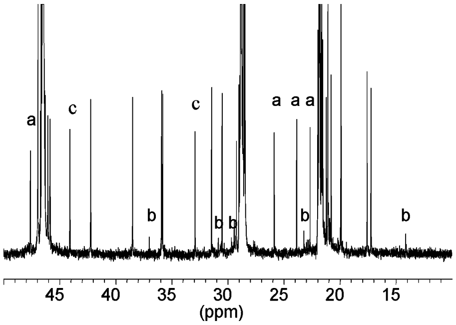
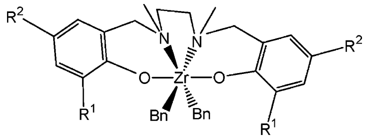


Figure 1. ^{13}C NMR (100 MHz) spectrum (in tetrachloroethane-1,2-d_2 solution at 120 °C) of an iPP sample obtained by quenching the reaction after 4 min. Resonances labeled with a, b, and c are due to ^{i}butyl, ^{n}butyl, and benzyl chain ends, respectively.[2,4−6]

that the behavior of model M−alkyl cations in tight association with $[MeB(C_6F_5)_3]^-$ at −80 °C is not representative of real M−polymeryl cations at practical temperatures and in looser ion couples, like those involving $[B(C_6F_5)_4]^-$ or the anion of methylalumoxane (MAO).[9]

We have addressed this question by taking advantage of a new class of nonmetallocene catalysts[10,11] (Chart 1; Bn = benzyl) able to polymerize propene with a high 1,2 regioselectivity (>99%) *in a controlled fashion.*[11] In particular, we have chosen the complex with R^1 = cumyl and R^2 = methyl, which upon activation with MAO/2,6-di-^{t}butylphenol,[12] affords an isotactic polypropylene ([*mmmm*] = 90%) containing 0.85 mol % regioirregular 2,1 units ($k_{pp}/k_{ps} = 1.2 \times 10^2$), with an average chain growth time of ca. 1 h at 25 °C and $[C_3H_6] = 1.36$ M (M_n = 180 kDa).[11]

Chart 1



In Figure 1, we report the ^{13}C NMR spectrum of a polypropylene sample obtained by quenching the reaction mixture after 4 min with methanol/HCl (M_n = 9.5 kDa). The resonances of the ^{i}butyl and ^{n}butyl chain ends resulting from the protonolysis of primary and secondary Zr−polymeryls are well evident, as are those of the initial benzyl ends. In particular, by full simulation of the spectrum, we estimated a fraction of terminal secondary Zr−polymeryls, $x_s^* = 20\%$, corresponding to a value of $k_{sp}/k_{ps} = 4$ (from eq 1). Identical results were obtained on polymers quenched at longer reaction times (up to 10 min). This indicates that secondary Zr−polymeryls undergo 1,2 propene insertion at a largely lower rate than primary ones ($k_{sp}/k_{pp} \sim 0.03$) and do accumulate, although in the present case, not to the point that the dormant chains outnumber the propagating ones.

Once k_{sp}/k_{ps} was measured, we determined k_{pE}/k_{sE} and k_{pH}/k_{sH} via propene/ethene copolymerization[3] and propene hydrooligomerization.[4a] The straight line through the copolymerization data points (Figure 2, left) extrapolates to a value of $(k_{sp}/k_{ps})(k_{pE}/k_{sE}) = 2.0$, which corresponds to $k_{pE}/k_{sE} = 0.5$; therefore, the assumption that ethene inserts with very similar rates into primary (albeit, β-substituted) and secondary M−polymeryl bonds[3] is correct. According to the copolymerization theory,[3] the slope of said line corresponds to the ratio of k_{pE}/k_{ps}; from the best-fit value of 1.8×10^3 and by substitution, it is immediate to calculate that $k_{sE}/k_{sp} = 9.0 \times 10^2$. This confirms that ethene inserts into secondary M−polymeryl bonds almost 1000-fold faster than propene (which is in fact at the foundation of the propene/ethene copolymerization approach).

The propene hydrooligomerization plot (Figure 2, right), in turn, extrapolates to $(k_{sp}/k_{ps})(k_{pH}/k_{sH}) = 0.2$; it follows that for the investigated catalyst, $k_{pH}/k_{sH} = 0.05$. According to the hydrooligomerization theory,[4a] the slope of the straight line through the data points corresponds to the ratio of k_{pp}/k_{ps}; the best fit value of 1.2×10^2 is indeed in perfect agreement with the observed polypropylene regioregularity.

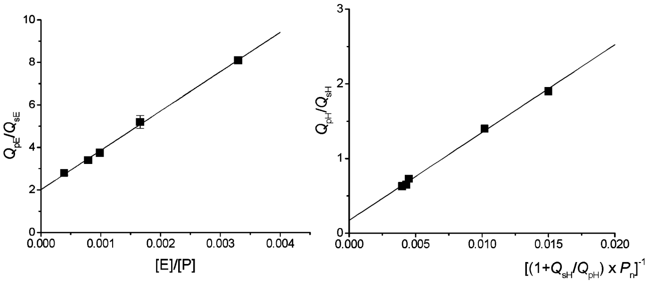


Figure 2. Propene/ethene copolymerization plot (left), and propene hydrooligomerization plot (right). For details, see text and refs 3 and 4.

In conclusion, the new results reported above (summarized in Table 1, system **4**) confirm the poor reactivity toward propene of authentic secondary M−polymeryls under realistic conditions and the possible accumulation of dormant chains in propene homopolymerization. Direct measurements of x_s^* are straightforward only for controlled polymerizations, like the one investigated here. In such a case, we could compare the actual value of x_s^* with those estimated via propene/ethene copolymerization ($x_s^*[C_3/C_2]$) and propene hydrooligomerization ($x_s^*[H_2]$) and conclude that $x_s^*[C_3/C_2]$ is fairly close to x_s^*, whereas $x_s^*[H_2]$ is substantially inflated. This probably reflects a general tendency ($k_{pE}/k_{sE} \sim 1$, $k_{pH}/k_{sH} < 1$), although the quantitative aspects seem to be critically dependent on the system considered (Table 1 and ref 8).

In the absence of direct information, we suggest that a strong catalyst activation in propene polymerization upon addition of low amounts of ethene or H_2, and a high tendency of the occasional 2,1 units to be isomerized to 3,1 units[1,2] (as is the case of systems **1** and **2**, and not of systems **3** and **4** in Table 1), should be regarded as important indirect indicators of a high dormancy.

Supporting Information Available: Experimental section. This material is available free of charge via the Internet at http://pubs.acs.org.

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