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Metallocene-Catalyzed Propene Polymerization: From Microstructure to Kinetics. C_s-Symmetric *ansa*-Zirconocenes

Vincenzo Busico,* Roberta Cipullo, Francesco Cutillo, Michele Vacatello, and Valeria Van Axel Castelli

Dipartimento di Chimica, Università di Napoli "Federico II", Via Cintia, 80126 Naples, Italy

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Polymer microstructure descends from polymerization kinetics; therefore, at least in principle, kinetic parameters can be extracted from microstructural data, e.g., by statistical analysis of sequence distributions in terms of the appropriate stochastic model of chain propagation. In a recent paper,[1] we have shown that this well-known concept, which finds application routinely in the determinations of reactivity ratios for the various possible (co)monomer additions/insertions, can be extended to cases in which chain propagation competes with one or more processes introducing "defects" of known and recognizable nature in the growing chains. In such cases, polymer regularity results from the balance of the competing processes, and is usually a function of monomer concentration which can be modeled with very useful results.

As a first example, we investigated propene polymerization promoted by two well-known isotactic-selective C_2-symmetric *ansa*-zirconocenes[2] for which a second-order kinetics had been reported,[3] and attributed by some to the participation ot two monomer molecules in the insertion transition state ("trigger" hypothesis).[4] From the dependence on propene concentration of the relative rates of propene polyinsertion and of *growing chain epimerization* (an intramolecular reaction leading to the racemization of last-inserted monomeric units),[5] we proved instead that the former has a simple first-order rate law, and that the apparent higher order kinetics can be traced to the presence of one or more resting states in the catalytic cycle.[1] In this communication, we extend the approach to C_s-symmetric (cyclopentadienyl)(fluorenyl) metallocenes.[2]

The concept of chain-migratory insertion in transition metal-mediated propene polymerization dates back to the 1960s, when it was proposed by Cossee for the heterogeneous Ziegler−Natta catalysts (Scheme 1).[6]

Although highly plausible and in agreement with the general principle of the least nuclear motion, it remained purely speculative until, in 1988, highly syndiotactic chain propagation in the presence of C_s-symmetric *ansa*-zirconocenes[2,7] provided a compelling experimental demonstration; a regular alternation of monomer insertions at the two enantiotopic active sites of the cationic catalytic species is indeed a necessary condition for the observed stereoselectivity.

With the prototypical system $Me_2C(Cp)(9\text{-fluorenyl})ZrCl_2$ (**1-Cl$_2$**)/MAO (MAO = methylalumoxane), at low temperature and high propene concentration ($T_p < 25$ °C, $[C_3H_6] > 1$ M, indicatively) the said condition is almost perfectly matched, and the polymers produced contain only low amounts of *mm* stereodefects (Chart 1A) due to occasional faults of propene enantioselection. With rising T_p and/or lowering $[C_3H_6]$, on the other hand, *site epimerization* (Scheme 2A), i.e., chain swinging between the two metal coordination sites, becomes competitive with monomer insertion, and increasing amounts of *m* stereodefects (Chart 1B) are generated as a result of consecutive insertions at the same active site ("skipped" insertions).[2,7]

In principle, growing chain epimerization may also contribute to this trend. However, by ^{2}H NMR we detected no scrambling of D in a sample of poly(propene-2-*d*) prepared at very low $[C_3H_5D]$ in the presence of $Ph_2C(Cp)(9\text{-fluorenyl})ZrCl_2$[2,8] (**2-Cl$_2$**, a homologue of **1-Cl$_2$** characterized by a higher stability and affording polymers of higher average molecular mass; see Supporting Information). This indicates[5] that for the said catalyst the effects of chain epimerization are negligible, which makes it simple to derive the analytical dependence of polymer stereoregularity on propene concentration.

The rates of propene insertion and of site epimerization are given by

$$v_{\text{ins}} = k_{\text{ins}}C^*[C_3H_6]$$
$$v_{\text{epi}} = k_{\text{epi}}C^*$$

where C^* is the concentration of active centers. Under conditions of negligible chain transfer, the stochastic probabilities of the two competing events are

$$P_{\text{ins}} = v_{\text{ins}}/(v_{\text{ins}} + v_{\text{epi}})$$
$$P_{\text{epi}} = v_{\text{epi}}/(v_{\text{ins}} + v_{\text{epi}}) = 1 - P_{\text{ins}}$$

and the fractional abundance of *r* diads in the polymer therefore is

$$\begin{aligned}[r] = [r°]P_{\text{ins}}^2 + (0.5 + [r°])P_{\text{ins}}P_{\text{epi}} + 0.5P_{\text{epi}}^2 &= \\ ([r°] - 0.5)P_{\text{ins}} + 0.5 &= \\ ([r°] - 0.5)\{[C_3H_6]/([C_3H_6] + k_{\text{epi}}/k_{\text{ins}})\} + 0.5 & \quad (1)\end{aligned}$$

where $[r°]$ is the upper limit of $[r]$ for $P_{\text{ins}} \to 1$ (i.e., in the absence of site epimerization).

Thus, $[r°]$ and $k_{\text{epi}}/k_{\text{ins}}$ for a given catalyst system at a given temperature can be calculated by interpolation of an experimental plot of $[r]$ vs $[C_3H_6]$ in terms of eq 1. Moreover, the difference in the activation parameters of monomer insertion and site epimerization can be estimated from the temperature dependence of $k_{\text{epi}}/k_{\text{ins}}$.

We applied this protocol to catalyst **2-Cl$_2$**, activated either with MAO or with $[HMe_2NC_6H_5][B(C_6F_5)_4]/Al(isobutyl)_3$ (**3**). For each system, we carried out three series of propene polymerizations in toluene at $T_p = 30$, 50, and 80 °C, varying $[C_3H_6]$ in the range 0.05−7 mol/L (see Experimental Section in the Supporting Information). The three sets of $([r], [C_3H_6])$ data points for **2-Cl$_2$**/MAO, along with the interpolating curves in terms of eq 1, are shown in Figure 1. All best-fit values of $[r°]$ and $k_{\text{epi}}/k_{\text{ins}}$ are given in Table 1 (entries 1−6).

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* Corresponding author. E-mail: busico@chemistry.unina.it.

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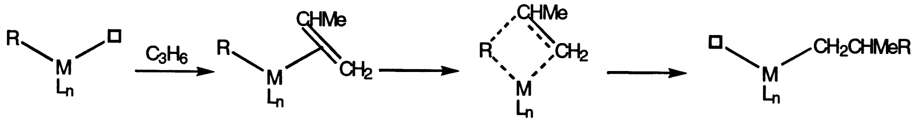
Scheme 1



Scheme 2

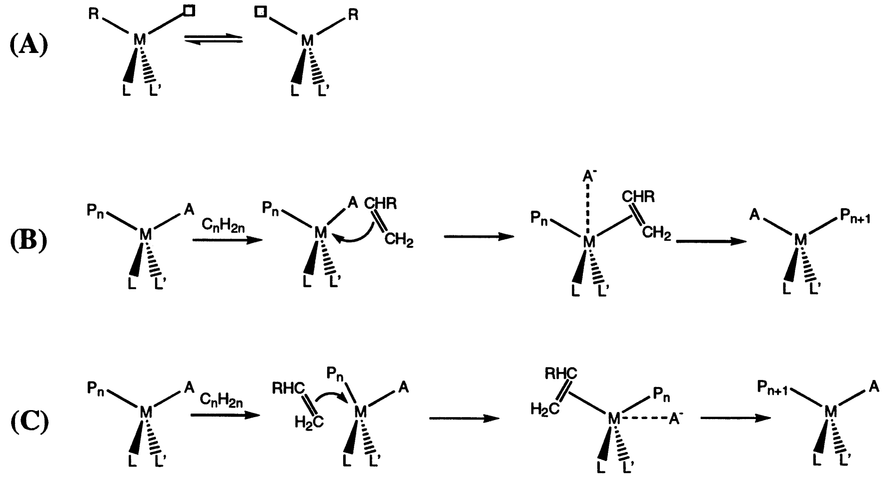
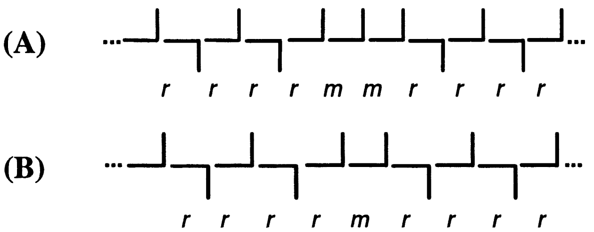


Chart 1



Very similar trends were observed for the two systems, with the expected[2,7] robust increase of k_{epi}/k_{ins} and slight decrease of $[r°]$ with increasing T_p.

Let us define now as σ and $1 - \sigma$ the probabilities that the monomer inserts with a given enantioface at the two enantiotopic active sites.[2b] It is easy to measure σ precisely by stochastic modeling of the ^{13}C NMR stereosequence distributions (see Supporting Information).[9] In the last column of Table 1, for each series of polymers we report the average value of $[r°]_{enantio} = \sigma^2 + (1 - \sigma)^2$, which represents the fraction of *r* diads formed in the hypothesis of ideal chain migratory propagation; the fact that this is practically coincident with $[r°]$ confirms that in the limit of $P_{ins} = 1$ (i.e., of negligible site epimerization) only *mm* stereodefects (Chart 1A) are left in the polymer.

The logarithm of the ratio of specific rates $k_{epi}/(k_{ins}[C_3H_6])$ at $[C_3H_6] = 1.0$ mol/L was then plotted against $1/T$, and the values of $\Delta E^{\#} = E^{\#}_{epi} - E^{\#}_{ins}$, and $\Delta S^{\#} = S^{\#}_{epi} - S^{\#}_{ins}$ ($E^{\#}$ = activation energy, $S^{\#}$ = activation entropy) were obtained as the slope and intercept at $1/T_p = 0$ of the straight line through the experimental points. For both systems, $\Delta E^{\#} = 11(1)$ kcal mol^{-1} and $\Delta S^{\#} = -28(1)$ cal K^{-1} mol^{-1}. Although absolute values of $E^{\#}_{ins}$ for C_s-symmetric *ansa*-zirconocenes are not known, for other classes of metallocenes in toluene they are typically in the range 10−15 kcal/mol;[2a,10] therefore, one can roughly estimate that $E^{\#}_{epi} \approx 20-25$ kcal/mol. This is much higher than theoretical estimates of chain "swinging" at naked metallocene cations (10−12 kcal/mol),[11−13] but close to experimental[14,15] and theoretical[11] values for model metallocene−alkyl ion couples. The necessary conclusion is that, despite their reputation of being "poorly coordinating", in toluene the anion of MAO and $[B(C_6F_5)_4]^-$ are "always" bound to the active cation. The same conclusion was recently reached by Babushkin and Brintzinger, based on pulsed field-gradient NMR measurements on Cp_2ZrMe_2/MAO.[16]

On the other hand, when we repeated the polymerization experiments with **2-Cl₂**/**3** in a more polar solvent (namely, bromobenzene) and analyzed the microstructural data, we ended up with $\Delta E^{\#} \approx 5$ kcal mol^{-1}, $\Delta S^{\#} \approx -8$ cal K^{-1} mol^{-1}. To the best of our knowledge, no experimental values of $E^{\#}_{ins}$ are available in bromobenzene, but an educated guess is that they are somewhat lower than in toluene.[11,17] This points to an $E^{\#}_{epi} < 15$ kcal/mol, which is not far from the aforementioned theoretical estimates for site epimerization at "naked" cations,[11−13] and indicates a substantial loosening of the ion couple in this solvent, giving reason for the much higher values of k_{epi}/k_{ins}—and hence for the much lower stereoselectivity—compared with those observed in toluene (Table 1, entries 7, 8 and 4, 5).

At this point, it is clear that the close proximity of the counterion to the active cation is mandatory for a regular chain migratory insertion mechanism. Although the two cocatalysts used in the present investigation performed almost identically in this respect, it seems likely that a different choice of cocatalyst can result in a different stereoselectivity; as a matter of fact, appreciable cocatalyst effects on the performance of **1-Me₂** have recently been reported by Marks et al.[14,15]

Entries 9−11 of Table 1 give the best-fit values of k_{epi}/k_{ins}, $[r°]$, and $[r°]_{enantio}$ as extracted by us, in the way just illustrated on our own data, from those of ref 15 for catalyst systems **1-Me₂**/$[(C_6H_5)_3C][B(C_6F_5)_4]$ (**4**), **1-Me₂**/$[(C_6H_5)_3C][FAl(2\text{-}C_6F_5C_6F_4)_3]$ (**5**), and **1-Me₂**/$B(C_6F_5)_3$ (**6**) at 60 °C. When comparing all results in the table, one should keep in mind that (a) catalyst precursors **2-Cl₂** and **1-Me₂** give rise to active cations of virtually identical enantioselectivity;[2] (b) cocatalyst **4** generates the same anion of **3** (i.e., $[B(C_6F_5)_4]^-$), but in

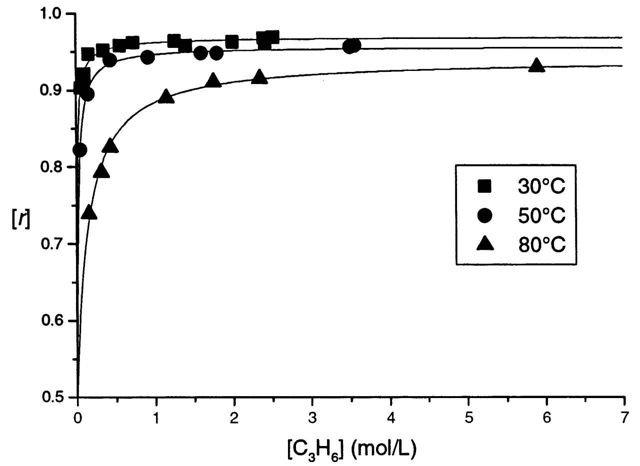


Figure 1. Fraction of *r* diads vs propene concentration in toluene for polypropylene samples produced with **2-Cl$_2$**/MAO at three different temperatures, with best-fit curves in terms of Eq 1.

Table 1. Values of k_{epi}/k_{ins}, [$r°$], and [$r°$]$_{enantio}$ (See Text) for Propene Polymerization in the Presence of Different Catalyst Systems

entry	catalyst/cocatalyst/ solvent/T_p	k_{epi}/k_{ins} (mol/L)	[$r°$] (eq 1)	[$r°$]$_{enantio}$ (^{13}C NMR)
1	**2-Cl$_2$**/MAO/toluene/30 °C	0.010(1)	0.968(2)	0.970
2	**2-Cl$_2$**/MAO/toluene/50 °C	0.022(1)	0.957(2)	0.963
3	**2-Cl$_2$**/MAO/toluene/80 °C	0.146(8)	0.940(4)	0.951
4	**2-Cl$_2$**/**3**/toluene/30 °C	0.017(1)	0.962(1)	0.964
5	**2-Cl$_2$**/**3**/toluene/50 °C	0.045(5)	0.948(5)	0.955
6	**2-Cl$_2$**/**3**/toluene/80 °C	0.21(1)	0.915(5)	0.935
7	**2-Cl$_2$**/**3**/bromobenzene/30 °C	0.34(3)	0.958(7)	0.965
8	**2-Cl$_2$**/**3**/bromobenzene/50 °C	0.57(8)	0.945(15)	0.960
9	**1-Me$_2$**/**4**/toluene/60 °C	0.14(1)	0.934(5)	0.946
10	**1-Me$_2$**/**5**/toluene/60 °C	0.0033(1)	0.940(1)	0.953
11	**1-Me$_2$**/**6**/toluene/60 °C	0.22(2)	0.879(7)	0.939

ref 15 it was introduced as a trityl rather than as a *N*,*N*-dimethylanilinium salt, and in the absence of Al(isobutyl)$_3$; (c) cocatalysts **5** and **6** lead to the formation of more coordinating anions (i.e., [FAl(2-C$_6$F$_5$C$_6$F$_4$)$_3$]$^-$ and [MeB(C$_6$F$_5$)$_3$]$^-$, respectively) than **3** and **4**.[14,15]

In our opinion, mainly three facts are notable:

(i) The value of k_{epi}/k_{ins} does not parallel the coordinating ability of the anion. Indeed, if it is true that, at similar T_p, k_{epi}/k_{ins} for **1-Me$_2$**/**5** is definitely lower than for **2-Cl$_2$**/**3** and **1-Me$_2$**/**4**, for **1-Me$_2$**/**6** instead it is much higher (entries 5, 9−11).

(ii) For a given system, the values of [$r°$] and [$r°$]$_{enantio}$ are *not* necessarily coincident. The most striking case is that of **1-Me$_2$**/**6**, for which at 60 °C we estimated [$r°$] = 0.879(7), [$r°$]$_{enantio}$ = 0.939.

(iii) Al(isobutyl)$_3$ and *N*,*N*-dimethylaniline have practically no effect on the stereoselectivity (compare entries 5 and 9, taking the different T_p into account).

A possible explanation to factual observations i and ii comes from recent results of quantum mechanical modeling of monomer insertion at metallocene cations, in which solvent and counterion effects were explicitly taken into account.[11] According to such studies, two main pathways for the incoming monomer to split the active ion couple are conceivable, depending on whether the approach is from the same side or from the opposite side with respect to the anion (Scheme 2, parts B and C).

It is important to realize that pathway C, which requires a smaller anion displacement than B,[11c] implies a "double" chain migration, and therefore ends up with the chain at the same coordination position. In the case of C_s-symmetry of the cation, this is indistinguishable, in terms of stereochemical consequences on the polymer, from a "skipped" insertion as defined before. Therefore, if this insertion path is competitive with that of Scheme 2B, *m* stereodefects continue to be generated even in the limit of $P_{ins} \rightarrow 1$. Most probably, this is what happens with [MeB(C$_6$F$_5$)$_3$]$^-$, possibly due to its relatively high coordinating ability coupled with the directional character of the B−(μ-Me)−Zr interaction.

In conclusion, highly syndiotactic propene polymerization in the presence of C_s-symmetric metallocene cations[2,7] is much less obvious than it may appear based on symmetry considerations alone. Effectively preventing the generation of *m* stereodefects requires the assistance of a counterion able to slow site epimerization more than monomer insertion, but also seconding chain-migratory insertion in such a way that the pathway of Scheme 2C is not competitive with that of Scheme 2B. It is remarkable that a good success in this delicate balance was achieved at the first attempt with MAO,[7] in turn serendipitously discovered.

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Supporting Information Available: Text giving the Experimental Section, Figure S1 showing the NMR spectrum of poly(propene-2-*d*), tables giving 150 MHz ^{13}C NMR stereosequence distributions of all polypropylene samples and results of their statistical analysis, and text and Figure S2 showing the application of eq 1 to the experimental data of ref 15. This material is available free of charge via the Internet at http://pubs.acs.org.

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