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Metallocene-Catalyzed Propene Polymerization: From Microstructure to Kinetics. 1. C_2-Symmetric *ansa*-Metallocenes and the "Trigger" Hypothesis

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ABSTRACT: A microstructural method for the determination of the reaction order with respect to the monomer in coordinated 1-alkene polymerizations is proposed. The method is applicable whenever enantioselective monomer polyinsertion competes with an *intramolecular* process introducing stereodefects of known and recognizable nature in the growing polymer chains at a rate independent of monomer concentration, [M] (e.g., chain or site epimerization for C_2-symmetric and C_s-symmetric *ansa*-metallocene catalysts, respectively). Indeed, in such cases, the stereoregularity of the polymer obtained at a given temperature results from the balance between the rates of the two competing processes, and is obviously a function of [M], because so is the rate of polyinsertion, $\langle v_p \rangle$. Therefore, from the way polymer stereoregularity changes with [M], the corresponding change of $\langle v_p \rangle$ can be inferred. Compared with the conventional macroscopic approach based on measurements of monomer consumption, the microstructural route is more reproducible, and allows one to discriminate between "authentic" and apparent higher-order polyinsertion rate laws. In this paper, in particular, we show that the "trigger" hypothesis invoked to explain the observed pseudo-second-order kinetics of propene polymerization promoted by C_2-symmetric *ansa*-metallocene catalysts is inconsistent with the experimental results and that an alternative explanation assuming first-order kinetics at catalytic species which interconvert between a propagating and a "resting" state is more plausible.

Introduction

The kinetics of Ziegler−Natta and related 1-alkene polymerizations[1,2] is still poorly understood, for a discoragingly high number of reasons:

(i) The catalytic species are extremely reactive, and easily deactivated by a variety of ubiquitous contaminants, including water and oxygen.

(ii) As a rule, and also due to point i, only a fraction of the transition metal species used as catalyst precursor becomes involved in catalysis, and all approaches proposed to now for the determination of active site concentrations (such as quenched-flow[3−5] and radiotagging[6,7] techniques) have serious drawbacks which make them potentially flawed.

(iii) Most catalysts show a decay of activity with time, which is often extensive and fast.[1,2a]

(iv) The polymerization process is highly exothermic, which easily results in a poor temperature control, particularly with heterogeneous systems.

(v) Heterogeneous catalysts always have several types of active species with different productivities and selectivities.[1] Homogeneous catalysts, in turn, may well have one single active species, but only in a few special cases are the two coordination sites involved in the reaction equivalent.[2]

(vi) With the only exception of ethene, a 1-alkene monomer can insert in a growing chain in (at least) four different modes, which results in an equal number of metal−alkyl species widely differing in reactivity.[8,9]

(vii) A variety of catalytic processes (including several pathways of chain transfer[1,2] and a number of isomerizations of the growing polymer chain[2,10,11] and/or of the catalytic species[2,12]) compete with monomer polyinsertion.

(viii) Catalyst productivity may depend, inter alia, on the concentration of the cocatalyst (usually an Al−alkyl species also used as a scavenger). For methylalumoxane-activated metallocene catalysts, in particular, this dependence can be dramatic (for reasons still waiting to be clarified).[2]

All this results in the fact that the so-called polymerization rate, v_p (i.e., the rate of monomer consumption) is a macroscopic parameter which, in addition to being poorly reproducible and time-dependent, represents almost invariably a complicated average over a wide distribution of active sites with unknown absolute and relative concentrations and as such is hard to interpret in molecular terms. Therefore, it is not surprising that most fundamental questions on the polymerization kinetics, including the nature of the rate-limiting step and the molecularity of monomer insertion, are still unanswered.

One of the most puzzling observations concerns the apparent reaction order with respect to the monomer. For a long time after the initial discovery of $TiCl_3$-based catalysts, it was found (assumed?) that in the rate law

$$\langle v_p \rangle = -d[M]/dt = \langle k_p \rangle C_p^*[M]^\alpha \qquad (1)$$

(where [M] and C_p^* are the concentrations of monomer and propagating chains, respectively) the value of the α-exponent is—reasonably—1.[1,13] Later observations, however, pointed out that this is not always the case. In the mid-1980s, for instance, Pino et al. measured α values up to 1.3 for propene polymerization with a number of $MgCl_2/TiCl_4$ supported "high-yield" catalysts.[14] Also moving from these findings, Ystenes proposed a mechanism according to which monomer insertion would be "triggered" by a second monomer molecule.[15] Much more recently, values of α close to 2

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have actually been reported for some of the new, well-defined homogeneous metallocene catalysts.[16] This prompted Prosenc et al. to investigate the "trigger" hypothesis theoretically for a model metallocene cation, and their DFT calculations did provide some basis for it, although with a number of caveats.[17]

On the other hand, less exotic explanations are well possible. In particular, it should be noted that eq 1 assumes that the (inevitable) occurrence of chain initiation and termination (transfer) processes has no effect on the propagation rate, which—however—cannot be taken for granted. According to Tait,[18] in addition to chain propagation (assumed to obey a first-order rate law)

$$\langle v_{\mathrm{p}}\rangle = -\mathrm{d}[\mathrm{M}]/\mathrm{d}t = \langle k_{\mathrm{p}}\rangle C_{\mathrm{p}}{}^*[\mathrm{M}] \tag{2}$$

the following reactions should also be considered:

•Chain transfer:

$$\langle v_{\mathrm{t,H}}\rangle = \langle k_{\mathrm{t,H}}\rangle C_{\mathrm{p}}{}^* \quad \text{(intramolecular } \beta\text{-H elimination)}$$

$$\langle v_{\mathrm{t,M}}\rangle = \langle k_{\mathrm{t,M}}\rangle C_{\mathrm{p}}{}^*[\mathrm{M}] \quad \text{(monomer-assisted } \beta\text{-H elimination)}$$

$$\langle v_{\mathrm{t,Al}}\rangle = \langle k_{\mathrm{t,Al}}\rangle C_{\mathrm{p}}{}^*[\mathrm{Al}]^{0.5} \quad \text{(chain transfer to the Al−alkyl)}$$

•Chain initiation:

$$\langle v_{\mathrm{i,H}}\rangle = \langle k_{\mathrm{i,H}}\rangle C_{\mathrm{i,H}}{}^*[\mathrm{M}] \quad \text{(into an initial Mt−H bond)}$$

$$\langle v_{\mathrm{i,M}}\rangle = \langle k_{\mathrm{i,M}}\rangle C_{\mathrm{i,M}}{}^*[\mathrm{M}] \quad \text{(into an initial Mt−C}_n\text{H}_{2n}\text{−H bond)}$$

$$\langle v_{\mathrm{i,Al}}\rangle = \langle k_{\mathrm{i,Al}}\rangle C_{\mathrm{i,Al}}{}^*[\mathrm{M}] \quad \text{(into an initial Mt−alkyl bond)}$$

Set

$$C^* = C_{\mathrm{p}}{}^* + \textstyle\sum_j C_{\mathrm{i},j}{}^*$$

(where C^* is the total concentration of transition metal species that can have catalytic activity, $C_{\mathrm{p}}{}^*$ the concentration of propagating ones, and $C_{\mathrm{i},j}{}^*$ that of transition metal species originating from the jth chain transfer process and waiting for the first monomer insertion in order to initiate a new chain), the stationary-state condition on $C_{\mathrm{p}}{}^*$

$$\mathrm{d}(C_{\mathrm{p}}{}^*)/\mathrm{d}t = 0$$

requires that

$$\textstyle\sum_j \langle v_{\mathrm{i},j}\rangle = \sum_j \langle v_{\mathrm{t},j}\rangle$$

and (plausibly) that

$$\langle v_{\mathrm{i,H}}\rangle = \langle k_{\mathrm{i,H}}\rangle C_{\mathrm{i,H}}{}^*[\mathrm{M}] = \langle v_{\mathrm{t,H}}\rangle = \langle k_{\mathrm{t,H}}\rangle C_{\mathrm{p}}{}^*$$

$$\langle v_{\mathrm{i,M}}\rangle = \langle k_{\mathrm{i,M}}\rangle C_{\mathrm{i,M}}{}^*[\mathrm{M}] = \langle v_{\mathrm{t,M}}\rangle = \langle k_{\mathrm{t,M}}\rangle C_{\mathrm{p}}{}^*[\mathrm{M}]$$

$$\langle v_{\mathrm{i,Al}}\rangle = \langle k_{\mathrm{i,Al}}\rangle C_{\mathrm{i,Al}}{}^*[\mathrm{M}] = \langle v_{\mathrm{t,Al}}\rangle = \langle k_{\mathrm{t,Al}}\rangle C_{\mathrm{p}}{}^*[\mathrm{Al}]^{0.5}$$

From this, one can immediately derive

$$\begin{aligned} C_{\mathrm{p}}{}^* = C^*/\{1 + \langle k_{\mathrm{t,H}}\rangle/(\langle k_{\mathrm{i,H}}\rangle[\mathrm{M}]) &+ \\ \langle k_{\mathrm{t,M}}\rangle/\langle k_{\mathrm{i,M}}\rangle &+ \langle k_{\mathrm{t,Al}}\rangle[\mathrm{Al}]^{0.5}/(\langle k_{\mathrm{i,Al}}\rangle[\mathrm{M}])\} \end{aligned} \tag{3}$$

Substituting $C_{\mathrm{p}}{}^*$ from eq 3 in eq 2 gives

$$\begin{aligned} \langle v_{\mathrm{p}}\rangle = \langle k_{\mathrm{p}}\rangle C_{\mathrm{p}}{}^*[\mathrm{M}] = \langle k_{\mathrm{p}}\rangle C^*[\mathrm{M}]^2/\{[\mathrm{M}] + \langle k_{\mathrm{t,H}}\rangle/\langle k_{\mathrm{i,H}}\rangle &+ \\ + \langle k_{\mathrm{t,M}}\rangle[\mathrm{M}]/\langle k_{\mathrm{i,M}}\rangle + \langle k_{\mathrm{t,Al}}\rangle[\mathrm{Al}]^{0.5}/\langle k_{\mathrm{i,Al}}\rangle\}& \end{aligned} \tag{4}$$

It is easy to realize that eq 4 simulates a second-order chain propagation law when

$$([\mathrm{M}] + \langle k_{\mathrm{t,M}}\rangle[\mathrm{M}]/\langle k_{\mathrm{i,M}}\rangle) \ll (\langle k_{\mathrm{t,H}}\rangle/\langle k_{\mathrm{i,H}}\rangle + \langle k_{\mathrm{t,Al}}\rangle[\mathrm{Al}]^{0.5}/\langle k_{\mathrm{i,Al}}\rangle) \tag{5}$$

whereas it reduces to a first-order kinetics when

$$([\mathrm{M}] + \langle k_{\mathrm{t,M}}\rangle[\mathrm{M}]/\langle k_{\mathrm{i,M}}\rangle) \gg (\langle k_{\mathrm{t,H}}\rangle/\langle k_{\mathrm{i,H}}\rangle + \langle k_{\mathrm{t,Al}}\rangle[\mathrm{Al}]^{0.5}/\langle k_{\mathrm{i,Al}}\rangle) \tag{6}$$

Intermediate conditions obviously result in apparent reaction orders between 1 and 2.

Conceptually similar kinetic schemes have been subsequently proposed, e.g. by Richardson et al.,[19] and more recently by Resconi et al.[20] The latter authors, in particular, postulated the existence of a catalyst "resting" state, not (necessarily) related with chain transfer and (re-) initiation, which would form from the propagating state at a rate, $\langle v_{\mathrm{f,rest}}\rangle$, independent of [M] but would then be returned to it by (slow) monomer insertion:

$$\langle v_{\mathrm{f,rest}}\rangle = \langle k_{\mathrm{f,rest}}\rangle C_{\mathrm{p}}{}^*$$

$$\langle v_{\mathrm{d,rest}}\rangle = \langle k_{\mathrm{d,rest}}\rangle C_{\mathrm{rest}}{}^*[\mathrm{M}]$$

This means that an additional, and possibly dominating, $\langle k_{\mathrm{f,rest}}\rangle/\langle k_{\mathrm{d,rest}}\rangle$ term should be added into eqs 3 and 4:

$$\begin{aligned} C_{\mathrm{p}}{}^* = C^*/\{1 + \langle k_{\mathrm{t,H}}\rangle/(\langle k_{\mathrm{i,H}}\rangle[\mathrm{M}]) + \langle k_{\mathrm{t,M}}\rangle/\langle k_{\mathrm{i,M}}\rangle &+ \\ + \langle k_{\mathrm{t,Al}}\rangle[\mathrm{Al}]^{0.5}/(\langle k_{\mathrm{i,Al}}\rangle[\mathrm{M}]) + \langle k_{\mathrm{f,rest}}\rangle/(\langle k_{\mathrm{d,rest}}\rangle[\mathrm{M}])\}& \end{aligned} \tag{3$'$}$$

$$\begin{aligned} \langle v_{\mathrm{p}}\rangle = \langle k_{\mathrm{p}}\rangle C_{\mathrm{p}}{}^*[\mathrm{M}] = \langle k_{\mathrm{p}}\rangle C^*[\mathrm{M}]^2/\{[\mathrm{M}] + \langle k_{\mathrm{t,H}}\rangle/\langle k_{\mathrm{i,H}}\rangle &+ \\ + \langle k_{\mathrm{t,M}}\rangle[\mathrm{M}]/\langle k_{\mathrm{i,M}}\rangle + \langle k_{\mathrm{t,Al}}\rangle[\mathrm{Al}]^{0.5}/\langle k_{\mathrm{i,Al}}\rangle &+ \\ \langle k_{\mathrm{f,rest}}\rangle/\langle k_{\mathrm{d,rest}}\rangle\}& \end{aligned} \tag{4$'$}$$

which makes the condition for (apparent) second-order kinetics (eq 5′ below)

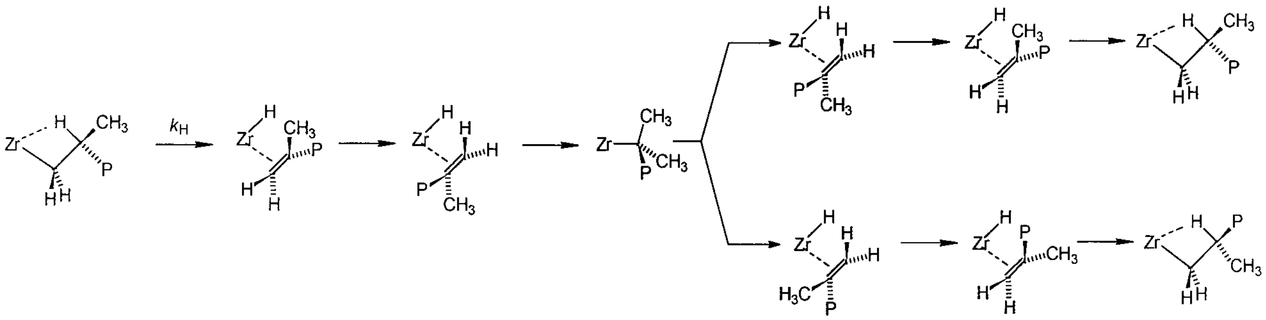
$$\begin{aligned} ([\mathrm{M}] + \langle k_{\mathrm{t,M}}\rangle[\mathrm{M}]/\langle k_{\mathrm{i,M}}\rangle) \ll& \\ (\langle k_{\mathrm{t,H}}\rangle/\langle k_{\mathrm{i,H}}\rangle + \langle k_{\mathrm{t,Al}}\rangle[\mathrm{Al}]^{0.5}/\langle k_{\mathrm{i,Al}}\rangle &+ \\ + \langle k_{\mathrm{f,rest}}\rangle/\langle k_{\mathrm{d,rest}}\rangle)& \end{aligned} \tag{5$'$}$$

more likely to be matched (compared with eq 5). For propene polymerization promoted by metallocene catalysts, it was tentatively proposed[20b] that the "resting" species be an α-branched Mt−polymeryl bond formed by growing chain isomerization,[10] although very many alternatives can be conceived as well.

Even more recently, Schaper et al. analyzed propene polymerization data for a number of *ansa*-zirconocene catalysts making use of a genetic algoritm[21] and concluded not only that one or more catalyst "resting" states need to be included in the reaction scheme in order to reproduce the experimental rate law but also that the possibility of monomer "trigger" cannot be ruled out.

To solve the impasse, we propose a *microstructural* approach to the problem, applicable to cases in which

Scheme 1



enantioselective 1-alkene polyinsertion competes with an *intramolecular* process introducing stereodefects of known and recognizable nature in the growing polymer chains, at a rate independent of monomer concentration. For propene polyinsertion, such a process can be, e.g., chain epimerization, which generates *rr*-type stereodefects in the isotactic chains growing at C_2-symmetric *ansa*-zirconocene species,[10] or site epimerization at C_s-symmetric *ansa*-zirconocene species, originating *m*-type stereodefects in growing syndiotactic chains.[2,12] At each given temperature, the stereoregularity of the polymer obtained results from the balance between the rates of the two competing processes and is obviously a function of [M], because so is the rate of polyinsertion. Therefore, from the way polymer stereoregularity changes with [M], the corresponding change of $\langle v_p \rangle$ can be inferred.

In our opinion, this approach is highly advantageous, compared with more conventional ones, for two main reasons:

Discrimination between an authentic and an apparent higher-order polyinsertion rate law is possible. Indeed, if the "trigger" hypothesis[15] is correct, one has to expect that polymer stereoregularity will be a function of $[M]^\alpha$, whereas a linear dependence should always be observed, also when $\alpha > 1$ in eq 1, in case the (apparent) higher-order kinetics has to be traced to the co-presence of "resting" and propagating transition metal species (eqs 3′−5′).[18,20]

Determining the degree of stereoregularity of a poly(1-alkene) sample by means of ^{13}C NMR[22] is much more reliable and reproducible than measuring a polymerization rate from monomer consumption. In particular, properly run independent quantitative spectra of a given polypropylene sample are virtually superimposable, once the accumulation time is long enough. Moreover, catalyst deactivation phenomena, or possible changes of active site concentration (C^*) with changing [M], are not expected to be influent on the microstructure of the polymer produced.[10f]

In the present paper, we report the results of the proposed method, as applied to isotactic propene polymerization promoted by two representative C_2-symmetric *ansa*-zirconocenes, for which it had been reported that α is close to 2 in eq 1.[16] In a subsequent paper, we will present similar results for syndiotactic propene polymerization in the presence of a C_s-symmetric *ansa*-zirconocene catalyst; in this second case, we will show how the microstructural approach can also be used to measure differences in the activation parameters for the catalytic processes in competition (in the considered case, polyinsertion and site epimerization), with important mechanistic implications.[23]

Results and Discussion

For this investigation, we chose two well-known isotactic-selective Si-bridged zirconocenes with C_2-symmetry—namely, *rac*-$Me_2Si(2\text{-}Me\text{-}1\text{-}indenyl)ZrCl_2$[24] (**I**) and *rac*-$Me_2Si(2\text{-}Me\text{-}benz[e]\text{-}1\text{-}indenyl)ZrCl_2$[16b] (**II**)—among the very few for which reliable investigations of catalyst productivity as a function of propene concentration have been reported in the literature, and an apparent reaction order α close to 2 has been determined. For **I**/MAO (MAO = methylalumoxane), in particular, Wester et al. measured α = 1.7 at 80 °C and 1.0 bar ≤ $p(C_3H_6)$ ≤ 2.5 bar;[16a] according to Stehling et al., for **II**/MAO, it is also α = 1.7 at 40 °C and 1.0 bar ≤ $p(C_3H_6)$ ≤ 5.0 bar.[16b]

For all known bis(indenyl) C_2-symmetric *ansa*-zirconocene catalysts, the process of isotactic propene polyinsertion competes with a concurrent reaction of epimerization of the growing chain, which consists of the racemization of a last-inserted monomeric unit, most probably according to the mechanism shown in Scheme 1.[10] This generates *rr*-type stereodefects, which sum up to those deriving from monomer insertion with the "wrong" enantioface.

The rate of chain epimerization, $\langle v_{epim} \rangle$ is given by[10f]

$$\langle v_{epim} \rangle = \langle k_{epim} \rangle C_p^* \qquad (7)$$

Therefore, if chain transfer and (re-) initiation processes are not considered (which is licit when the analysis is restricted to inner chain microstructure), the probability that, under certain experimental conditions, a given monomeric unit was not subjected to epimerization can be expressed as[10f]

$$P_{ins} = \langle k_{ins} \rangle [M]^\beta / (\langle k_{ins} \rangle [M]^\beta + \langle k_{epim} \rangle) = [M]^\beta / ([M]^\beta + \langle k_{epim} \rangle / \langle k_{ins} \rangle) \qquad (8)$$

where β is the "true" reaction order of monomer insertion, intended as an elementary process (which explains why, in eq 8, we used the symbols $\langle k_{ins} \rangle$ and β, rather than $\langle k_p \rangle$ and α of eq 1).

The probability that both monomeric units of a given diad did not undergo epimerization is obviously P_{ins}^2. From this, it follows immediately that the fraction of *meso* diads in the polymer, [*m*] (far from the chain ends), depends on [M] according to the following simple expression[10f]

$$[m] = [m^\circ] P_{ins}^2 + 0.5(1\text{-}P_{ins}^2) = ([m^\circ] - 0.5) P_{ins}^2 + 0.5 = ([m^\circ] - 0.5)\{[M]^\beta / ([M]^\beta + \langle k_{epim} \rangle / \langle k_{ins} \rangle)\}^2 + 0.5 \qquad (9)$$

Table 1. ^{13}C NMR Fraction of *meso* Diads, [*m*], as a Function of Propene Concentration, [C_3H_6], for Polypropylene Samples Prepared at 80 °C in the Presence of Catalyst System I/MAO[a,b]

sample no.	[C_3H_6] (M)	[*m*]
1	0.062(6)	0.72(1)
2	0.098(6)	0.79 (1)
3	0.118(6)	0.78(1)
4	0.151(8)	0.82(1)
5	0.193(8)	0.85(2)
6	0.34(3)	0.91(1)
7	0.45(3)	0.908(4)
8	0.67(3)	0.931(6)
9	1.48(3)	0.949(6)
10	2.24(3)	0.956(9)
11	2.41(3)	0.960(4)
12	3.72(17)	0.959(8)

[a] [Zr] = 1.0×10^{-6} to 5.0×10^{-5} M; [Al]/[Zr] = $(3-20) \times 10^3$. [b] Experimental uncertainty on last significant digit(s) in parentheses.

Table 2. ^{13}C NMR Fraction of *meso* Diads, [*m*], as a Function of Propene Concentration, [C_3H_6], for Polypropylene Samples Prepared at 80 °C in the Presence of Catalyst System II/MAO[a,b]

sample no.	[C_3H_6] (M)	[*m*]
1	0.050(17)	0.82(2)
2	0.101(17)	0.89(2)
3	0.165(6)	0.91(1)
4	0.221(17)	0.92(1)
5	0.28(3)	0.924(2)
6	0.39(3)	0.940(6)
7	0.56(3)	0.953(2)
8	0.56(3)	0.95(1)
9	0.67(3)	0.960(6)
10	1.37(6)	0.962(4)
11	2.35(6)	0.970(4)

[a] [Zr] = $(1-5) \times 10^{-6}$ M; [Al]/[Zr] = 1.5×10^4. [b] Experimental uncertainty on last significant digit(s) in parentheses.

where [m^o] is the limiting value of [*m*] for $P_{ins} \rightarrow 1$ (i.e., under conditions in which the rate of chain epimerization is negligible compared with that of monomer insertion, and polymer stereoregularity is only dependent on catalyst enantioselectivity).

Therefore, from ^{13}C NMR measurements of [*m*] on a series of polymers prepared with a certain catalyst at variable [M] (under otherwise identical experimental conditions), one can calculate in terms of eq 9 the best-fitting values of the adjustable parameters [$m°$] (if not known independently), $\langle k_{epim}\rangle/\langle k_{ins}\rangle$, and β.

This is what we did for the two investigated zirconocenes. We chose to operate at 80 °C, a temperature at which the effect of growing chain epimerization on the stereoselectivity is appreciable up to comparatively high [M]. We explored the whole range of [M] from virtually 0 (actually, 0.03 mol/L in toluene, below which we were unable to achieve an accurate propene pressure control) up to 3−4 mol/L (above which our temperature control became problematic). Upon doing this, we found it impossible to keep a number of experimental parameters at fixed values, as would have been desirable. In particular, the concentrations of Zr and Al, as well as the polymerization time, had to be adjusted in order to result in polymerization rates compatible with a temperature control within ±0.5 °C and in enough product for the microstructural characterization. In consequence, we could not make use of polymerization yields to extract trends of average catalyst productivity vs [M] (which was however out of our scope). On the other hand, in previous investigations[10a,f,g] we had already noted that, at least in the case of C_2-symmetric *ansa*-zirconocene catalysts, polymer stereoregularity at fixed [M] is practically insensitive to changes in [Zr] and [Al] over wide ranges (5×10^{-6} M ≤ [Zr] ≤ 5×10^{-4} M; 0.025 M ≤ [Al] ≤ 0.25 M), even when catalyst productivity strongly depends on them. This finding is not trivial, and suggests that the said dependence should be traced to C_p*, rather than to $\langle k_p\rangle$ ($\langle k_{ins}\rangle$); preliminary quenched-flow investigations performed in our laboratory seem to be consistent with such interpretation.[25]

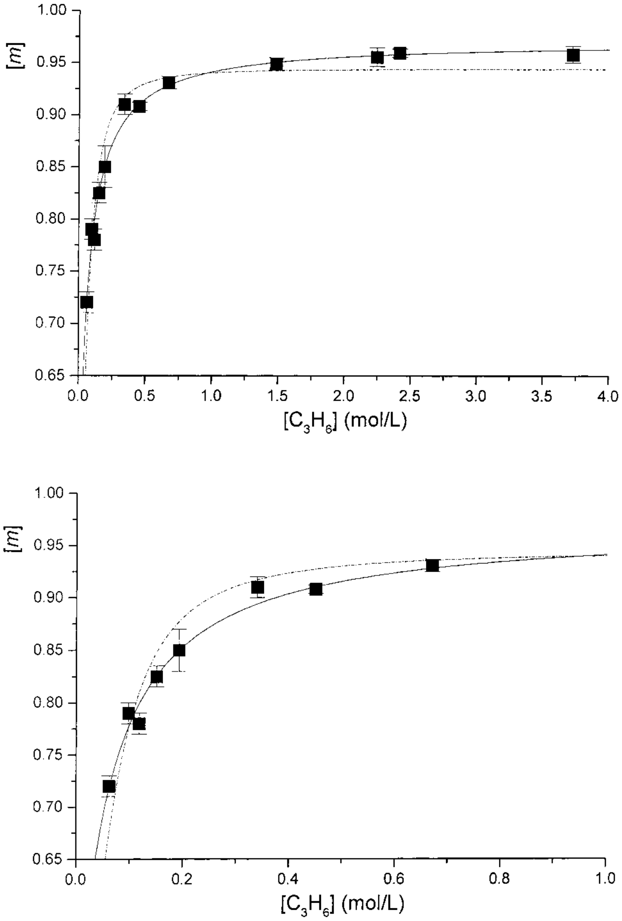


Figure 1. Fraction of *meso* diads, [*m*], vs propene concentration, [C_3H_6], for polypropylene samples prepared at 80 °C in the presence of catalyst system **I**/MAO: (top) complete plot; (bottom) expansion in the region 0−1 M. Continuous and dashed best-fitting curves correspond to minimization under cases a and b, respectively (see text).

Tables 1 and 2 list the polymerization runs carried out for the two catalyst systems, along with the [*m*] values measured by ^{13}C NMR on the polymers obtained. The corresponding plots of [*m*] vs [M] are given in Figures 1 and 2. In each plot, two best-fitting curves are shown, corresponding to the following two cases: (a) all three adjustable parameters in eq 9 were optimized (continuous curve); (b) only [$m°$] and $\langle k_{epim}\rangle/\langle k_{ins}\rangle$ were optimized, whereas β was imposed to coincide with the literature value of the apparent reaction order α in eq 1.

We are well aware that the comparison is delicate and that appreciable differences between the two fits can be expected mainly at low [M], where the function is steeper (and more stringent is the need for an extremely accurate reaction control).[26] In our opinion, however, the number of data points and their experimental accuracy are high enough to draw significant conclusions. As a

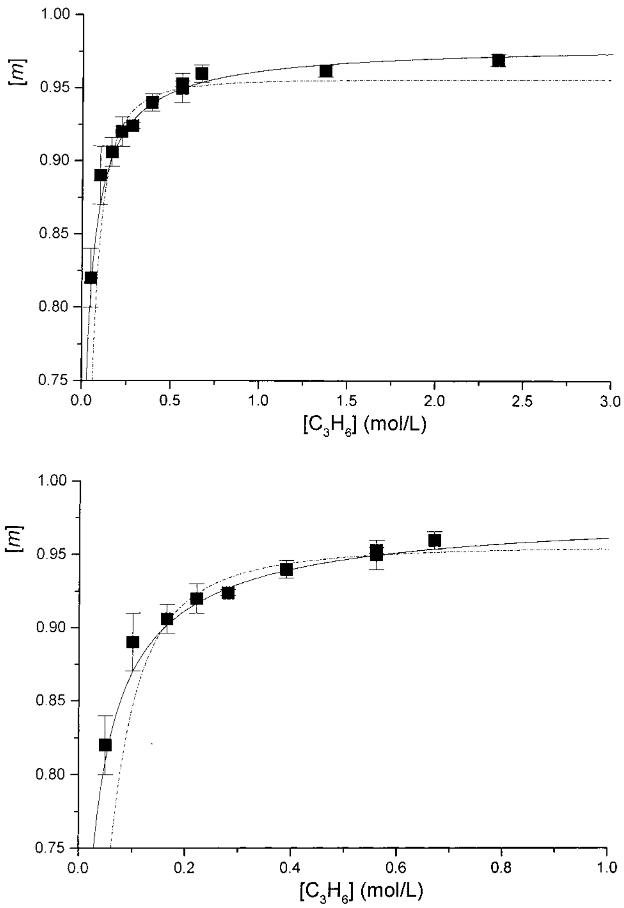


Figure 2. Fraction of *meso* diads, [*m*], vs propene concentration, [C_3H_6], for polypropylene samples prepared at 80 °C in the presence of catalyst system **II**/MAO: (top) complete plot; (bottom) expansion in the region 0−1 M. Continuous and dashed best-fitting curves correspond to minimization under cases a and b, respectively (see text).

Table 3. Best-Fit Values[a] of the Adjustable Parameters in Eq 9 for the Experimental Data in Tables 1 and 2 (See Text) and Corresponding Values of the χ_r^2 Function

catalyst system	β	$\langle k_{epim}\rangle/\langle k_{ins}\rangle(M^{\beta})$	[m°]	χ_r^2
I/MAO	0.94(7)	0.034(6)	0.972(6)	0.99
	1.7[b]	0.0052(7)	0.945(7)	8.5
II/MAO	0.80(12)	0.023(7)	0.984(7)	1.2
	1.7[b]	0.0030(8)	0.957(5)	9.1

[a] Standard deviation (σ) in parentheses. [b] Imposed (see text).

matter of fact, already on inspection of the plots it can be realized that case b results in a much worse fit. A quantitative confirmation comes from the values of the reduced-χ^2 function reported in Table 3: indeed, for each catalyst system these are 1 order of magnitude lower in case a than in case b, and in the former case, they are ≈1, as they should be for a "good" model.

In the same Table 3, we also give the best-fit values of the three (case a)) or two (case b)) adjustable parameters. *What is crucial to note for this investigation is that, in case a, β turned out to be very close to 1* (actually, lower than 1 by roughly 1σ for catalyst **I**, by roughly 2σ for catalyst **II**). *Therefore, we conclude that the rate of monomer insertion has a first-order dependence on [M], and that the "trigger" hypothesis[15] is not consistent with our data.* Conversely, an interpretation of the apparent second-order polymerization kinetics[16] in terms of eqs 3′−5′[18,20] may well hold.

The best-fit values of [m°] and $\langle k_{epim}\rangle/\langle k_{ins}\rangle$ in Table 3 also deserve a comment. For each catalyst system, largely different $\langle k_{epim}\rangle/\langle k_{ins}\rangle$ ratios—both numerically and dimensionally—were obtained under cases a and b, but this is mainly due to the different rate law used for monomer insertion. More interesting, instead, is the fact that the limiting stereoselectivity was also found to depend slightly on the choice of the minimization criterium and that for each catalyst a higher [m°] was estimated in case a than in case b. Looking at the plots in Figures 1 and 2, it can be seen that, at 80 °C, chain epimerization lowers appreciably polymer stereoregularity up to fairly high [M] and that the true catalyst enantioselectivity can only be measured by extrapolation in terms of eq 9. The result obviously depends on the rate law of monomer insertion; in particular, setting $\beta = \alpha$ (case b)) leads one to underestimate [m°].

In conclusion, we believe that the microstructural approach introduced in the present paper is an useful tool for investigating the kinetics of isotactic propene polymerization promoted by C_2-symmetric *ansa*-metallocene catalysts. In the second part of this series, we will show how the approach can be extended successfully to syndiotactic propene polymerization in the presence of C_s-symmetric *ansa*-zirconocenes, and aimed at investigating additional important mechanistic features, such as—in particular—the effect of catalyst/cocatalyst interaction on the dynamics of the catalytic species.

Experimental Section

rac-$Me_2Si(2\text{-}Me\text{-}1\text{-}indenyl)_2ZrCl_2$ was purchased from Boulder Scientific Co.; a sample of *rac*-$Me_2Si(2\text{-}Me\text{-}benz[e]\text{-}1\text{-}indenyl)_2ZrCl_2$ was received from Prof. H. H. Brintzinger (Universität Konstanz).

All polymerization experiments were carried out in a 2 L magnetically stirred stainless steel reactor (Brignole AU-2), equipped with a glass vial holder-breaker. Dry toluene (Aldrich, 0.5 L) and MAO (Witco GmbH, 10 wt % solution in toluene) were introduced into the reactor, which was thermostated at 80 °C and pressurized with propene at a given partial pressure.[27] The reaction was started by breaking a glass vial containing the appropriate amount of solid catalyst (previously sealed under argon in a Vacuum-Atmospheres glovebox), and allowed to proceed at constant propene concentration, making use of an electronic pressure controller (Brooks model 5866-E) mounted on the feeding line. In case of polymerization runs performed at [C_3H_6] < 0.3 M, the composition of the gas phase was also monitored by on-line Gas-Chromatographic analysis. Catalyst and cocatalyst concentrations were adjusted in such a way that monomer conversion (measured on-line with a Brooks 5850-E mass-flowmeter) never exceeded 1.0 g/min; this enabled us to achieve a temperature control of the liquid phase within ±0.5 °C. After an appropriate time, the polymerization was stopped by quickly venting the reactor. The polymer was coagulated with acidified methanol, filtered, and vacuum-dried.

Quantitative ^{13}C NMR spectra were recorded with a Varian VXR 200 spectometer operating at 50.3 MHz, on 100 mg/mL polymer solutions in tetrachloroethane-1,2-d_2 at 100−120 °C. Conditions: 5 mm probe; 76° pulse; acquisition time, 1.2 s; relaxation delay, 1.2 s; 10−15K transients. Peak integration was carried out by means of full simulation, with the SHAPE2000 software package.[28] The fractions of *meso* diads were evaluated as explained in ref 10f; the confidence intervals were estimated using the Monte Carlo simulation routine of the CONFSTAT suite (Ver. 2.3 for Windows),[29] accepting all solutions of the enantiomorphic-sites model with a value of the χ_r^2 function up to 1.2 times that at the absolute minimum.

The best-fit of the experimental data in Tables 1 and 2 on the basis of eq 9 was carried out with the curve-fitting routine of the Microcal Origin (Ver. 5.0) software package.

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