A Possible Interpretation of the Nonlinear Propagation Rate Laws for Insertion Polymerizations: A Kinetic Model Based on a Single-Center, Two-State Catalyst

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ABSTRACT: A kinetic model for chain propagation that can account for reaction orders higher than one on monomer concentration, observed for several insertion polymerizations, is discussed. This model is based on the presence of a "single-center, two-state catalyst" system, where the slower state is of lower energy and the interconversion rate between the two states is intermediate between the fast and slow propagation rates. This kinetic model fits available experimental data on polymerization rates, as a function of propene concentration, in the presence of zirconocene catalysts. Different possibilities for the chemical nature of the two catalyst states are discussed.

Introduction

In catalytic olefin polymerization the propagation rate (that is catalyst activity) is dependent on monomer concentration, provided that the transition metal−olefin complex is not the resting state, and each elementary insertion step at a given active site must obey the simple relationship

$$R_p = k_p[C][M] \qquad (1)$$

where [C] is the concentration of active sites and [M] is the concentration of the monomer.

However, the reaction order on monomer concentration has been reported to be higher than 1 for several catalytic systems for propene,[1−5] ethene,[5] styrene,[6] and diene[7] polymerizations:

$$R_p = k_p[C][M]^n \quad (1 < n < 2)$$

As for propene polymerizations by zirconocenes,[1−3] all indirect reasons, such as mass- or heat-transfer limitations, have been ruled out by careful experiments by Mülhaupt and co-workers,[3] who pointed out that "equilibria involving the active species are responsible for this effect" and that "propene might be involved in an equilibrium between dormant and active catalyst sites". Moreover, secondary (2,1) insertions cannot be held responsible for this "overreaction" because this is observed also for the highly regiospecific $Me_2C(Cp)(Flu)ZrCl_2$ catalyst,[1,2] and the total amount of secondary units (including terminations after a secondary unit insertion) in the case of the *rac*-[ethylenebis(1-indenyl)]$ZrCl_2$ appears to be constant with propene concentration.[8]

To account for the reaction order higher than the first, some kinetic models assuming reaction intermediates presenting the coordination to the catalytic metal center of two monomer molecules have been proposed.[5,9]

In the present paper, a kinetic model for chain propagation that can account for the reaction order higher than the first, without the need of invoking double monomer coordination, is proposed. The possible validity of this model for propene polymerization by stereospecific zirconocenes has been tested by comparison with published experimental data.

Polymerization Activity

The inconsistency between the experimental activity/monomer concentration dependence (apparently nonlinear) and eq 1 (linear) can be overcome by assuming that, in the steady state, a catalytic center has two active states which differ in either their monomer insertion or coordination rates, that is, having two different propagation rate constants, a faster state, C_{fast},with the propagation rate constant for primary insertion $k_{p,fast}$ and a slower one, C_{slow},with the propagation rate constant for primary insertion $k_{p,slow}$. Each state inserts a monomer according to eq 1, and the overall propagation rate law is

$$R_p = k_{p,fast}[C_{fast}][M] + k_{p,slow}[C_{slow}][M] \qquad (2)$$

Without specifying the nature of the two different catalytic states, but assuming that their interconversion does not involve the monomer and that the monomer insertion transforms a slow center into a fast one, a general kinetic scheme can be written (see Scheme 1), where k_p are the rate constants for primary propagation (monomer coordination followed by insertion), $k_{f\to s}$ and $k_{s\to f}$ indicate the rates of interconversion between the two states, and n and $n + 1$ indicate the number of monomeric units inserted in the growing chain at the active center.

In Scheme 1 the propagation constant of each center is considered independent from the degree of polymerization. Hence, in the following discussion we assume

$$[C_{fast}] = \sum_{n=1}^{\infty}[C_{fast,n}] \quad \text{and} \quad [C_{slow}] = \sum_{n=1}^{\infty}[C_{slow,n}]$$

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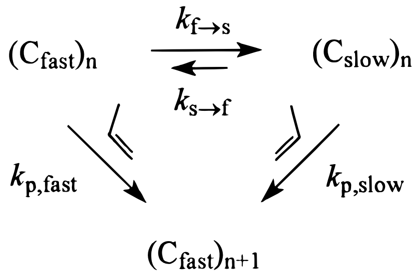
Scheme 1



For the sake of simplicity, as often assumed for chain polymerization mechanism, the contributions to the polymerization rate from the initiation reactions have been neglected.

It is also worth noting that the slow state of Scheme 1 is not necessarily a resting state, and its propagation rate constant is not assumed to be in absolute slow but only slower than the propagation rate constant of the faster one.

If the steady-state approximation is applied to C_{slow} or to C_{fast}

$$k_{f\to s}[C_{fast}] = k_{s\to f}[C_{slow}] + k_{p,slow}[C_{slow}][M] \qquad (3)$$

then

$$\frac{[C_{slow}]}{[C_{fast}]} = \frac{k_{f\to s}}{k_{s\to f} + k_{p,slow}[M]} \qquad (4)$$

It is apparent that, unless the conversion of the slow center into fast center is much faster than the propagation at the slow center ($k_{s\to f} \gg k_{p,slow}[M]$), the concentration of the slow centers will increase by reducing monomer concentration.

If [C] is the overall concentration of the active centers,

$$[C_{fast}] + [C_{slow}] = [C] \qquad (5)$$

then

$$[C_{fast}] = [C]\frac{k_{s\to f} + k_{p,slow}[M]}{k_{f\to s} + k_{s\to f} + k_{p,slow}[M]} \qquad (6)$$

and

$$[C_{slow}] = [C]\frac{k_{f\to s}}{k_{f\to s} + k_{s\to f} + k_{p,slow}[M]} \qquad (7)$$

and

$$\frac{R_p}{[C]} = \frac{\left(k_{f\to s} + \frac{k_{p,fast}k_{s\to f}}{k_{p,slow}}\right)[M] + k_{p,fast}[M]^2}{\frac{k_{f\to s} + k_{s\to f}}{k_{p,slow}} + [M]} \qquad (8)$$

Hence, for the kinetic Scheme 1, the propagation rate law is of the kind

$$\frac{R_p}{[C]} = \frac{A[M] + k_{p,fast}[M]^2}{B + [M]} \qquad (9)$$

where A and B are apparent constants, composed of combinations of kinetic constants. Of course, only the concentration of the catalytic metal C_{Mt} can be easily known, and

$$\frac{R_p}{[C]} = \frac{R_p}{\alpha C_{Mt}}$$

where α is the fraction of metal atoms that are active in the polymerization.

It is worth noting that eq 8 converts to the first reaction order for $k_{s\to f} \geq k_{f\to s}$, or $k_{p,slow}[M] \gg k_{f\to s}$, $k_{s\to f}$, for which $R_p \approx k_{p,fast}[C][M]$.

On the other hand, eq 8 approaches the second reaction order, $R_p \approx k_{p,fast}[C][M]^2$, when $k_{p,fast}[M] \gg k_{f\to s} \gg k_{p,slow}[M] \gg k_{s\to f}$.

Hence, eq 8 corresponds to a reaction order higher than 1 on monomer concentration for $k_{p,fast}[M] > k_{f\to s} > k_{p,slow}[M] > k_{s\to f}$, that is, when the slower state of the catalytic center is of lower energy with respect to the faster one, and the interconversion rate between the fast and the slow state is intermediate between the fast and the slow chain propagation rates.

A propagation rate law, formally equal to eq 9, is derived in Appendix 1 for a more general kinetic scheme including reversible monomer coordinations to catalytic centers in a fast or a slow state and irreversible monomer insertions starting from alkene-bound intermediates.

The fitting of experimental activity data with eq 9 allows, in favorable cases, to determine $\alpha k_{p,fast}$ (or $k_{p,fast}$ in the limit $\alpha = 1$) as well as the apparent kinetic constants αA (A in the limit $\alpha = 1$) and B. On the basis of these values, it is possible to determine the kinetic constant ratios:

$$\frac{k_{f\to s}}{k_{p,slow}} = \frac{Bk_{p,fast} - A}{k_{p,fast} - k_{p,slow}/\alpha} \approx B - A/k_{p,fast} \qquad (10)$$

$$\frac{k_{s\to f}}{k_{p,slow}} = B - \frac{k_{f\to s}}{k_{p,slow}} \approx A/k_{p,fast} \qquad (11)$$

From these kinetic constant ratios, the fractions of the centers in the fast and in the slow state can be determined. In fact, from eqs 6 and 7

$$X_{fast} = \frac{[C_{fast}]}{[C]} = \frac{\frac{k_{s\to f}}{k_{p,slow}} + [M]}{\frac{k_{s\to f}}{k_{p,slow}} + \frac{k_{f\to s}}{k_{p,slow}} + [M]} \qquad (12)$$

$$X_{slow} = \frac{[C_{slow}]}{[C]} = \frac{\frac{k_{f\to s}}{k_{p,slow}}}{\frac{k_{s\to f}}{k_{p,slow}} + \frac{k_{f\to s}}{k_{p,slow}} + [M]} \qquad (13)$$

Moreover, since the limiting upper value of $k_{f\to s}$ is A (see eqs 8 and 9), an estimate of the limiting upper value for $k_{p,slow}$ can be obtained from eq 10: $(k_{p,slow})_{up} \approx (k_{f\to s})_{up}/(B - A/k_{p,fast}) = A/(B - A/k_{p,fast})$.

For instance, for the case of the syndiospecific catalytic system $Me_2C(Cp)(Flu)ZrCl_2$/MAO,[2] by assuming $\alpha = 1$ and by weighting the experimental data with the function $1/Y = C_{Zr}/R_p$ (curve fitting b of Figure 1), it has been found that $A = 170$ s^{-1}, $B = 7.12$ mol/L, $k_{p,fast} = 189$ L/(mol s), $k_{f\to s}/k_{p,slow} \approx 6$ mol/L, $k_{s\to f}/k_{p,slow} \approx 0.89$ mol/L, and $(k_{p,slow})_{up} \approx 27$ L/(mol s).

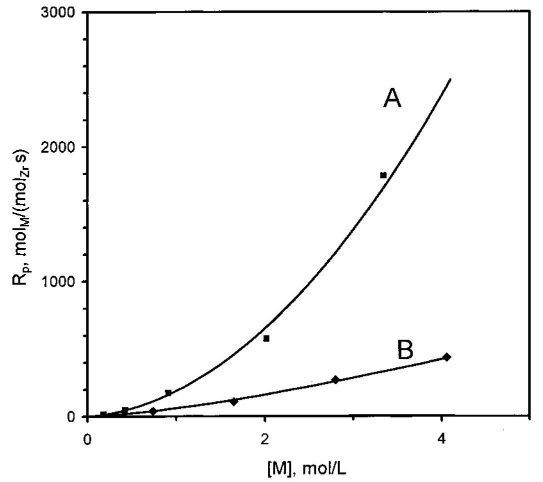


Figure 1. (A) Activity of the $Me_2Si(2\text{-}Me\text{-}Benzind)_2ZrCl_2$/MAO catalyst; data from ref 3 (■) and best fit from eq 9. (B) Activity of the $Me_2C(Cp)(Flu)ZrCl_2$/MAO catalyst; data from ref 2 (◆) and best fit from eq 9.

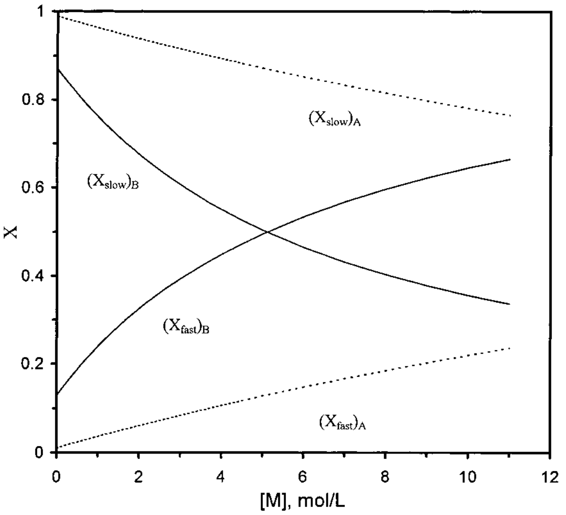


Figure 2. Fraction of catalytic centers in the fast state (X_{fast}) and in the slow state (X_{slow}) plotted as a function of monomer concentration. They have been calculated on the basis of eqs 12 and 13 by assuming the kinetic constants derived for a syndiospecific (solid lines) and an isospecific (dashed lines) zirconocene based catalytic systems. In the latter case, as an example, $k_{p,fast}$ has been assumed equal to 5000 mol/(L s) (see text).

The X_{fast} and X_{slow} values calculated by assuming the two kinetic constant ratios reported above are plotted in Figure 2, as a function of [M]. It is apparent that in the framework of our model the fraction of the slow state increases by decreasing monomer concentration.

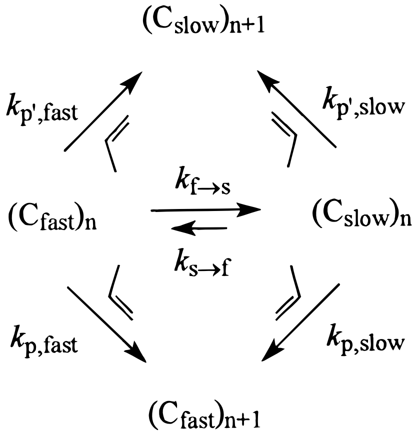
For the case of the isospecific catalytic system $Me_2Si(2\text{-}Me\text{-}Benzind)_2ZrCl_2$/MAO,[3] interpolations of the available experimental data by eq 9 show that $B \gg [M]$, that is, $(k_{f\to s} + k_{s\to f}) \gg k_{p,slow}$, and eq 9 is reduced to

$$R_p/[C] = (A/B)[M] + (k_{p,fast}/B)[M]^2 \qquad (14)$$

In particular, by weighting the experimental data with the function $1/Y = C_{Zr}/R_p$ (curve fitting a of Figure 1), the interpolation by eq 14 gives

$$k_{p,fast}/B = k_{p,fast}k_{p,slow}/(k_{f\to s} + k_{s\to f}) = 135\ L^2/(mol^2\ s) \qquad (15)$$

Scheme 2



showing that $k_{p,fast} \gg (k_{f\to s} + k_{s\to f})$ and $A/B = (k_{f\to s}k_{p,slow} + k_{s\to f}k_{p,fast})/(k_{f\to s} + k_{s\to f}) = 55$ L/(mol s) $\approx k_{p,fast}k_{s\to f}/(k_{f\to s} + k_{s\to f})$. Hence, $k_{f\to s}/k_{p,slow} \approx k_{p,fast}/135$. $(A/B)/k_{p,fast}/B = 55/135$ mol/L $\approx k_{s\to f}/k_{p,slow}$, and in summary, for this isospecific system

$$k_{p,fast} \gg k_{f\to s} \gg k_{p,slow} \approx 2.5k_{s\to f} \qquad (16)$$

The X_{fast} and X_{slow} values calculated for this isospecific catalytic system, on the basis of eqs 12 and 13 by assuming as an example $k_{p,fast} = 5000$ mol/(L s), are plotted as dashed lines in Figure 2, as a function of [M]. As for the considered syndiospecific catalytic system, an increase (in this case nearly linear) of the fraction of the slow state by decreasing monomer concentration is apparent.

Possible Nature of the Two Different States

Scheme 1 requires two different alkene-free states of the catalyst active center: a higher energy state faster in monomer insertion and a lower energy state slower in monomer insertion, with the slower one converting into the faster one after monomer insertion.

In our view, these two states of the active center could differ in the conformation of the growing polymer chain. Several theoretical calculations have indicated that the kinetic product of monomer insertion is a γ-hydrogen agostic intermediate, while the resting state (more stable, hence less reactive) has the β-hydrogen agostic interaction.[10,11] It seems reasonable to assume that the site with the γ-hydrogen agostic bond, being higher in energy, has a higher rate for propene coordination and/or insertion than the one having the β-hydrogen agostic interaction.

A slightly different kinetic model, recently proposed by some of us, which introduced the concept of a single-center, two-state catalyst system, which fits the observed changes in molecular weights with [propene] in the case of propene polymerization with Brintzinger's C_2 symmetric zirconocene catalyst,[8] is now discarded.

It was postulated that the two different states correspond to two sites having the growing chain end of opposite chirality (generated by epimerization[8,12,13] in the case of C_2 symmetric metallocene precatalysts or by chain back-skip in the case of C_s symmetric ones), where the site with the "wrong" chirality of the growing chain end with respect to the catalyst enantioselectivity is the slow one (Scheme 2).

Following the usual procedure, it is possible to derive

$$R_p = [\mathrm{C}]\left\{\frac{(k_{p,\mathrm{fast}}k_{s\to f} + k_{p',\mathrm{fast}}k_{s\to f} + k_{p,\mathrm{slow}}k_{f\to s} + k_{p',\mathrm{slow}}k_{f\to s})[\mathrm{M}]}{k_{s\to f} + k_{f\to s} + (k_{p',\mathrm{fast}} + k_{p,\mathrm{slow}})[\mathrm{M}]} + \frac{(k_{p,\mathrm{fast}}k_{p,\mathrm{slow}} + 2k_{p',\mathrm{fast}}k_{p,\mathrm{slow}} + k_{p',\mathrm{fast}}k_{p',\mathrm{slow}})[\mathrm{M}]^2}{k_{s\to f} + k_{f\to s} + (k_{p',\mathrm{fast}} + k_{p,\mathrm{slow}})[\mathrm{M}]}\right\} \quad (17)$$

As already described for the propagation rate law (eq 8), eq 17 also can present the kinetic order in monomer in the range from 2 to 1 only when $k_{f\to s} \gg k_{s\to f}$.

For the kinetic model of Scheme 2, fast and slow states correspond to the same alkene-free active center having the growing chain end of opposite chirality, and it is reasonable to expect $k_{f\to s} \cong k_{s\to f.}$ In fact, all molecular mechanics studies relative to enantioselective catalytic models show that the energies of the alkene-free intermediates are essentially independent of the growing chain end.[14]

Furthermore, recent results from our laboratories tend to rule out this hypothesis: in fact, at least in one case, we observed nonlinearity in the activity/[propene] correlation even when no or very little epimerization was occurring.[15] Hence, epimerization seems to be a consequence, not the cause, of the formation of a slow catalyst state. More important, Chien's results[5] of a nonlinear reaction order in ethylene polymerization with an aspecific catalyst obviously cannot be explained with the above model, which hence has to be dismissed, as also pointed out by Chien.[5]

Other possibilities can be proposed to explain the nature of the slow state of an active polymerization center, which can be different for different catalytic systems, monomers, and experimental conditions. For instance, the faster state could correspond to cationic active centers solvent separated from the counterion. Correspondingly the lower energy slower state could be the tight ion pair.[16] The same effect could be generated by a coordinated $\mathrm{AlR_3}$ or neutral zirconocene species.[17] However, these hypotheses require some further assumptions imposing that the slow site becomes the fast site as a monomer is inserted.

It is also worth noting that when the terminations are not negligible with respect to the propagation, the slower state could correspond to initiation centers deriving from some kind of termination that does not involve the monomer (e.g., a β-hydrogen transfer to the metal rather than to a coordinated monomer molecule). In this case $k_{f\to s} \equiv k_{\mathrm{term}}$ and $k_{p,\mathrm{slow}} \equiv k_i$, and the occurrence of a nonlinear propagation rate law is discussed in ref 18.

Further experimental investigations are required in order to establish the precise nature(s) of such slow state(s) of the active center. In particular, the study of activity/[propene] and molecular weight/[propene] correlations for specific catalytic systems such as $\mathrm{Cp^*{}_2ZrCl_2}$/MAO and $\mathrm{Cp^*{}_2HfCl_2}$/MAO (propene oligomerization catalysts with chain transfer via the β-methyl group elimination, selectivity of 92% and 98%, respectively)[19] in comparison with $\mathrm{Cp_2ZrCl_2}$/MAO (propene oligomerization catalyst with chain transfer via the β-hydrogen elimination only) seems relevant. Such studies could help to clarify whether active centers having a β-hydrogen agostic interaction between the metal and the growing polymer chain end could, at least for some systems, be the slow states of the polymerization catalysts.

Conclusions

A kinetic model which assumes that a single catalytic center exists in two interconverting active states, differing in their monomer insertion rates, is able to explain the apparent reaction order higher than the first one in monomer concentration (eqs 8 and 9) without the need of invoking double monomer coordination.[9,20] In this framework, the reaction order higher than the first is achieved when the slower state is of lower energy with respect to the faster one and the interconversion rate between fast and slow states is intermediate between fast and slow chain propagation rates. The reaction order higher than the first would be due to the decrease of the concentration of the slower state as the monomer concentration increases (eq 4 and Figure 2). Possible kinetic constants relative to the proposed model are derived for an isospecific and a syndiospecific zirconocene-based catalytic system.

Some hypotheses relative to the nature of these fast and slow states are discussed. It is suggested that slow states could be related to less reactive growing chain conformations. For instance, for the case of olefin polymerization by stereorigid zirconocenes, slow states could be catalytic complexes presenting a β-hydrogen agostic bond of the growing chain to the metal. A previously proposed kinetic model for which the slow state presents a "wrong" growing chain chirality (although its propagation rate law is formally identical to eq 9) is unsuitable to account for the kinetic order in monomer higher than the first.

A possible choice between the hypotheses relative to the nature of the fast and slow states requires further experimental investigation.

Appendix 1

A general kinetic scheme for polymerization can include, besides the alkene-free intermediates $\mathrm{C_{slow}}$ and $\mathrm{C_{fast}}$, the alkene-bound intermediate C·M (see Scheme 3). In the following, eq 9 is derived for such a kinetic scheme, which includes separate monomer coordination and insertion steps.

$$\frac{\mathrm{d}[\mathrm{C_{fast}}]}{\mathrm{d}t} = k_{s\to f}[\mathrm{C_{slow}}] + k_i[\mathrm{C{\cdot}M}] + k_{d,\mathrm{fast}}[\mathrm{C{\cdot}M}] - k_{f\to s}[\mathrm{C_{fast}}] - k_{c,\mathrm{fast}}[\mathrm{C_{fast}}][\mathrm{M}] = 0 \quad (18)$$

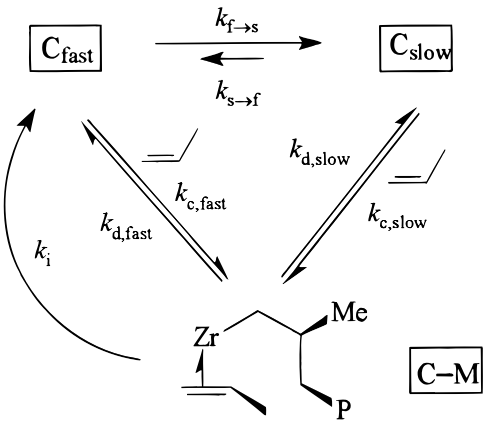
$$\frac{\mathrm{d}[\mathrm{C_{slow}}]}{\mathrm{d}t} = k_{f\to s}[\mathrm{C_{fast}}] + k_{d,\mathrm{slow}}[\mathrm{C{\cdot}M}] - k_{s\to f}[\mathrm{C_{slow}}] - k_{c,\mathrm{slow}}[\mathrm{C_{slow}}][\mathrm{M}] = 0 \quad (19)$$

$$\frac{\mathrm{d}[\mathrm{C{\cdot}M}]}{\mathrm{d}t} = k_{c,\mathrm{fast}}[\mathrm{C_{fast}}][\mathrm{M}] + k_{c,\mathrm{slow}}[\mathrm{C_{slow}}][\mathrm{M}] - (k_i + k_{d,\mathrm{slow}} + k_{d,\mathrm{fast}})[\mathrm{C{\cdot}M}] = 0 \quad (20)$$

From eq c we obtain

$$[\mathrm{C{\cdot}M}] = \frac{(k_{c,\mathrm{fast}}[\mathrm{C_{fast}}] + k_{c,\mathrm{slow}}[\mathrm{C_{slow}}])[\mathrm{M}]}{k_i + k_{d,\mathrm{fast}} + k_{d,\mathrm{slow}}} \quad (21)$$

Scheme 3gm



By substituting into eq 18

$$\frac{d[C_{fast}]}{dt} = k_{s\to f}[C_{slow}] + \frac{(k_i + k_{d,fast})k_{c,fast}[C_{fast}][M]}{k_i + k_{d,fast} + k_{d,slow}} + \frac{(k_i + k_{d,fast})k_{c,slow}[C_{slow}][M]}{k_i + k_{d,fast} + k_{d,slow}} - k_{c,fast}[C_{fast}][M] - k_{f\to s}[C_{fast}] = 0$$

thus

$$\frac{[C_{slow}]}{[C_{fast}]} = \frac{k_{f\to s} + \dfrac{k_{c,fast}k_{d,slow}[M]}{k_i + k_{d,fast} + k_{d,slow}}}{k_{s\to f} + \dfrac{(k_i + k_{d,fast})k_{c,slow}[M]}{k_i + k_{d,fast} + k_{d,slow}}} = \frac{k_{f\to s} + A[M]}{k_{s\to f} + B[M]} \tag{22}$$

Given that

$$[C_{fast}] = \chi_{fast}[C] \quad \text{and} \quad [C_{slow}] = \chi_{slow}[C] \quad \text{with } \chi_{fast} + \chi_{slow} = 1 \tag{23}$$

from eq 22 one obtains

$$\frac{[C_{slow}]}{[C_{fast}]} = \frac{\chi_{slow}[C](k_{f\to s} + A[M])}{\chi_{fast}[C](k_{s\to f} + B[M])}$$

Combining eqs 21 and 23

$$\chi_{fast} = \frac{k_{s\to f} + B[M]}{k_{s\to f} + k_{f\to s} + (A + B)[M]}$$

and

$$\chi_{slow} = \frac{k_{f\to s} + A[M]}{k_{s\to f} + k_{f\to s} + (A + B)[M]}$$

Hence, the propagation rate becomes

$$R_p = k_i[C\cdot M] = \frac{k_i k_{c,fast}\chi_{fast}[C][M]}{k_i + k_{d,fast} + k_{d,slow}} + \frac{k_i k_{c,slow}\chi_{slow}[C][M]}{k_i + k_{d,fast} + k_{d,slow}} = C\chi_{fast}[C][M] + D\chi_{slow}[C][M] = \frac{Ck_{s\to f} + BC[M]}{k_{s\to f} + k_{f\to s} + (A + B)[M]}[C][M] + \frac{Dk_{f\to s} + AD[M]}{k_{s\to f} + k_{f\to s} + (A + B)[M]}[C][M] = [C]\left(\frac{Ck_{s\to f} + Dk_{f\to s}}{k_{s\to f} + k_{f\to s} + (A + B)[M]}[M] + \frac{BC + AD}{k_{s\to f} + k_{f\to s} + (A + B)[M]}[M]^2\right) = [C]\frac{k_1'[M] + k_2'[M]^2}{k_3' + k_4'[M]}$$

which is eq 9.

Appendix 2

Molecular Weight. The average polymerization degree $\bar{P}_n$ of the polymer is determined by both the chain propagation rates and the chain-transfer rates:

$$\bar{P}_n = \sum R_p / \sum R_t$$

The dependence of polymer molecular weights on monomer concentration varies depending on the types of chain-transfer reactions, which are different for different catalysts. Thus, accurate molecular weight data together with the knowledge of the mechanisms of chain transfer provide an excellent tool for the kinetic analysis.

Let us assume that, in the first approximation, only the slow active centers C_{slow} can undergo chain transfer by both unimolecular β-transfer to the metal and bimolecular β-transfer to the monomer.

In the case of the simplified kinetic Scheme 1, we have

$$R_t = [C_{slow}](k_{to} + k_{t_1}[M]) \tag{24}$$

By substituting eq 7 into eq 24

$$R_t = \frac{k_{f\to s}[C](k_{to} + k_{t1}[M])}{k_{f\to s} + k_{s\to f} + k_{p,slow}[M]} \tag{25}$$

From eqs 8 and 25

$$\bar{P}_n = \frac{R_p}{R_t} = \frac{(k_{p,slow}k_{f\to s} + k_{p,fast}k_{s\to f})[M] + k_{p,slow}k_{p,fast}[M]^2}{k_{f\to s}(k_{t0} + k_{t1}[M])} \tag{26}$$

Hence, the number-average degree of polymerization can be described as

$$\bar{P}_n = \frac{k_1'[M] + k_2'[M]^2}{k_3' + k_4'[M]} \tag{27}$$

where again k' are combinations of kinetic constants.

The dependence of molecular weights on propene concentration for the more general kinetic scheme including reversible monomer coordinations to catalytic centers in a fast or a slow state is given by[8]

$$R_t = [\mathrm{C}_{\mathrm{slow}}](k_{t0} + k_{t1}[\mathrm{M}]) = [\mathrm{C}]\chi_{\mathrm{slow}}(k_{to} + k_{t1}[\mathrm{M}]) = \frac{k_{f\rightarrow s} + A[\mathrm{M}]}{k_{s\rightarrow f} + k_{f\rightarrow s} + (A + B)[\mathrm{M}]}(k_{t0} + k_{t1}[\mathrm{M}])[\mathrm{C}] = [\mathrm{C}]\left(\frac{k_{t0}k_{f\rightarrow s} + (Ak_{t0} + k_{t1}k_{f\rightarrow s})[\mathrm{M}] + Ak_{t1}[\mathrm{M}]^2}{k_{s\rightarrow f} + k_{f\rightarrow s} + (A + B)[\mathrm{M}]}\right) = [\mathrm{C}]\left(\frac{k'_5 + k'_6[\mathrm{M}] + k'_7[\mathrm{M}]^2}{k'_3 + k'_4[\mathrm{M}]}\right)$$

By combining the latter equation with eq 9, the law determining the number-average degree of polymerization $\bar{P}_n$ is obtained:

$$\bar{P}_n = \frac{k'_1[\mathrm{M}] + k'_2[\mathrm{M}]^2}{k'_5 + k'_6[\mathrm{M}] + k'_7[\mathrm{M}]^2} \qquad (28)$$

If eq 1 holds, we have the normal correlation between molecular weight and monomer concentration:

$$\bar{P}_n = \frac{k_p[\mathrm{M}]}{k_{t0} + k_{t1}[\mathrm{M}]} \qquad (29)$$

which can be linearized:

$$\frac{1}{\bar{P}_n} = \frac{k_{t1}}{k_p} + \frac{k_{t0}}{k_p}\frac{1}{[\mathrm{M}]} \qquad (30)$$

Molecular weight data, which are intrinsically much less affected by experimental error than the measure of catalyst activity, were obtained with good reproducibility for the isotactic polypropene samples produced with the chiral *rac*-C_2H_4(1-indenyl)$_2$$ZrCl_2$/MAO catalyst. Equation 27 provided a good fit of the molecular weights, while eq 30 did not (Figure 3 in ref 8).

For a given catalytic system, the k'_1 through k'_4 values obtained by fitting the experimental molecular weight data, in combination with the k_1 through k_4 values obtained by fitting the activity data (eq 9), could be used to derive all the kinetic constants relative to the simplified kinetic model of Scheme 1, as well as the kinetic constants relative to termination reactions.

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