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Zirconocene-Catalysed Propene Polymerisation: Kinetics, Mechanism, and the Role of the Anion

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Summary: The olefin polymerisation activity of metallocene catalysts strongly depends on the counteranion provided by the activator system. The relative activities of a number of new diborate anions $[Z(BAr_3)_2]^-$ have been quantified (Z = CN, NH_2, $N(CN)_2$; Ar = C_6F_5 or *o*-$C_6F_4C_6F_5$). The kinetic parameters for the initiation, propagation and termination steps of propene polymerisations catalysed by (SBI)$ZrCl_2$ have been determined using quenched-flow kinetic and batch techniques [SBI = *rac*-$Me_2Si(1\text{-}Ind)_2$]. Comparison of two activator systems, (i) $CPh_3[B(C_6F_5)_4]$ / triisobutylaluminium (TIBA) and (ii) methylaluminoxane (MAO) shows, surprisingly, that the concentration of species actively involved in chain growth at any one time is comparable for both systems, although the MAO-activated catalyst is about 20 times less active than the borate system. It is concluded that the counteranion remains sufficiently strongly bound to the metal centre throughout the chain growth sequence to modulate the energetics of monomer insertion. A model suggesting that the monomer binding follows an associative interchange (I_a) mechanism is proposed.

Keywords: anion effects; kinetics; mechanism of polymerisation; metallocenes; propene polymerisation

Introduction

Although many aspects of metallocene catalysed 1-alkene polymerisations such as the relationship between ligand structure and polymer stereochemistry are well understood and quantifiable,[1-4] the relationship between catalyst structure and one of the most important catalyst properties, its activity, is much less certain. It is commonly accepted that the use of a variety of activator systems, such as methylaluminoxane (MAO), $B(C_6F_5)_3$, or trityl and ammonium salts of non-coordinating borates all lead to similar active species, generally formulated as ion pairs $[L_2M\text{-}R]^+[X]^-$, where the degree of ion interactions may range from molecular zwitterions as in $L_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3$ to ion pairs of less distinct nature where the anion is thought to be sufficiently remote from the electron-deficient cationic metal alkyl

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species not to impede the uptake of the 1-alkene monomer.[5,6] This view seems supported by the observation that catalytic activity increases as the nucleophilicity of the anion decreases.[7-9]

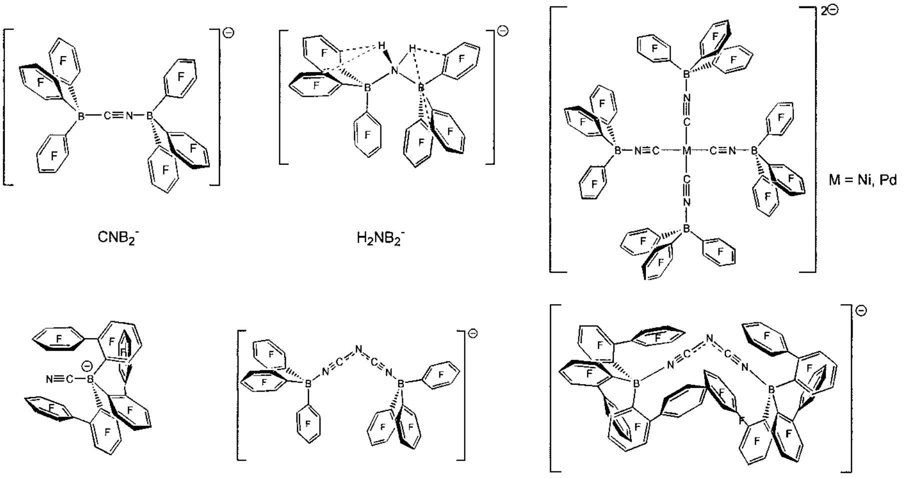
Our interest in the problem of quantitatively assessing the factors that control catalyst activity originated in the observation that the activity of the same metallocene precursor under comparable conditions could be increased by a factor of 30 – 40 by changing the activator from MAO to a trityl borate salt. Our initial assumption was that this was primarily the consequence of the differing concentrations of active species in these systems, as the result of a dissociation equilibrium:[5, 7-9]

$$L_2ZrR(X) \overset{K}{\rightleftharpoons} [L_2ZrR]^+ + X^- \tag{1}$$

Results and Discussion

Significant research effort by a number of groups has concentrated on anion engineering, with the aim of maximising the potential of metallocene catalysts.[6,9-15] Some more recent examples of such anions prepared in our laboratory are shown in Chart I.[16-19]

Chart I



CNB_2^-

$H_2NB_2^-$

M = Ni, Pd

$NCPBB^-$

CAB_2^-

$CAPBB^-$

For ethene polymerisations, the activity sequence under normalised conditions (20 °C, 1 bar, toluene) is $CNB_2 \approx CAPBB > H_2NB_2 \approx B(C_6F_5)_4 > CAB_2 \approx NCPBB$. A similar sequence is found for propene: $CNB_2 \approx CAPBB > H_2NB_2 \approx B(C_6F_5)_4 >> CAB_2$. The trityl salts of all these anions, combined with $AlBu^i_3$ as scavenger, give significantly higher propene polymerisation activities than $B(C_6F_5)_3$; for example, while comparative tests with $(SBI)ZrMe_2$ / $AlBu^i_3$ / $CPh_3[X]$ had to be terminated after 30 – 60 s to prevent the effects of monomer depletion and system heterogenisation, reactions with $B(C_6F_5)_3$ required reaction times of 10 – 30 min. Typical activity profiles as a function of catalyst concentration are shown in Figure 1. Extrapolation to zero catalyst concentration enables concentration-independent activity data to be determined. From such data, the contribution of the counteranion to the activation barrier of propene polymerisation can be derived (Figure 2).[18]

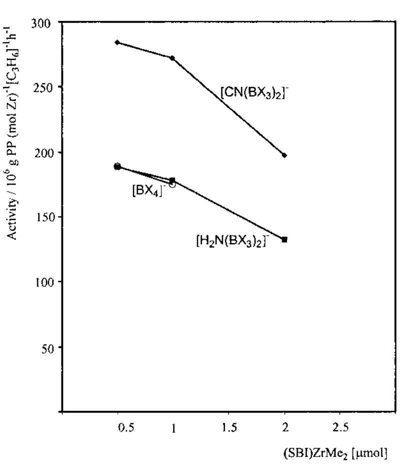


Figure 1. Anion dependence of propene polymerisation activity for selected anions (X = C_6F_5). Conditions: $(SBI)ZrMe_2$ / $AlBu^i_3$ (100 mmol) / toluene (100 mL), CPh_3:Zr = 1, 1 bar, 20 °C, 30 s.

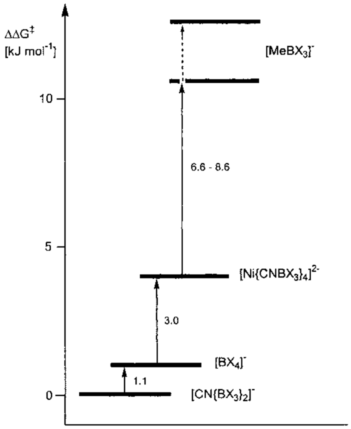


Figure 2. Contribution of borate anions to the activation barrier for propene polymerisation in batch reactions, relative to CNB_2^- as arbitrary reference point.

While these studies support the assumption that more strongly coordinating anions, such as $[MeB(C_6F_5)_3]^-$, give the least active catalysts, the activities proved *independent* of total anion concentration. For example, the addition of $[PhCH_2NEt_3][B(C_6F_5)_4]$ up to a B/Zr ratio of 20:1 had no effect on the polymerisation rate.

Kinetics provide a more detailed insight into the role of anions during the chain growth process.[20] The (SBI)ZrMe$_2$ / AlBu$^i_3$ / CPh$_3$[CN{B(C$_6$F$_5$)$_3$}$_2$] system (1:100:1) was chosen for quenched-flow kinetic studies at 25.0±0.1 °C to explore the early phase (t = 0.2 – 5 s) of the polymerisation reaction.[21] Since at the initial stages the kinetics follows non-steady state conditions, the conversion of the precursor complex to the active species (initiation, k_i) must be taken into account, eq (2):

$$\frac{-\,\mathrm{d}[M]}{\mathrm{d}t} = k_i[C_0][M] + k_p[C][M] \qquad (2)$$

where [C$_0$] = initial concentration of the precursor and [C] = catalyst concentration. The polymer mass Y collected at flow rate F over time t_c is given by eq (3) (m = molar mass of monomer, [M]$_0$ = initial propene concentration = 0.59 mol L^{-1}).

$$Y = F\,m\,t_c\,[C]_0\,[(1 - e^{-k_i[M]_0 t}) + k_p[M]_0\,(t + \frac{1}{k_i[M]_0}\,e^{-k_i[M]_0 t} - \frac{1}{k_i[M]_0})] \qquad (3)$$

Figure 3 shows the time dependence of polymer yield for several zirconocene concentrations.

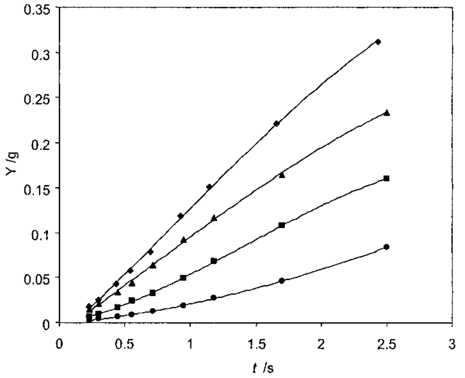


Figure 3. Time dependence of PP yield for the borate system. [Zr] = 2.38 × 10^{-5} (●); 4.76 × 10^{-5} (■); 7.14 × 10^{-5} (▲) and 9.52 × 10^{-5} mol L^{-1} (◆). The positive curvature at higher [Zr] and longer t indicates the effects of monomer depletion. [M]$_0$ = 0.59 mol L^{-1}, toluene, 25.0±01 °C.

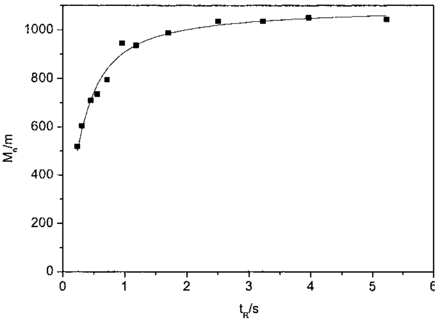


Figure 4. Time dependence of $\bar{M}_n$; (SBI)ZrMe$_2$/AlBu$^i_3$/CPh$_3$[CN{B(C$_6$F$_5$)$_3$}$_2$, toluene, 25.0±01 °C.

In their pioneering kinetic studies on the Cp$_2$TiCl$_2$/AlEt$_2$Cl ethene polymerisation system, Fink et al. have suggested an "intermittent growth" model the polymerisation process, where the active species are in equilibrium with (observable) resting (dormant) states.[22] While over the duration of a polymerisation reaction all metal centres can become involved in the production of polymer chains (save those deactivated by impurities),[23] the percentage of total metallocene actively involved in polymer chain growth at any one time is not known for most systems but may vary widely. It was of obvious interest to quantify the distribution between active and dormant states, by measuring the time evolution of the number-average molecular weight $\bar{M}_n$ (Figure 4).

Very similar behaviour was found for the system (SBI)ZrCl$_2$ / MAO (Al:Zr = 2500:1), although the lower activity made it necessary to conduct the polymerisations at 40 °C for longer reaction times ([M] = 0.42 mol L^{-1}) (Figures 5 and 6).

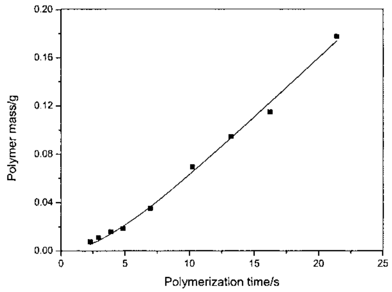


Figure 5. Time dependence of PP yield for the (SBI)ZrCl$_2$ / MAO system.

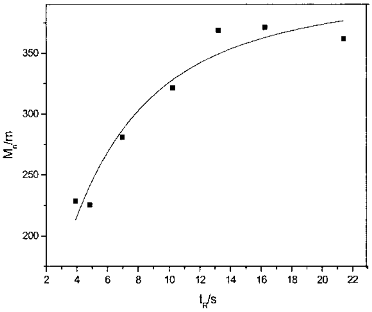
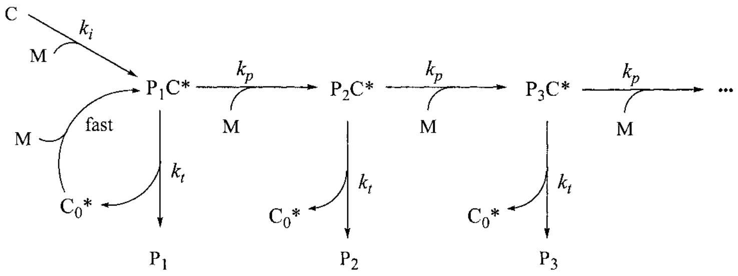


Figure 6. Time dependence of $\bar{M}_n$ for the (SBI)ZrCl$_2$ / MAO system.

We interpret these observations assuming an intermittent growth model where the precursor reacts with the monomer to give an active species at rate k_i, followed by chain propagation with rate constant k_p and involving active Zr species carrying polymeryl chains of varying chain length, P_zC^*. The k_p values for different P_zC^* are assumed to be identical. Chain termination (k_t) may take place from any of the species P_zC^* (z = 1, 2, 3…), with $k_t << k_p$ (Scheme 1). The parameters k_i and k_p were estimated by curve fitting. Tests show that the data for k_p are rather insensitive to the value of k_i.



Scheme 1.

The number-average degree of polymerisation $<n>$ is defined by eq (4).

$$<n> = \frac{\overline{M}_n}{m_M} = \frac{\Sigma z P_z}{\Sigma P_z} \qquad (4)$$

It can be shown that the time dependence of $\overline{M}_n$ is given by eq (5).

$$\langle n \rangle = \frac{\frac{(k_p[M]_0 + k_t)t}{k_t} + \frac{k_p[M]_0 + k_t - k_i[M]_0}{k_i[M]_0(k_t - k_i[M]_0)}(e^{-k_i[M]_0 t} - 1) - \frac{k_p[M]_0 k_i[M]_0}{k_t^2(k_t - k_i[M]_0)}(e^{-k_t t} - 1)}{t + \frac{1}{k_i[M]_0} e^{-k_i[M]_0 t} - \frac{1}{k_i[M]_0}} \qquad (5)$$

Assuming that $k_i << k_p$ and $k_t << k_i[M]_0$, this equation simplifies to eq (6) which was used for modelling $\overline{M}_n$.

$$\langle n \rangle = \frac{k_p[M]_0}{k_t} \bullet \frac{t + \frac{k_t}{k_i[M]_0(k_t - k_i[M]_0)}(e^{-k_i[M]_0 t} - 1) - \frac{k_i[M]_0}{k_t(k_t - k_i[M]_0)}(e^{-k_t t} - 1)}{t + \frac{1}{k_i[M]_0}(e^{-k_i[M]_0 t} - 1)} \qquad (6)$$

Applying steady-state conditions with respect to initiation and termination, i.e. $\exp(-k_i[M]_0 t) \rightarrow 0$ and $\exp(-k_t t) \rightarrow 0$, eq (6) simplifies to eq (7) which has been ascribed to Natta and Pasquon[24] and has frequently been used to describe $<n>$ but is not applicable under the present reaction conditions.

$$\langle n \rangle = \frac{k_p[M]_0 t}{1 + k_t t} \qquad (7)$$

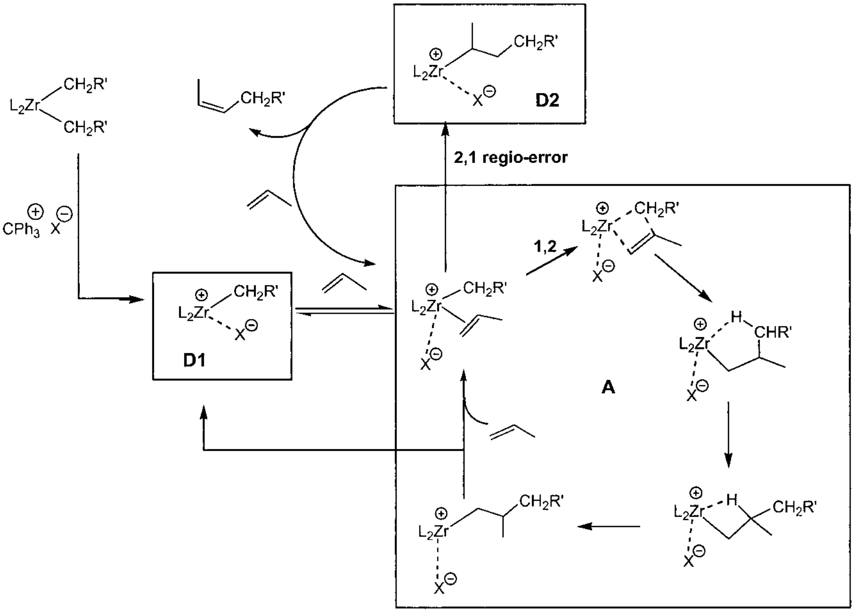
Curve fitting using eq (6) gives another set of data for k_p and k_i. Since the data in Figure 4 are derived from fewer measurements, the value of k_i is less certain but very comparable to that determined from *Y(t)*. On the other hand, the k_p value is an order of magnitude larger. To differentiate, we will refer to the propagation rate constant derived from polymer mass measurements as the *apparent* propagation rate k_p^{app}, since it assumes that 100% of the initially added zirconocene did indeed become catalytically active, while k_p will denote the rate constant derived from $\bar{M}_n$, eq (6). Pertinent kinetic parameters for the borate and the MAO-activated systems are given in Table 1.

The ratio k_p^{app}/k_p should then be a measure of the proportion of total zirconocene that was involved in chain growth at any one time. Surprisingly, this value was found to be almost identical in both the borate and the MAO-activated systems, ca. 0.08; i.e. under the given conditions less than 10% of the total zirconocene concentration may be regarded as "active species" P_zC^* in the sense of Scheme 1.

Table 1. Comparison of kinetic parameters for the (SBI)ZrMe$_2$ / borate and the (SBI)ZrCl$_2$ / MAO systems.

	L_2ZrR_2 / CPh_3^+		L_2ZrCl_2 / MAO	
	Yield vs Time	M_n *vs Time*	*Yield vs Time*	M_n *vs Time*
k_p^{app}, L mol^{-1}s^{-1}	1320 ± 20		48 ± 3	
k_p, L mol^{-1}s^{-1}		17,200 ± 1400		600 ± 230
k_i, L mol^{-1}s^{-1}	5.2 ± 0.6	2.5 ± 3.2	0.25 ± 0.05	0.8 ± 2.6
k_t, s^{-1}		9.4 ± 0.7		0.6 ± 0.2
k_p^{app}/k_p	0.08		0.08	

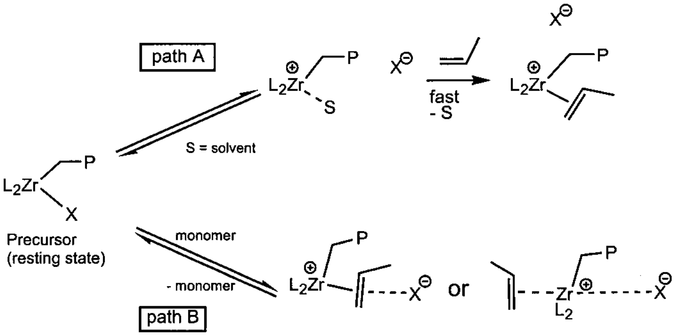
Current thinking about the nature of active and dormant species is depicted in Scheme 2. Alkylation of the zirconocene precursor with $AlBu^i_3$ followed by activation with a trityl borate is thought to lead primarily to a zirconocene alkyl tight ion pair, a resting state **D1** that is observable and stable for $CH_2R' = CH_3$.[18] Removal of the anion from the equilibrium position provides entry into the catalytic cycle, consisting of an assembly of active species involved in chain growth, as depicted in box **A** of Scheme 2. Other dormant states are possible, such as that derived from 2,1-misinsertion of propene, to give a *sec*-alkyl (**D2**).[2] Further possibilities include the formation of a Zr-CMe$_2$P *tert*-alkyl formed by chain epimerisation.[25] Both *sec*- and *tert*-alkyls will be slow to insert further monomer.



Scheme 2. Active and dormant states in zirconocene-catalysed alkene polymerisations.

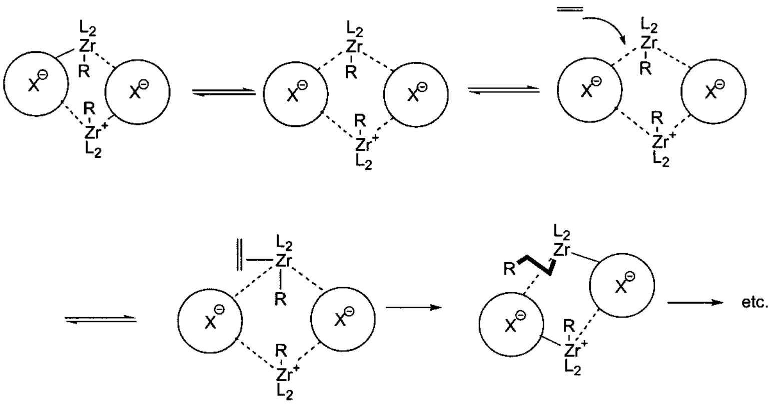
Since the kinetic results suggest similar concentrations of active species for the borate and the MAO system, the differences in activity must relate to the rate with which the monomer insertion cycle is completed. In a low-dielectric medium such as toluene it is only to be expected that the anion remains associated with the metallocenium cation throughout the cycle, i.e. there is no dissociation equilibrium of the type shown in eq (1). This assumption is further supported by the absence of an anion concentration effect, which indicates that in a low-polarity hydrocarbon medium ions do not diffuse freely. The associated anion will influence the lifetime of one or more of the intermediates.

Two possible scenarios of monomer insertion are represented in Scheme 3. Path A involves anion dissociation, followed by solvent coordination and substitution by monomer. Path B involves the direct substitution of the anion by monomer, either by approach from the same side as the anion to lead, effectively, to an insertion of the monomer between the metal and the anion,[26] or by approach from the opposite side to the anion, which, in view of the considerable size of tetraarylborate anions, seems more likely. Path A may play a role in half-sandwich complexes where toluene coordination has been shown to be preferred to anion coordination, at least in the case of zirconium and hafnium.[27] For bis-Cp complexes of the type investigated here, however, the kinetic data rule out path A and favour path B.



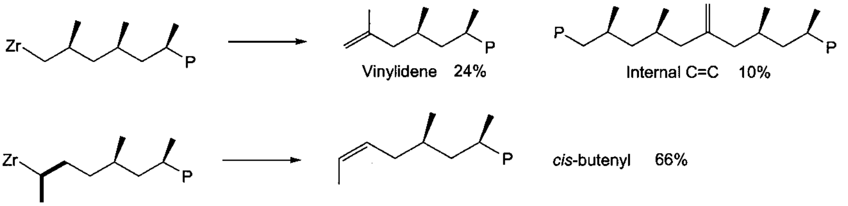
Scheme 3.

Brintzinger et al. have argued that, at least in the case of the relatively ionic zirconocenium $[B(C_6F_5)_4]^-$ salts, ion quadruples or higher aggregates may be present in hydrocarbon solutions.[28] Anion exchange rates determined by NMR methods for the borate system are of the same order of magnitude as the monomer insertion rates found here from the time dependence of $\overline{M}_n$. It is tempting to speculate, therefore, that the two processes may be related: in such an ion quadruple, the energy required to weaken the cation-anion interaction in the course of monomer coordination is balanced by the energy gained as a second anion approaches (Scheme 4). In such a case, monomer binding and anion displacement follows the path of an S_N2 reaction; it would be immediately followed by anion re-coordination. These mechanistic features are in fact those typical of an associative interchange, I_a, mechanism.



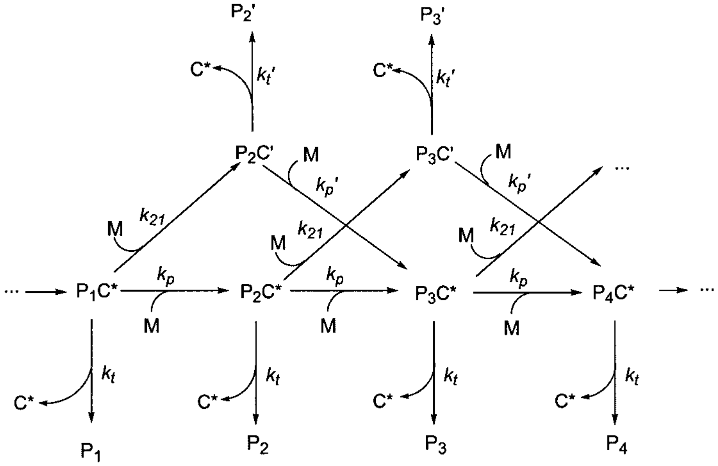
Scheme 4. Hypothetical monomer insertion mechanism coupled with anion exchange in ion quadruples.

Information about the nature of the main resting states is available by polymer end group analysis. Three different types of unsaturated polymers are found in this catalyst system, vinylidene, *cis*-butenyl, and internal C=C (Scheme 5).[29] The latter arise via C-H activation and formation of an η^3-allyl intermediate; in spite of the complex mechanism of their formation they are already apparent at reaction times of <1 s.



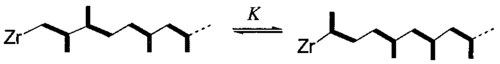
Scheme 5. PP end groups.

The main type of unsaturated end group is *cis*-butenyl, formed by β-H elimination from *sec*-alkyl Zr species following 2,1-propene misinsertion. The polymer also contains about 0.2 mol-% enchained 2,1-misinsertions. Since 1,2-insertion following a 2,1 stereoerror is slow compared with the main propagation step, 2,1-misinsertions tie up a significant percentage of total zirconocene as dormant species, while the fact that 2,1-enchainments are present in the main polymer chain argues that termination following misinsertion is also comparatively slow. The mechanism shown in Scheme 1 should therefore be elaborated to take account of these findings, Scheme 6, where k_{21} and k_p' indicate, respectively, a 2,1-insertion into a Zr-*prim*-alkyl and 1,2-insertion into a Zr-*sec*-alkyl bond.



Scheme 6.

If one neglects differences in polymeryl chain lengths and considers all P_zC^* as one species, and all P_zC' as another, one can formulate a hypothetical equilibrium between a Zr-*sec*-alkyl and its product following propene 1,2-insertion: $K = \Sigma[P_zC']/\Sigma[P_zC^*] = k_{21}/k_p'$ (Scheme 7). The value for K is estimated to be about 12, which may be regarded as a quantitative measure for the steric repulsion of two adjacent methyl groups in the PP chain and the relative stabilities of primary and secondary alkyls.



Scheme 7.

Conclusion

Quenched-flow kinetic techniques have allowed the quantification of the concentration of active species in metallocene-catalysed propene polymerisations. The rate constants for catalyst initiation, chain propagation and chain termination have been estimated. Surprisingly, this value is not strongly dependent on the nature of the catalyst activator, at least for the catalyst system described here. Catalyst productivity, as a function of the time taken for the completion of a monomer insertion cycle, is strongly influenced by the counteranion. The data suggest that the anion remains closely associated during the transition state and influences the residence times of one or more catalytic intermediates in the assembly of active species that constitute the catalytic cycle. The non-active proportion of total [Zr] consists mainly of species produced by propene 2,1-misinsertions, with the rate of 2,1-misinsertion being about 500 times slower than that of 1,2-insertion. The overall polymerisation mechanism is consistent with an intermittent chain growth model with an equilibrium between dormant and active states; it is proposed that the anion re-coordinates after each monomer insertion step, in a manner reminiscent of an associative interchange mechanism.

Acknowledgement

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