The influence of methylalumoxane (MAO) on the isoselective propene polymerization with the homogeneous metallocene Me$_2$Si(Benz[e]Ind)$_2$ZrCl$_2$

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Abstract

The isoselective propene polymerization using the homogeneous Me$_2$Si(Benz[e]Ind)$_2$ZrCl$_2$/MAO catalyst system was investigated. The influence of the concentrations of metallocene and MAO activator on polymerization kinetics and microstructure of the resulting polymer was studied. Catalyst activity was found to be independent of zirconocene concentration and only a function of total MAO concentration. Polypropene microstructure was not affected by either MAO or zirconocene concentration. The polymerization behavior is compared to that of Me$_2$Si(2-Me-Benz[e]Ind)$_2$ZrCl$_2$/MAO. A model is presented to account for the equilibria present in the polymerization medium. This model takes into account the interactions between metallocene cation and excess MAO, thus explaining the influence of MAO concentration on catalyst activity in propene polymerization.

Keywords: Homogeneous catalysis; Kinetics; Polymerization; MAO; Metallocene; Propene; Ziegler–Natta catalysts; Zirconium; Complexation

1. Introduction

Forty years after the discovery of the stereoselective polymerization of 1-olefins catalyzed by transition metal compounds, the development of metallocene catalysts has led to new insights into the basic reactions of the polyinsertion mechanism [1–26]. Polymerization with homogeneous metallocene catalysts requires an extraordinarily high excess of the cocatalyst methylalumoxane (MAO) in order to reach satisfactory activities. A ratio of Al/Ti or Al/Zr, respectively, of more than 1,000 is typical for the reaction conditions employed. Because of the ill-defined structure of the oligomeric substance MAO [27], the reasons for this required excess are not yet elucidated in detail.

The objective of our research was to gain a deeper understanding of the interaction of MAO with the catalytically active metallocene site and the dependence of both polymer microstructure and polymerization kinetics upon the cocatalyst addition. Here we present our research on the isoselective propene polymerization using the

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homogeneous catalyst system $Me_2Si(Benz[e]Ind)_2ZrCl_2$/MAO, aiming at better understanding of the interactions controlling catalyst activity and polymer microstructure. Special attention will be paid to a comparison with the results obtained with the related $Me_2Si(2\text{-}Me\text{-}Benz[e]Ind)_2ZrCl_2$/MAO system [28–31].

2. Experimental part

All operations were performed in an argon atmosphere using Schlenk techniques. All the glass equipment was stored at 150°C and heated in vacuum prior to use. Argon (99.99%, Messer-Griesheim) was purified by passing over activated Cu_2O (BASF AG) and over a molecular sieve (0.4 nm).

Rac-dimethylsilylene-bis(benz[e]indenyl)zirconiumdichloride was prepared by U. Stehling in the group of Prof. Dr. H.-H. Brintzinger at the University of Konstanz, Germany, and stored at 5°C in an argon atmosphere.

Toluene (> 99.7%, Roth) was stored over Al_2O_3 (Merck) for some days and filtrated over Al_2O_3. To 3.5 l of the filtrate, 2 g *n*-butyllithium (Aldrich or Riedel-de-Haen) was added. The mixture was refluxed over $LiAlH_4$ for some hours. After rectification, it was refluxed over Na/K for two days and distilled prior to use. MAO was supplied by Witco. Propene (polymerization grade, BASF) was condensed into a 10 l steel bomb containing a solution of tri-isobutylaluminium in toluene (25 wt%, Aldrich) and stored there.

The polymerizations were performed in a Büchi 2 l glass autoclave at 2 bar total pressure and 40°C. Temperature was controlled by means of two independent thermostats. Propene pressure was kept constant by feeding the monomer from a pressure tank thermostated at 60°C by means of a selenoid valve connected to a pressure sensor in the autoclave. Catalyst activity was determined by monitoring the pressure drop

in the thermostated tank as described previously [29,30]. Polymerizations were performed at 2 bar total pressure and 40°C. Under these conditions, propene partial pressure is 1.922 bar, and propene concentration in toluene is 910 mmol/l [32].

3. Results and discussion

Concentration of methylalumoxane (MAO) cocatalyst exerts a marked influence on reaction kinetics. Fig. 1 shows the catalytic activity for three polymerizations with varying MAO concentrations (5–40 mmol/l) and constant zirconium concentration (2 μmol/l). All curves show a maximum activity after approximately 10 min followed by a more or less rapid decay. Measurements at [Zr] = 1 μmol/l show a very similar pattern, as displayed in Fig. 2. Polymerization activities are displayed in Table 1. A detailed analysis of the catalyst activity/time profiles indicates that the curves measured at 1 μmol/l differ mainly in three points from those recorded at twice the zirconocene concentration: maximum activities are higher, they are reached later and deactivation is slower.

Maximum polymerization activity is observed at an aluminium concentration of 20
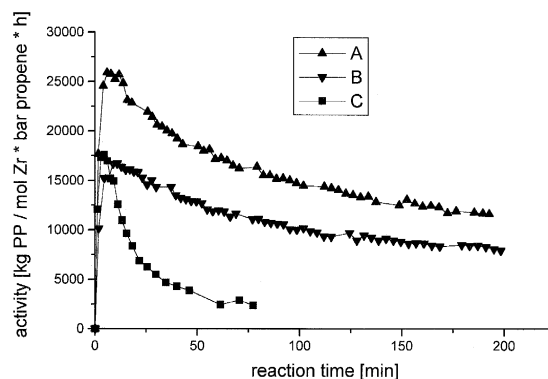

Fig. 1. Comparison of polymerization activity for propene polymerizations using the $Me_2Si(Benz[e]Ind)_2ZrCl_2$/MAO system at 40°C, 2 bar total pressure and [Zr] = 2 μmol/l in 600 ml of toluene, [Pr] = 910 mmol/l. A: [Al] = 20 mmol/l; B: [Al] = 40 mmol/l; C: [Al] = 5 mmol/l.
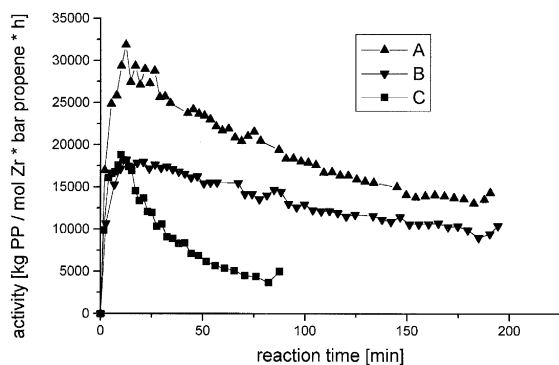
Fig. 2. Comparison of polymerization activity for propene polymerizations using the $Me_2Si(Benz[e]Ind)_2ZrCl_2$ /MAO system at 40°C, 2 bar total pressure and [Zr] = 1 μmol/l in 600 ml of toluene, [Pr] = 910 mmol/l. A: [Al] = 20 mmol/l; B: [Al] = 40 mmol/l; C: [Al] = 5 mmol/l.
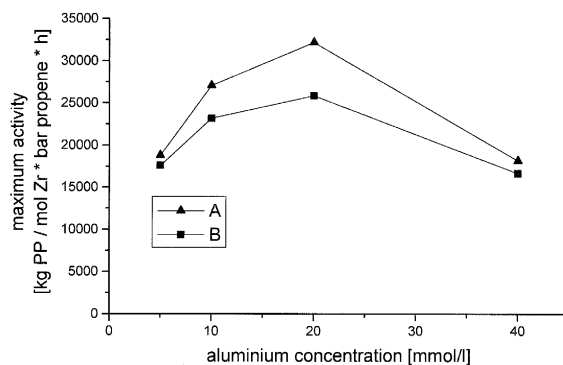

Fig. 3. Maximum polymerization activity as a function of MAO concentration for propene polymerizations at 40°C and 2 bar total pressure in 600 ml of toluene using the $Me_2Si(Benz[e]Ind)_2ZrCl_2$ /MAO catalyst, [Pr] = 910 mmol/l. A: [Zr] = 1 μmol/l; B: [Zr] = 2 μmol/l.

mmol/l independent from metallocene concentration and thus from the Al/Zr molar ratio. Fig. 3 shows maximum activity as a function of the concentrations of zirconocene and cocatalyst. Fig. 4 displays the polymerization activity found after one hour related to the maximum activity for different concentration of metallocene and MAO. One can clearly notice the slower deactivation at higher MAO-concentrations and lower zirconocene concentrations.

Polymerization activity (A) is proportional to the number of active sites. Thus, if the deactivation is first order with respect to the active center, one observes a decay of activity which is

proportional to the activity itself. Integration results in

$$\ln(A) = -k_1 * t + const_1 \qquad (1)$$

Therefore, a plot of $\ln(A)$ versus time should be linear. If the deactivation reaction is second order, the decay of activity is proportional to the square of the activity. From this follows by integration:

$$1/A = k_2 * t + const_2 \qquad (2)$$

This would result in a linear plot of $1/A$ versus time. From the respective plot (Fig. 5), we believe deactivation to be bimolecular with respect to the active center.

Table 1
Polymerization activities for propene polymerization using the $Me_2Si(Benz[e]Ind)_2ZrCl_2$/MAO catalyst [a]

Run	Zirconocene concentration (μmol/l)	Aluminium concentration (mmol/l)	Maximum activity (kg PP/mol Zr * bar propene * h)	Activity after 1 h (kg PP/mol Zr * bar propene * h)
SK013	2	5	17600	2600
SK009	2	10	23200	11000
SK010	2	20	25900	17200
SK012	2	40	16700	12000
SK017	1	5	18800	5400
SK016	1	10	27100	14400
SK015	1	20	32200	22000
SK014	1	40	18200	15500

[a] Polymerization at 40°C and 2 bar total pressure in 600 ml toluene, [Pr] = 910 mmol/l.

In contrast to its influence on polymerization kinetics, the concentrations of zirconocene and cocatalyst do not exert a remarkable influence on the molecular masses and the microstructure of the polypropylene produced with $Me_2Si(Benz[e]Ind)_2ZrCl_2$/MAO as shown in Table 2. Number-average molecular masses are in the range of 40,000 to 50,000 g/mol with narrow distributions of $M_w/M_n = 1.7$ to 1.9. Melting points vary between 142 and 146°C.
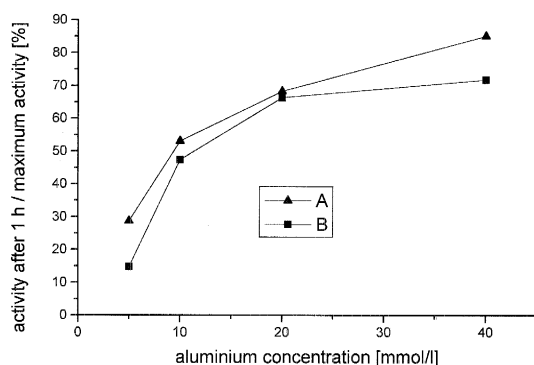

Fig. 4. Polymerization activity left after one hour related to maximum activity as a function of MAO concentration for propene polymerizations at 40°C and 2 bar total pressure in 600 ml of toluene using the $Me_2Si(Benz[e]Ind)_2ZrCl_2$/MAO catalyst, [Pr] = 910 mmol/l. A: [Zr] = 1 μmol/l; B: [Zr] = 2 μmol/l.

Melting enthalpies are in the range of 91 to 98 J/g, corresponding to a crystallinity of approximately 45% [33]. ^{13}C-NMR-spectroscopy reveals a stereoselectivity of about 92.5% mmmm-pentads and a relatively high amount of isotactic 2,1-insertions (ca. 0.7%). The NMR spectrum also shows signals corresponding to racemic 2,1-insertions estimated to be about 0.1–0.2% of the methyl signal intensity. In all cases, variations are within the experimental error. No correlation between metallocene and MAO concentrations and molecular weights, thermal properties and microstructure of the polymer can be established. In contrast to this, MAO concentration exerts a significant influence on polymerization kinetics.

For the basic reaction steps of the catalytic cycle, the interactions of the active species with other metallocenes, the counterion and the large amount of neutral MAO are of special importance. Based on these interactions, the model in Scheme 1 might account for the dependence of polymerization features on the concentrations of the different species present in the polymerization medium. The metallocene dichloride **1** employed as catalyst precursor is inactive in the sense of chain propagation. With MAO as Lewis

Table 2
Molecular weights, melting temperatures, melting enthalpies, microstructure and the polypropylenes produced with $Me_2Si(Benz[e]Ind)_2ZrCl_2$/MAO [a]

Run	Zirkonocene concentration (μmol/l)	Aluminium concentration (mmol/l)	M_w [b] (g/mol)	M_n [b] (g/mol)	M_η [c] (g/mol)	M_w/M_n [b]	T_m [d] (°C)	ΔH_m [d] (J/g)	% mmmm [e]	% m-2,1 [f]
SK013	2	5	45100	25100	37300	1.8	145.0	94.9	92.5	0.71
SK009	2	10	41600	22800	38300	1.8	145.7	91.9	92.5	0.64
SK010	2	20	50000	27500	33600	1.8	145.2	98.0	93.0	0.76
SK012	2	40	39900	23000	31800	1.7	144.7	97.6	92.3	0.71
SK017	1	5	46000	24900	34500	1.8	145.0	91.7	92.4	0.65
SK016	1	10	42900	23000	31800	1.9	143.8	92.2	92.5	0.71
SK015	1	20	41900	23500	38300	1.8	142.7	92.0	92.9	0.68
SK014	1	40	41400	24000	32700	1.7	144.3	93.7	93.2	0.65

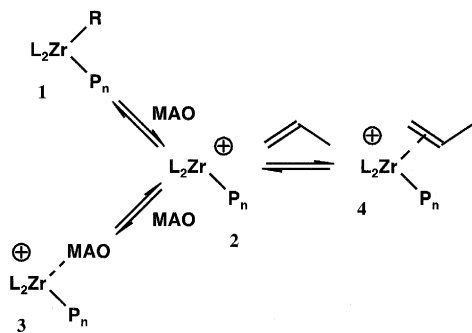[a] Polymerization at 40°C and 2 bar total pressure in 600 ml toluene, [Pr] = 910 mmol/l.
[b] Determined via SEC.
[c] Determined via viscosimetry.
[d] Determined via DSC.
[e] Determined via ^{13}C-NMR, intensity of the mmmm pentad signal related to the total methyl pentad intensity.
[f] Determined via ^{13}C-NMR, intensity of the *meso*-2,1 insertions related to the total methyl pentad intensity.

Scheme 1. Model for the species present in the polymerization medium.

acid, it is converted into a d^0-14-electron-cation **2** active in polymerization catalysis. An equilibrium in favor of **1** could account for the low activities observed in the case of low MAO concentrations. Upon increasing the MAO concentration, the oxygen functions of MAO could serve as a donor leading to a reversible deactivation of the active center **2** resulting in the structure **3**. Nevertheless, chain propagation can only occur from the cationic complex **4** formed by complexation of propene to the d^0-system **3**.

Termination of the growing polypropylene chain in the catalyst system $Me_2Si(Benz[e]Ind)_2ZrCl_2$/MAO takes place by the transfer of a β-hydrogen to a coordinated propene molecule [31] and thus only in complex **4**. The rate of chain termination *via* β-H-elimination can be neglected compared to the rate of termination via β-H-transfer in **4**. As complexes **1**, **2** and **3** are not active in the sense of chain propagation, **4** is the only species from which both chain propagation and termination can occur. Therefore, a shift of the equilibria shown in Scheme 1 results in a change of catalytic activity, but not in a change of the molecular mass of the polymer.

This situation is fundamentally different from polymerizations using the homogeneous $Me_2Si(2\text{-}Me\text{-}Benz[e]Ind)_2ZrCl_2$/MAO catalyst. In this system, the polymer chain is not terminated by β-H-transfer to monomer. This is prevented by the steric demands of the ligand system [31]. All metallocene cations in Scheme 1 undergo β-H-elimination, whereas chain propagation only occurs from **4**. Therefore, a shift of the equilibria to structure **4** at optimum MAO concentrations resulting in higher activities also accounts for a raise of molecular weight.

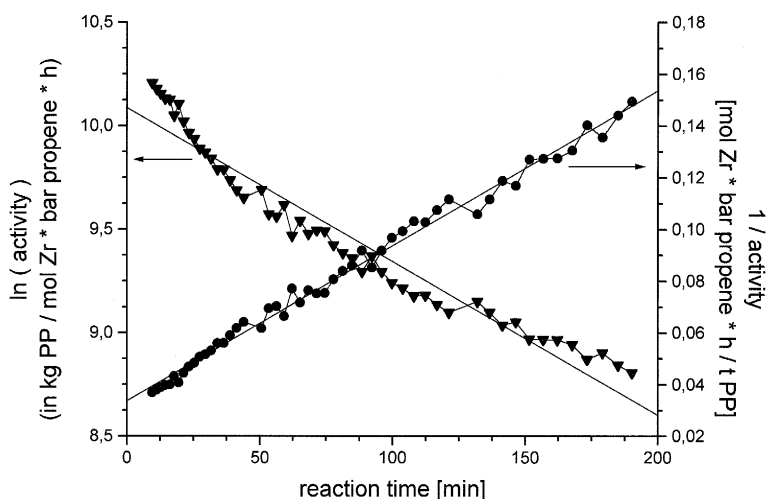The microstructure of the polymer produced using the $Me_2Si(2\text{-}Me\text{-}Benz[e]Ind)_2ZrCl_2$/MAO system is as well in-

Fig. 5. Kinetic analysis of propene polymerization at 40°C and 2 bar total pressure in 600 ml of toluene, [Pr] = 910 mmol/l, [Zr] = 1 μmol/l, [Al] = 10 mmol/l using the $Me_2Si(Benz[e]Ind)_2ZrCl_2$/MAO catalyst. Left *y* axis: plot of ln (activity) versus time (first order deactivation); right *y* axis: plot of 1/activity versus time (second order deactivation).

Table 3
Comparison of polypropylenes produced using the $Me_2Si(Benz[e]Ind)_2ZrCl_2$/MAO (SBI) and the $Me_2Si(2-Me-Benz[e]Ind)_2ZrCl_2$/MAO (SMBI) [31] system, respectively [a]

Run	Metal-locene	Aluminium concentration (mmol/l)	Maximum activity [b]	M_n [c]	% mmmm [d]
JP132	SMBI	2.5	3000	91000	94.4
JP131	SMBI	5	54000	213000	96.1
JP120	SMBI	10	23000	209000	96.0
JP082	SMBI	20	14000	138000	96.6
SK017	SBI	5	18800	24900	92.4
SK016	SBI	10	27100	23000	92.5
SK015	SBI	20	32200	23500	92.9
SK014	SBI	40	18200	24000	93.2

[a] Polymerization at 40°C and 2 bar total pressure in 600 ml toluene, [Pr] = 910 mmol/l, [Zr] = 1 μmol/l.
[b] In kg PP/mol Zr∗bar propene∗h.
[c] Determined via SEC.
[d] Determined via ^{13}C-NMR, intensity of the mmmm pentad signal related to the total methyl pentad intensity.

fluenced by the MAO concentration as shown in Table 3. At higher MAO concentrations, one observes a higher stereoselectivity. The formation of stereo errors has been attributed to isomerization of the chain end via termination and subsequent reinsertion [34]. In contrast to the $Me_2Si(2-Me-Benz[e]Ind)_2ZrCl_2$/MAO system, both chain termination and reinsertion in the case of $Me_2Si(Benz[e]Ind)_2ZrCl_2$ are only possible at the metallocene **4**. For the same reasons as with respect to molecular masses, stereoselectivity does not depend on the ratio of the different zirconocenes, which is influenced by a change of the MAO concentration. Thus, the microstructure of the resulting polypropene is independent of the cocatalyst concentration.

The higher catalytic activities observed at lower zirconocene concentrations could be explained by Ostwald's law for the dissociation of electrolytes assuming that an ion pair of zirconocene cation and MAO counterion preferably dissociates at lower concentrations, thus leading to higher activities as it is also observed when going to a solvent with higher polarity [35]. An alternative explanation is based on the deactivation reaction assumed to be bimolecular with respect to the active center. A higher reac-

tion order would account for slower deactivation and thus increased activities at lower zirconocene concentrations.

The slower deactivation observed at higher MAO concentrations could be explained by the reversible coordination of *neutral* MAO to the very lewis-acid zirconocene cation, thus reducing it in its electrophilicity. A reversibly coordinated metallocenium cation is expected to react less with other Lewis-basic substances in the reaction medium as, for example, the MAO *counterion*.

Nevertheless, an observation still to be explained is the dependence of the activity (as related to the zirconocene concentration) on the *absolute* MAO-concentration, but not on the Al/Zr molar ratio.

The response of a catalyst system to variations of catalyst and activator concentrations differs for different metallocenes. For polymerizations with Cp_2ZrCl_2, $(NmCp)_2ZrCl_2$ (Nm = neomenthyl) and $C_2H_4(Ind)_2ZrCl_2$ activated by MAO, a monotonous dependence of catalytic activity was observed upon increasing the Al/Zr molar ratio [36–41]. For analogous polymerizations using the MAO-activated zirconocenes $C_2H_4(THInd)_2ZrCl_2$ (THInd = tetrahydroindenyl), $Me_2Si(Ind)_2ZrCl_2$, $Me_2C(Cp)(Flu)ZrCl_2$ and $Me_2C(3-Me-Cp)(Flu)ZrCl_2$ there is a certain Al/Zr ratio leading to maximum activities [42–45]. Upon increasing this ratio even more, activities decrease again. For $Me_2Si(Ind)_2ZrCl_2$ and $Me_2C(Cp)(Flu)ZrCl_2$, Herfert observed a linear dependence of conversion upon catalyst concentration and thus a constant activity (related to the catalyst concentration) when varying this in the range of 4.4 to 70 μmol/l though MAO concentration was kept constant at 11.2 and 22.4 mmol/l, respectively, thus varying the Al/Zr molar ratio over a wide range [42,43]. Similar results were obtained by Jüngling using the $Me_2Si(2-Me-Benz[e]Ind)_2ZrCl_2$/MAO catalyst [30].

This response, namely the dependence of catalyst activity upon the *absolute* MAO concen-

tration, cannot be explained by the law of mass action. Therefore, we chose a strictly statistical approach to account for the obtained results considering an isolated zirconocene cation and calculating the extent of electrostatic interactions with the Lewis-basic donor MAO in dependence on the concentration of the latter. In other words, we consider the coordinating power of a MAO solution at a given concentration.

The electrostatic interaction energy with dipols E is normally described by [46]

$$E \sim -1/r^6 \tag{3}$$

i.e. the interaction is inversely proportional to the sixth power of the distance of the respective dipols. It is obvious that coordination of the polar MAO particles to the electron-deficient zirconocene increases with increasing MAO content of the polymerization medium and, therefore, with decreasing distances between the coordinating particles. Thus, we consider the distance between the oligomeric MAO molecules as the fundamental aspect for the extent of electrostatic interaction between a zirconocenium cation and MAO.

By means of simple geometrical considerations, it can be shown that the mean distance between two particles in an n-dimensional space is inversely proportional to the nth root of their concentration, i.e.:

$$r \sim c^{-1/n} \left(= c^{-1/3}\right) \tag{4}$$

To clarify this, we consider a rectangular parallelepiped of sides x, y and z, respectively. If the distance between two arbitrary points or particles in this epiped shall be reduced by the factor of 2, all three sides have to be reduced by this factor, too. Thus, the volume is reduced by the factor of 2^3, in which the exponent represents the dimensionality of the three-dimensional space. Therefore, the concentration of the particles contained in this volume is increased by the same factor. This idea can be generalized to give Eq. (4). It is important to notice that this model is purely statistical and does not rely on any particular distribution of the particles.

By combination of Eq. (3) and Eq. (4) follows

$$E \sim c^2 \tag{5}$$

This means that the energy of the electrostatic interaction between a zirconocenium cation and MAO molecules in solution is proportional to the square of MAO concentration. Thus, this interaction is especially strong at high activator concentration. This is in agreement with the experimental results. Moreover, Eq. (5) shows that the electrostatic interaction depends only upon absolute MAO concentration, which is also confirmed by the experiments.

If we assume that the activating effect of MAO as a Lewis acid is first order with respect to MAO, then the dependence of activity A upon cocatalyst concentration can be expressed by

$$A = \alpha * c * \exp\left(-\beta * c^2\right) \tag{6}$$

In this expression, α represents a parameter for the response of the metallocene to *activation* by MAO as a Lewis acid, whereas β is a measure of the sensitivity of the active site against *coordination* by MAO as a Lewis base, i.e. its electrophilicity. Upon choosing appropriate values for α and β, a semi-quantitatively satisfac-

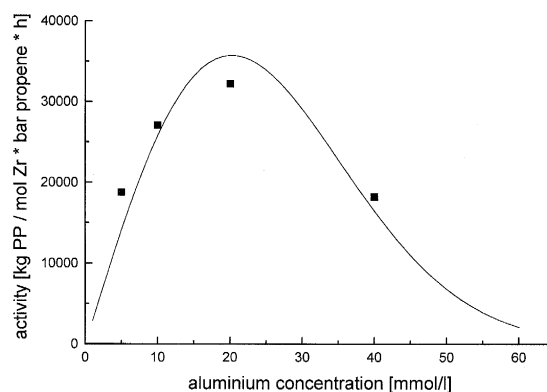Fig. 6. Comparison of experimental data for polymerization activity at 40°C and 2 bar total pressure in 600 ml of toluene using the $Me_2Si(Benz[e]Ind)_2ZrCl_2$/MAO catalyst, $[Pr] = 910$ mmol/l, $[Zr] = 1$ μmol/l and varying aluminium concentrations with data calculated according to [7] with $\alpha = 2919$ kg PP l/mol Zr*bar propene*h*mol Al and $\beta = 0.001225$ l^2/(mol Al)^2.

tory fit with the experimental data is obtained (Fig. 6).

Nevertheless, it still remains unclear why this reversible deactivation of the active center by high MAO concentrations is not observed with all metallocene catalysts. For example, the activity of the Cp_2ZrCl_2/MAO system increases monotonously with increasing MAO content in the solution [36]. Thus, it is necessary to distinguish between steric and electronic effects at the metallocene center to assess the extent of Lewis acidity and basicity of methyl alumoxane towards the active species.

4. Conclusions

Measurements of propene polymerization kinetics using homogeneous MAO-activated metallocene catalysts provide the basis for a better understanding of the role of the aluminum activator. The metallocene catalyst $Me_2Si(Benz[e]Ind)_2ZrCl_2$/MAO shows maximum activity at a MAO concentration of 20 mmol/l independent of zirconocene concentration. The polymerization behavior of the $Me_2Si(Benz[e]Ind)_2ZrCl_2$/MAO system can be explained by Eq. (6) and the equilibria in Scheme 1. The comparison to the related $Me_2Si(2-Me-Benz[e]Ind)_2ZrCl_2$/MAO catalyst indicates that the differences between these systems are based on the different mechanisms of chain termination. Nevertheless, more research is necessary to explore the very complex role and function of methyl alumoxane in homogeneous olefin polymerization.

Acknowledgements

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