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Kinetics and mechanistic insight into propylene polymerization with different metallocenes and various aluminium alkyls as cocatalysts

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Abstract

The influence of successive replacement of MAO by different aluminium alkyls in a metallocene catalyzed homogeneous polymerization is discussed. An activating effect was found by the addition of TIBA and TBA, whereas TMA and TEA have a deactivating effect. Propylene polymerizations were carried out with different substituted metallocenes of the general formula $Me_2C[3\text{-RCpFlu}]ZrCl_2$, where R is H, methyl, *i*-propyl or *t*-butyl. With increasing the size of the substituent, the polymerization activity decreased. Besides, it was found that the deactivating effect of methylaluminoxane (MAO) during the polymerization was compensated with more bulky substituents. Using $Me_2C[3\text{-}t\text{-BuCpFlu}]ZrCl_2$ for the propylene polymerization, a deactivating effect was no longer observed. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Stereorigide group 4 ansa-metallocenes are of growing interest as stereospecific Ziegler-catalysts with methylaluminoxane (MAO) as cocatalyst. Brintzinger's synthesis of rac-Et[Ind-$H_4]_2ZrCl_2$ in 1985 was the first step in a development still going on [1,2]. Metallocenes allow the synthesis of well-defined macromolecules with controlled microstructure.

With regard to the cocatalyst MAO, there are indeed conceptions that explain the activation of the metallocene compound L_2MCl_2 through MAO to form the polymerization active cation, but only a few mechanistic knowledge are known about the role of MAO during the polymerization.

Known MAO forms, as of this writing, in solution complex and dynamic cluster structures [3,4] always contain parts of free TMA in equilibrium.

This paper deals with the influence of MAO during a polymerization process with different metallocenes of the general structure Me_2C-

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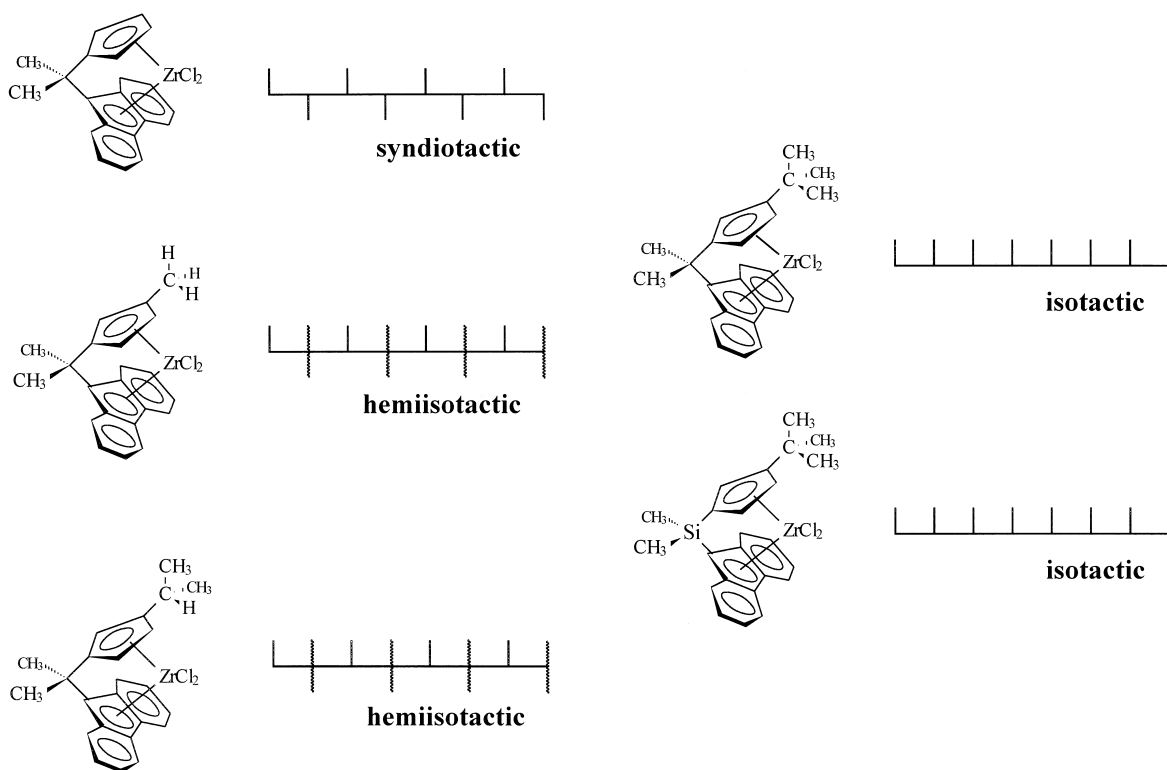
Fig. 1. Influence of metallocene structure on the polymer microstructure in propylene polymerization.

[RCpFlu]ZrCl$_2$, where R is H, Me, *i*-propyl or *t*-butyl (Fig. 1).

The successive replacement of MAO by different aluminium alkyls is another aspect which will be reported in this paper.

2. Experimental

2.1. Materials

All solvents and air-sensitive compounds where handled under argon using standard Schlenk technique. The propylene gas was purified by being passed through a series of columns of NaAl(Et)$_4$ to remove residual traces of moisture and oxygen. Toluene was purified by distillation under argon over NaAl(Et)$_4$.

2.2. Catalysts

Me$_2$Si[Ind]$_2$ZrCl$_2$ was synthesized according to Herrmann et al. [5]. Me$_2$Si[2-Me-4,5-Benzo-Ind]$_2$ZrCl$_2$ was obtained from industry. Me$_2$C-[RCpFlu]ZrCl$_2$ was synthesized according to literature [6,7]. TIBA was obtained from Schering. TMA, TEA, TBA and MAO (10 wt.% solution in toluene) were obtained from Witco.

2.3. Propylene polymerization procedures

The polymerizations were performed in a 0.25 dm^3 glass autoclave at 2.0 bar propylene pressure. The temperature was varied from 25°C to 60°C. A propeller-like stirrer was used at 1200 rpm to stir the reaction mixture. The reactor was filled with toluene and MAO, ther-

mostated and saturated with propylene gas. The preactivated metallocene was injected in the reactor with an argon overpressure of 4.0 bar. The total volume of the liquid phase was 110 ml in a typical experiment. The monomer consumption was measured by mass flowmeters. The reaction was stopped through addition of methanol. The precipitated polymer was stirred in a mixture of methanol and hydrochloric acid overnight. The polymer was filtered, washed with methanol and dried via vacuum.

3. Results and discussion

The influence of MAO is not yet fully understood. As so far known, a first rate increasing effect of the MAO compound is overcompensated at high [Al]/[Zr]-ratios through a rate inhibiting effect, Fig. 2a and b [8].

Fig. 2a and b demonstrate the ethylene and propylene polymerization rate with $Me_2C[CpFlu]ZrCl_2/MAO$ and the $Me_2Si[Ind]_2ZrCl_2/MAO$ catalyst systems in dependence on the ratio [Al]/[Zr]. The polymerization rate passes through a maximum with both catalyst systems and both monomers. But this maximum appears with the $Me_2Si[Ind]_2ZrCl_2$ catalyst in ethylene polymerization at a [Al]/[Zr]-ratio of 27 000/1 and in propylene polymerization at a [Al]/[Zr]-ratio of 11 000/1. With the $Me_2C[CpFlu]ZrCl_2$ catalyst, however, the maxima appear at smaller [Al]/[Zr]-ratios, namely 5100/1 in the ethylene polymerization and 1300/1 in the propylene polymerization. We suggested the inhibiting effect of MAO may be due to a blocking of the active zirconocene center through the complexed MAO compound. Through the more intensive interaction between metallocene and MAO compound (tight contact pair) at higher [Al]/[Zr]-ratios, the space available for the monomer addition becomes smaller. Therefore, for both catalyst systems, the rate maximum appears at higher [Al]/[Zr]-ratios in

the ethylene polymerization than in propylene polymerization. Furthermore, the catalysts have different ligand geometry. The $Me_2C[CpFlu]$-ligand has a shorter bridge and therefore, a larger angle between the planes of the π-ligand systems than the $Me_2Si[Ind]_2$-ligand. Therefore, in the $Me_2C[CpFlu]ZrCl_2$, the Zr atom is less shielded by the ligand system and the interaction with the MAO compound is still more efficient. Hence, and again as a consequence of the tight contact pair between Zr and MAO compound, the maxima appear at much lower [Al]/[Zr]-ratios with the $Me_2C[CpFlu]ZrCl_2$ catalyst for both monomers.

Using the $Me_2C[3\text{-}MeCpFlu]ZrCl_2/MAO$ catalyst system for propylene polymerization, the rate maximum appears at a still lower ratio [Al]/[Zr] of 500/1. It seems that the Cp-ring methyl group acts as an additional hindrance and so confirms the specific shielding effect of the MAO compound.

In this context, it was interesting to see how the ratio [Al]/[Zr] acts in the polymerization with the two catalysts with the more bulky Cp-ring *t*-butyl group shown in Fig. 1.

In Figs. 3 and 4 the dependency of the propylene polymerization rate on the ratio [Al]/[Zr] for two different metallocenes, namely $Me_2C[3\text{-}t\text{-}BuCpFlu]ZrCl_2$ and $Me_2Si[3\text{-}t\text{-}BuCpFlu]ZrCl_2$, is shown.

In both cases, the increasing effect of the MAO at low [Al]/[Zr]-ratios is not overcompensated at higher ratios, and after reaching the maximum polymerization rate at a [Al]/[Zr]-ratio of 750/1 in case of the $Me_2C[3\text{-}t\text{-}BuCpFlu]ZrCl_2/MAO$-system and 6700/1 in case of $Me_2Si[3\text{-}t\text{-}BuCpFlu]ZrCl_2/MAO$-system, the polymerization rate is independent of the amount of MAO.

Obviously, the bulkier *t*-butyl group is able to prevent the building of a tight contact ion pair because of sterical reasons. Therefore, the blocking of the active zirconocene center is suppressed.

Using the $Me_2C[3\text{-}i\text{-}PrCpFlu]ZrCl_2/MAO$ catalyst system for propylene polymerization,

Fig. 5, a maximum polymerization rate is reached again but now at ratio [Al]/[Zr] of 210/1. However, the polymerization rate maximum is followed by a slow decrease of the polymerization rate.

It is remarkable that the activity of the metallocenes decreases with increasing size of the substituent at the Cp ring, Fig. 6.

These kinetic results will be explained after the discussion of the role of the different aluminium alkyls during the polymerization.

3.1. Polymerization with MAO / TMA

Systematic investigations were carried out on the effect of TMA on the metallocene activity and the molecular weight of the polypropylene. For these experiments, the cocatalyst MAO was successively replaced through TMA, without altering the total quantity of the cocatalyst, measured as the aluminium concentration. Fig. 7 shows the effect of TMA on the maximum polymerization rate of the system $Me_2Si[2-Me-$

(a) $v_p/([Zr] \cdot [monomer])$ [L/mols]

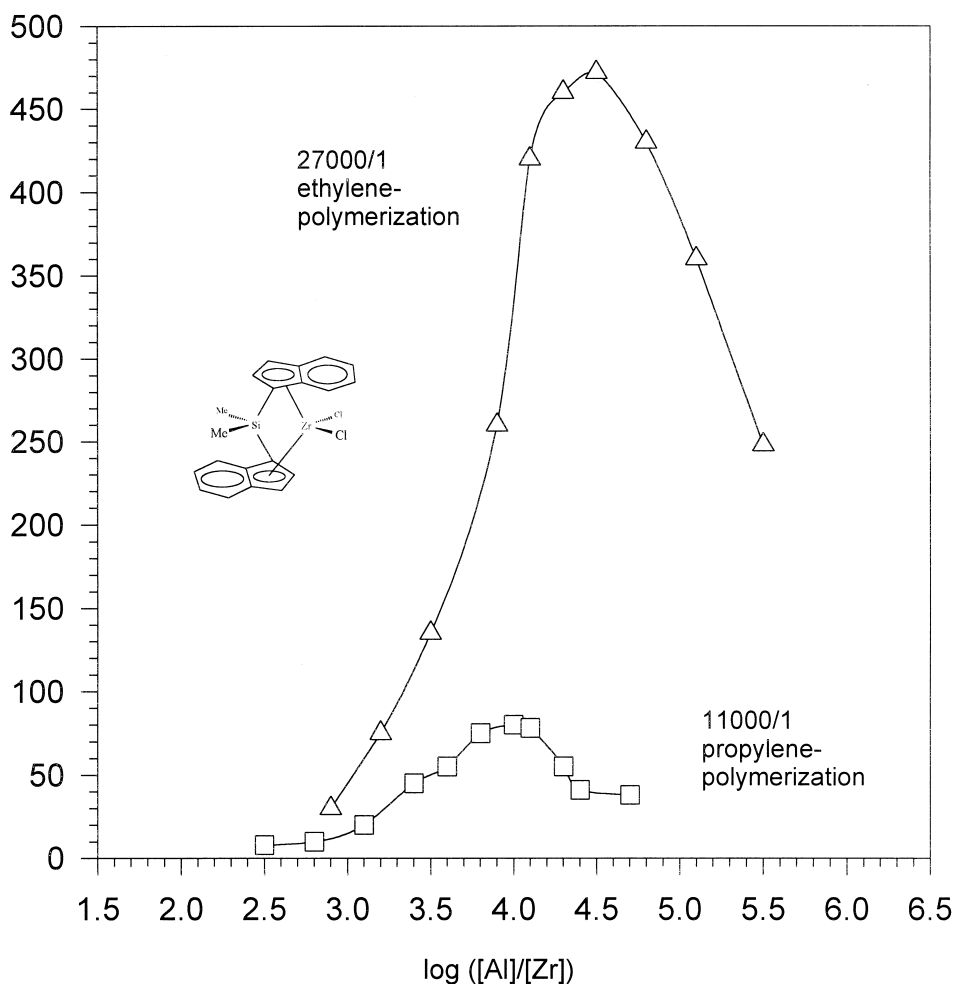27000/1 ethylene-polymerization

11000/1 propylene-polymerization

Fig. 2. (a) Ethylene and propylene polymerization rate in dependence on the ratio [Al]/[Zr] with $Me_2Si[Ind]_2ZrCl_2$/MAO. (b) Ethylene and propylene polymerization rate in dependence on the ratio [Al]/[Zr] with $Me_2C[FluCp]ZrCl_2$/MAO.
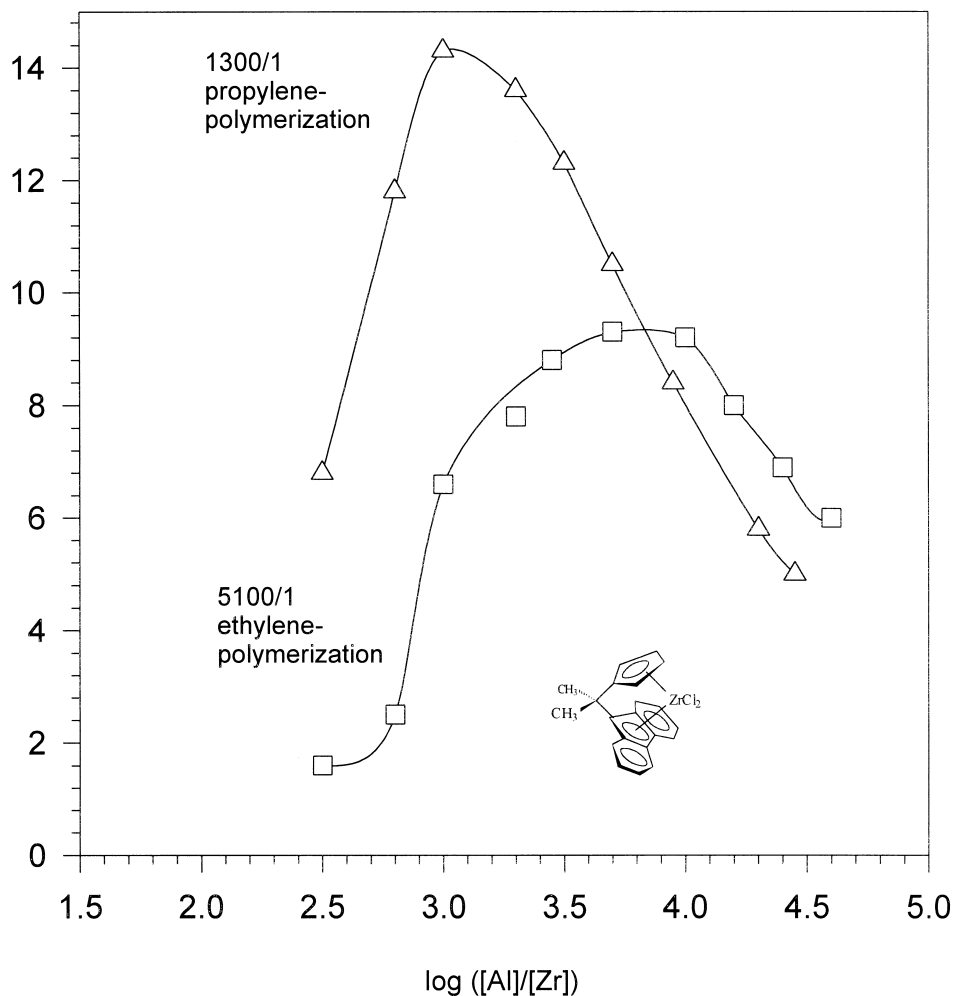
(b) $v_p/([Zr] \cdot [monomer])$ [L/mols]

Fig. 2 (continued).

4,5-BenzoInd]$_2$ZrCl$_2$/MAO/TMA for two different [Al]/[Zr]-ratios.

As expected, the maximum polymerization rate decreases with increasing quantity of added TMA. It is known that TMA has a deactivating effect on the polymerization by means of metallocene catalysts [9]. With 100% [Al] of TMA (0% [Al] of MAO), as expected, no further polymerization occurs.

The molecular weights of the polypropylenes (Table 1), which were produced with the system Me$_2$Si[2-Me-4,5-BenzoInd]$_2$ZrCl$_2$, decrease with increasing TMA content. This effect is particularly noticeable with a high ratio of [Al]/[Zr].

The replacement of MAO through TMA shows no effect on the molecular weight distribution of the polymers.
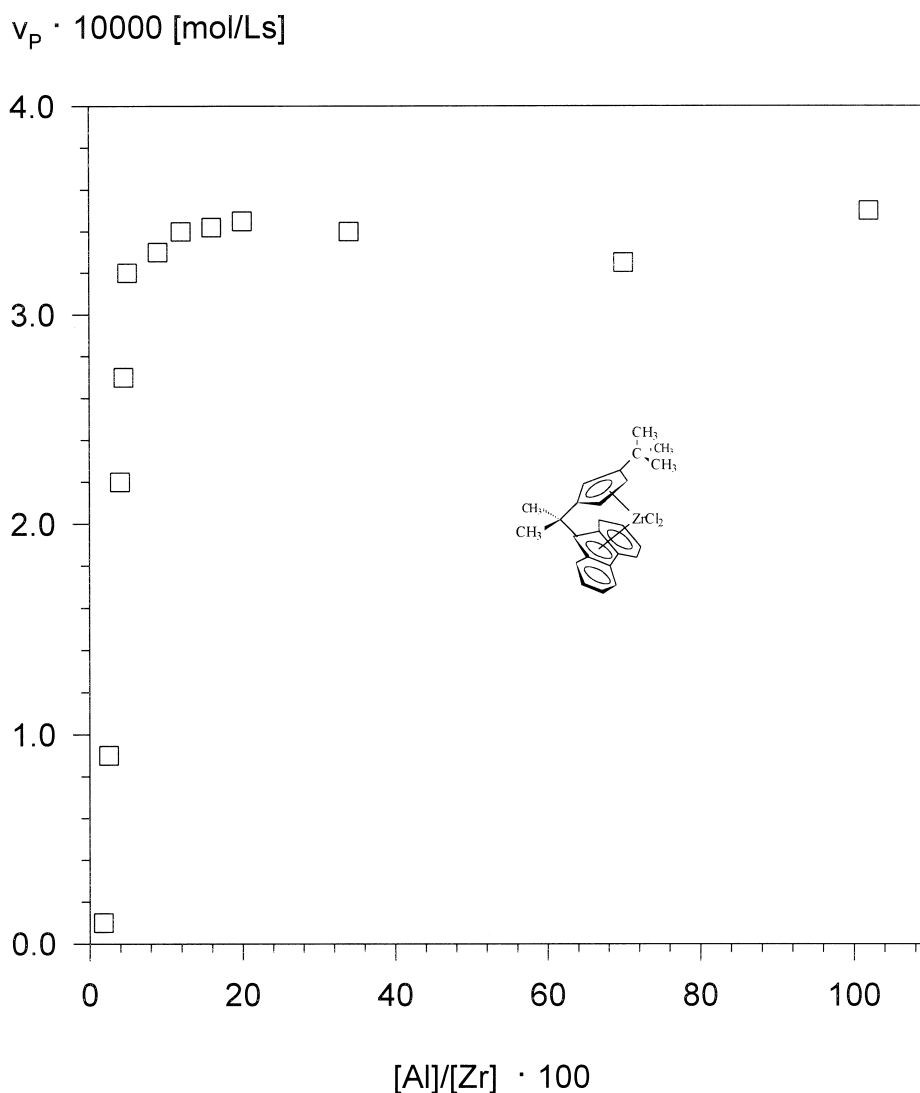
$v_P \cdot 10000$ [mol/Ls]

Fig. 3. Propylene polymerization rate independence on the ratio [Al]/[Zr] with $Me_2C[3\text{-}t\text{-}BuCpFlu]ZrCl_2$/MAO. Polymerization conditions: $p = 2$ bar, $T_p = 25°C$, [Zr] $= 4.4 \times 10^{-5}$ mol/l, solvent = toluene.

3.2. Polymerizations with MAO / ALR₃

The question arises now: what effect would other aluminium alkyls frequently used in Ziegler polymerization have on the polymerization? For this reason, additional investigations were carried out with the system $Me_2Si[2\text{-}Me\text{-}4,5\text{-}BenzoInd]_2ZrCl_2$, whereby MAO was now replaced for TIBA while retaining the total concentration of the cocatalyst. The investigations showed an increase in activity by an approximate factor of two, Fig. 8. This is even more

surprising, since the ratio [Al]/[Zr] in relation to the cocatalyst MAO was far below the optimum ratio. [1]

Additional polymerization should provide an indication of the extent by which the steric

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[1] The optimum [Al]/[Zr]-ratio of the system $Me_2Si[2\text{-}Me\text{-}4,5\text{-}BenzoInd]_2ZrCl_2$/MAO referring to 100% [Al] from MAO is 1715/1 [10]. The maximum rise in activity of the system $Me_2Si[2\text{-}Me\text{-}4,5\text{-}BenzoInd]_2ZrCl_2$/MAO/TIBA can be seen with about 70% [Al] from TIBA and 30% [Al] from MAO.
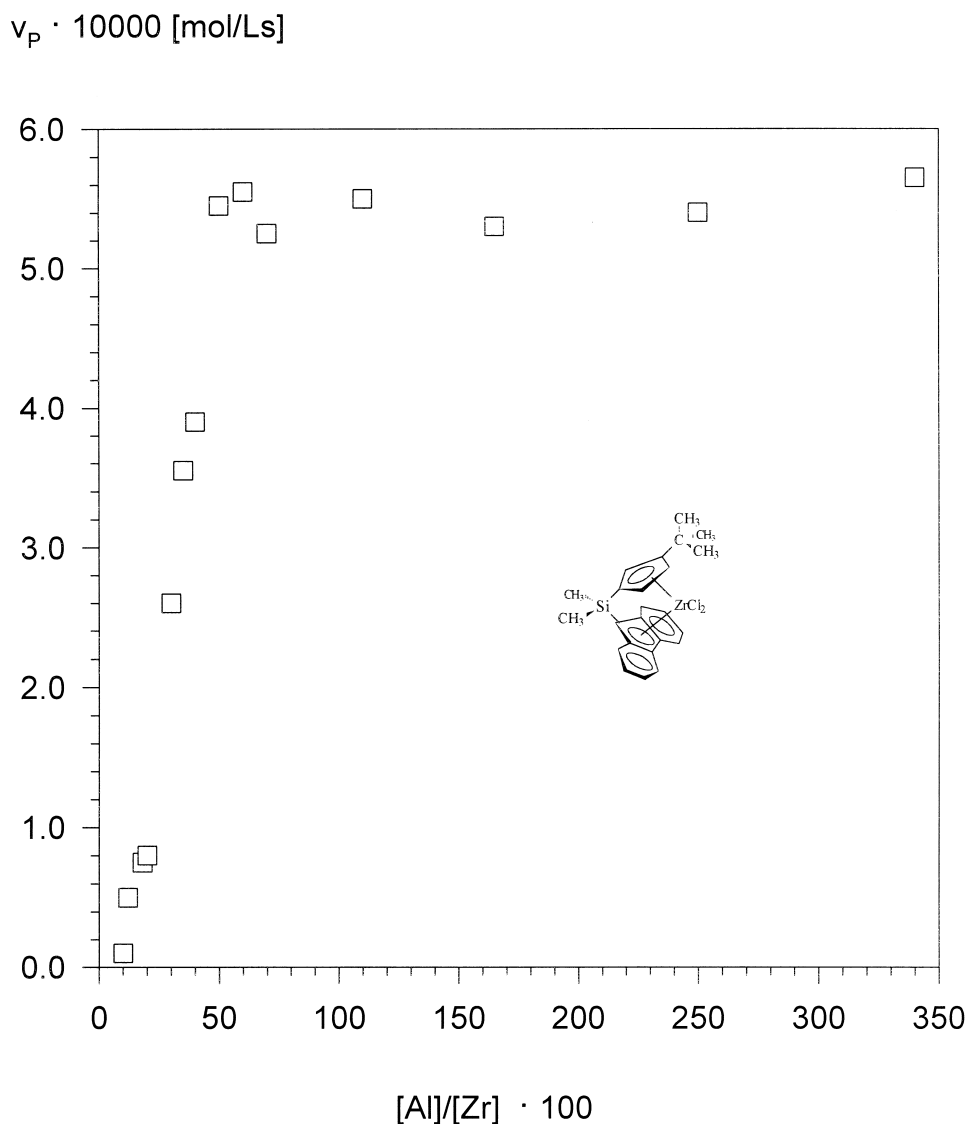
Fig. 4. Propylene polymerization rate independence on the ratio [Al]/[Zr] with Me$_2$Si[3-t-BuCpFlu]ZrCl$_2$/MAO. Polymerization conditions: p = 2 bar, T_p = 25°C, [Zr] = 1.8 × 10^{-5} mol/l, solvent = toluene.

demand of the aluminium alkyls exerts an effect on the increase in activity. The pertinent investigations for TEA and TBA are shown in Fig. 9.

Interestingly, only aluminium alkyls of medium size (TIBA, TBA) have an activating effect. [2] Deactivation occurs with TEA.

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[2] Maximum rise in activity of the system Me$_2$Si[2-Me-4,5-BenzoInd]$_2$ZrCl$_2$/MAO/TBA can be seen with about 44% [Al] from TBA and 56% [Al] from MAO.

The effect of the aluminium alkyls on the molecular weights of the polypropylenes is very different (Table 2); when the polymerizations were carried out with TEA, the molecular weights of the polypropylenes decreases dramatically. A weaker decrease in molecular weight is observed where polymerization takes place with TIBA and TBA, respectively.

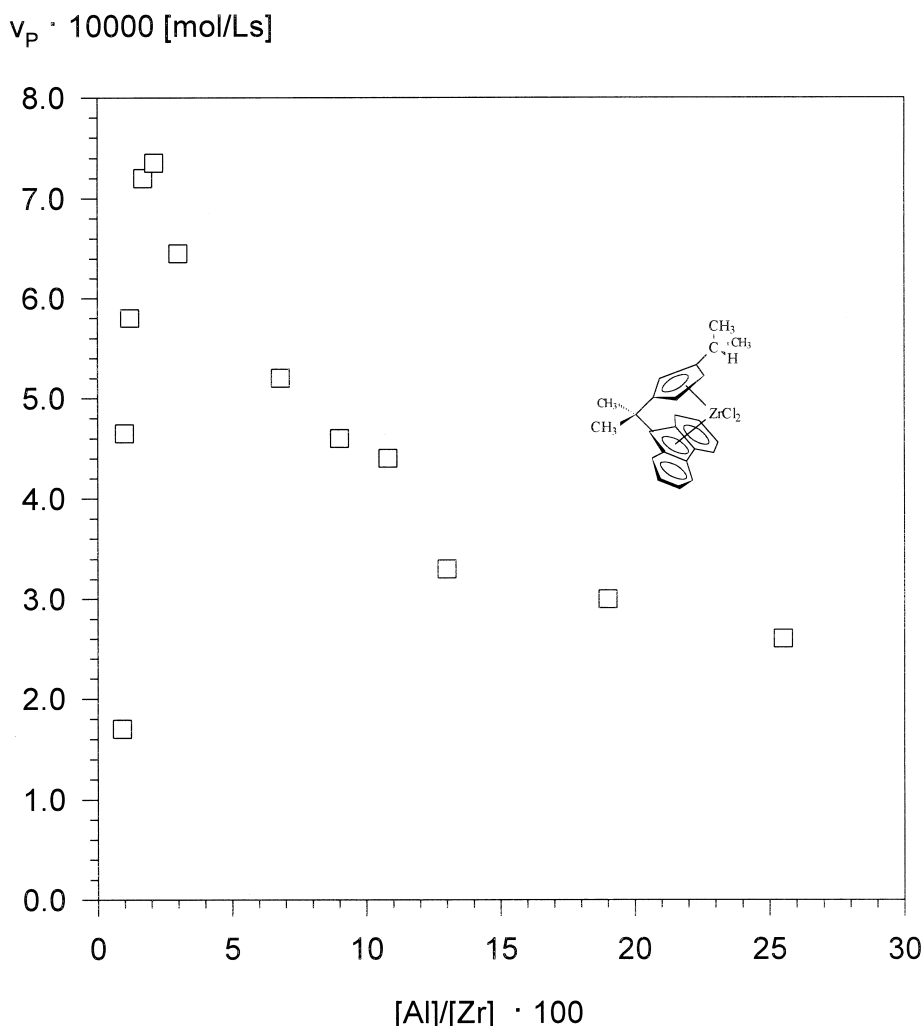The general accepted role of MAO during polymerization with metallocenes is the meth-

$v_P \cdot 10000$ [mol/Ls]

Fig. 5. Propylene polymerization rate in dependence on the ratio [Al]/[Zr] with $Me_2C[3\text{-}i\text{-}PrCpFlu]ZrCl_2/MAO$. Polymerization conditions: $p = 2$ bar, $T_p = 25°C$, [Zr] $= 7.4 \times 10^{-5}$ mol/l, solvent = toluene.

ylation of the metallocene and the abstraction of one methyl group, forming a cationic 'active species'. Deactivation occurs when the 'active species' reacts with one molecule of TMA to form a bimetallic complex, Fig. 10. [3]

These bimetallic complexes were investigated by Bochmann and were spectroscopically proven by NMR for the catalyst $Me_2Si[Ind]_2$-$ZrCl_2$ [9]. They are coordinately saturated and do not posses any free orbitals for the coordination of an olefin. A polymerization can only arise after dissociation of the bimetallic complex. Accordingly, the polymerization activity should decrease with an increasing TMA concentration. Bochmann detected for the system $Me_2Si[Ind]_2ZrMo_2/B(C_6F_5)_3/TMA$ a maximum of productivity at an [Al]/[Zr]-ratio of 1/1, while the productivity declines to about one fortieth through a 100-fold excess of TMA.

Intense research by Ziegler et al. [11] and Lehmkuhl and Ziegler [12], Hoffmann [13], Yamamoto and Hayamizu [14] and Rottler et al.
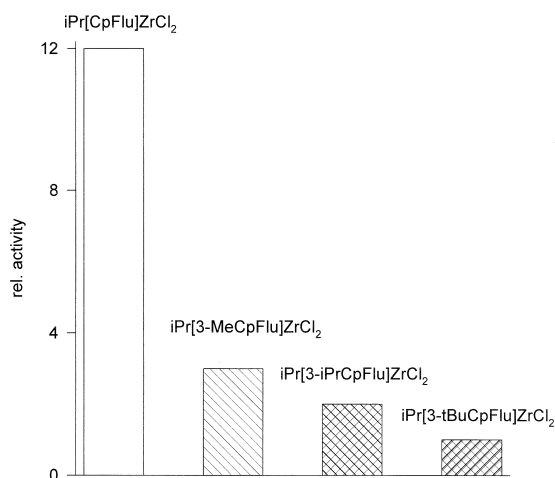
Fig. 6. Relative activities for different metallocenes of the general formula $Me_2C[RCpFlu]ZrCl_2$, where R is H, Me, *i*-propyl or *t*-butyl.

Table 1
Molecular weights of the polypropylene produced with $Me_2Si[2-Me-4,5-BenzoInd]_2ZrCl_2$ /MAO/TMA

% Al from TMA [Al]/[Zr] = 15500/1	M_w	% Al from TMA [Al]/[Zr] = 1715/1	M_w
0	665000	0	645000
21	453000	22	620000
50	365000	44	653000
70	353000	66	514000
89	305000	80	420000

Polymerization conditions: $p = 2$ bar, $T_p = 25°C$, $[Zr] = 6.0 \times 10^{-6}$ mol/l, solvent = toluene.

[15] dealt with the alkyl group exchange of aluminium alkyls. The mixed aluminium alkyls cannot be depicted in substance, but they can be verified by means of ^{1}H-NMR and ^{13}C-NMR
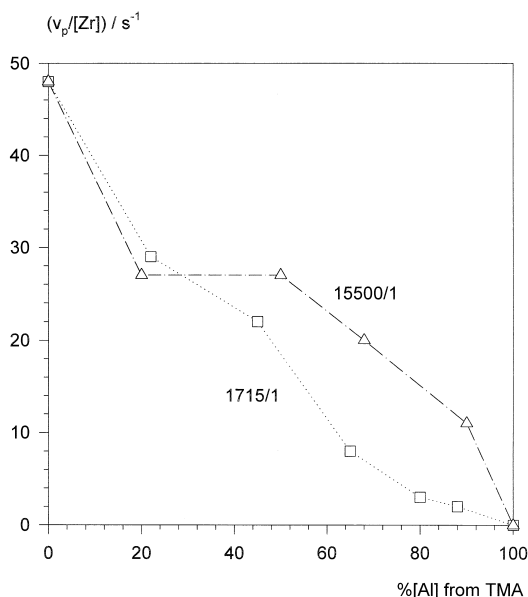

Fig. 7. Dependency of the polymerization rate on exchanged quantity of TMA for the system $Me_2Si[2-Me-4,5-BenzoInd]_2ZrCl_2$ with two different [Al]/[Zr]-ratios: 1715/1 and 15500/1. Polymerization conditions: $p = 2$ bar, $T_p = 25°C$, $[Zr] = 6.0 \times 10^{-6}$ mol/l, solvent = toluene.

spectroscopy. The ligand exchange takes place through dimeric aluminium complexes. For a mixture of TMA/TEA, the exchange takes place so rapidly that signals for the terminal and bridge building methyl and methylene groups, respectively, can only be detected at very low temperatures. Depending on the concentration ratio for a TMA/TIBA mixture, different mixed dimeric compounds could already be detected at room temperature. For steric reasons, methyl groups occur primarily in the bridge positions. However, with a high excess of TIBA, at least one of the two bridge positions can contain an isobutyl group, Fig. 11. When both bridge positions consist of an isobutyl group, the complex becomes unstable and disintegrates [13].

From ^{1}H-NMR investigations, Yamamoto and Hayamizu [14] proposed a bridge building factor for the tendency of an alkyl group to act as bridge for the series methyl:ethyl:*n*-propyl:*i*-butyl like 1:1/6:1/7:1/17. This tendency is based primarily on steric factors, and it can be concluded that the ability for intermolecular ligand exchange of the aluminium alkyls decreases in the sequence TMA > TEA > TIBA $\approx$ TBA. In addition, it can be presumed that the inhibition of the metallocenes also decreases for steric reasons in this sequence.

The consequences for the polymerization active species, are (a) TMA/TEA: The activated catalyst can be deactivated through the forma-
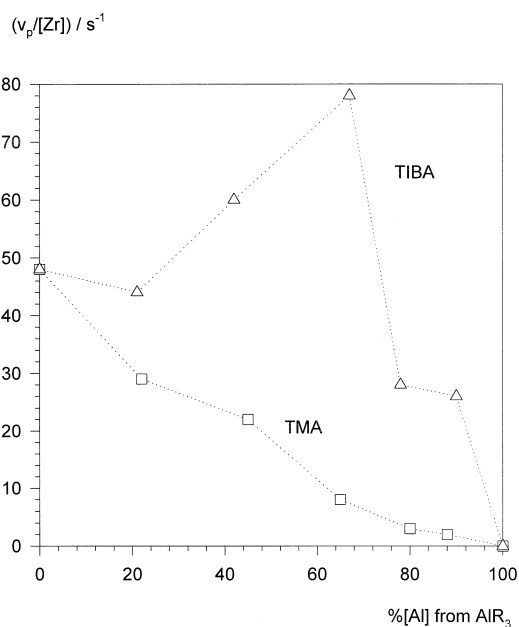
$(v_p/[Zr]) / s^{-1}$

Fig. 8. Dependency of the polymerization rate on exchanged quantity of TMA and TIBA, respectively, for the system $Me_2Si[2$-Me-4,5-BenzoInd$]_2ZrCl_2$. Polymerization conditions: $p = 2$ bar, $T_p = 25°C$, $[Al]/[Zr] = 1715/1$, $[Zr] = 6.0 \times 10^{-6}$ mol/l, solvent = toluene.

$(v_p/[Zr]) / s^{-1}$

Fig. 9. Dependency of the polymerization rate on the replaced quantity of TEA and TBA for the system $Me_2Si[2$-Me-4,5-Benzo-Ind$]_2ZrCl_2$. Polymerization conditions: $p = 2$ bar, $T_p = 25°C$, $[Zr] = 6.0 \times 10^{-6}$ mol/l, solvent = toluene.

tion of a bimetallic complex both with TMA, TEA as well as the mixed compounds $MeAlEt_2$ and Me_2AlEt. (b) TMA/TIBA: The active species can only be deactivated by TMA of the MAO solution. A part of the TMA is however trapped by the reaction with TIBA. $MeAl(i$-Bu$)_2$ and $Me_2Al(i$-Bu$)$ are formed as well as the abovementioned dimeric aluminium compounds in equilibrium. Due to their size, a smaller amount of $MeAl(i$-Bu$)_2$ and $Me_2Al(i$-Bu$)$ react with the active species. TIBA as well as TBA act also as a trapping reagent for the poly-merization inhibiting TMA.

Hence, the increase in activity in propylene polymerization with the addition of TIBA and TBA, respectively, can be explained by means of intermolecular ligand exchange, Fig. 12.

These results now allow an explanation for the different behavior of the different substi-tuted metallocenes by means of the dependency
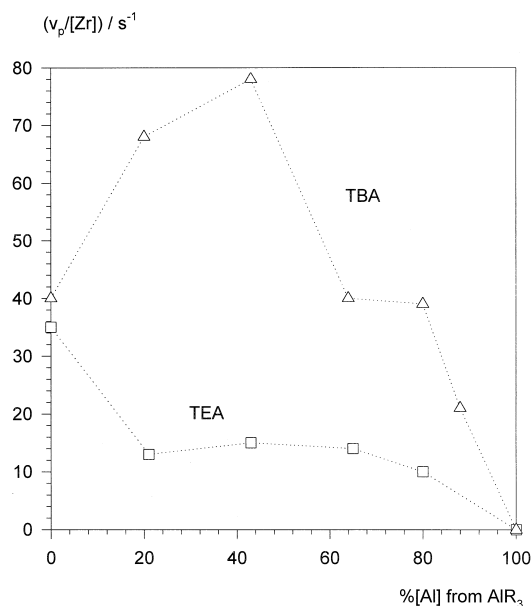
of the polymerization rate on the cocatalyst amount.

Fig. 13 shows a schematic comparison of the polymerization rate in dependence on the MAO amount for the four different above described metallocenes.

In the metallocene with the bulky Cp-ring t-butyl group and also, in a smaller extent, in

Table 2
Molecular weights of the polypropylene produced with $Me_2Si[2$-Me-4,5-BenzoInd$]_2ZrCl_2/MAO/AlR_3$

% Al from TEA	M_w	% Al from TIBA	M_w	% Al from TBA	M_w
0	572 000	0	642 000	0	558 000
22	181 000	22	537 000	22	542 000
44	132 000	44	530 000	44	457 000
66	98 800	66	665 000	66	341 000
80	98 400	80	747 000	80	370 000
		88	574 000	88	336 000

Polymerization conditions: $p = 2$ bar, $T_p = 25°C$, $[Zr] = 6.0 \times 10^{-6}$ mol/l, $[Al]/[Zr] = 1715/1$, solvent = toluene.

Activation:

MAO

"active species"
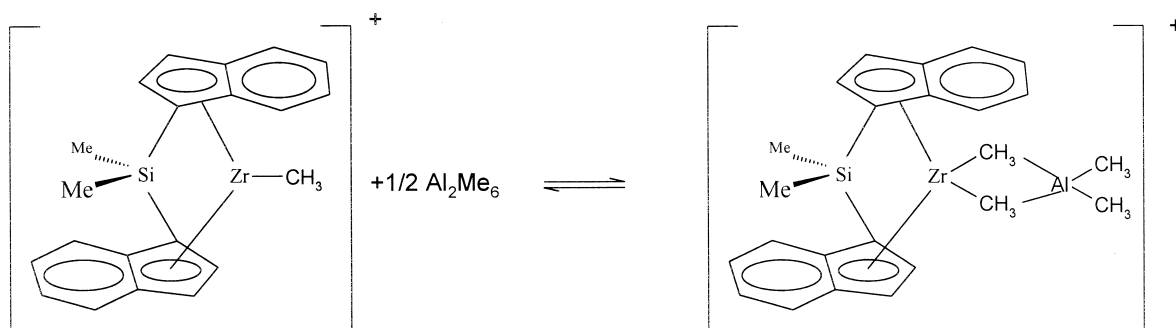
Deactivation:

+1/2 Al$_2$Me$_6$ ⇌
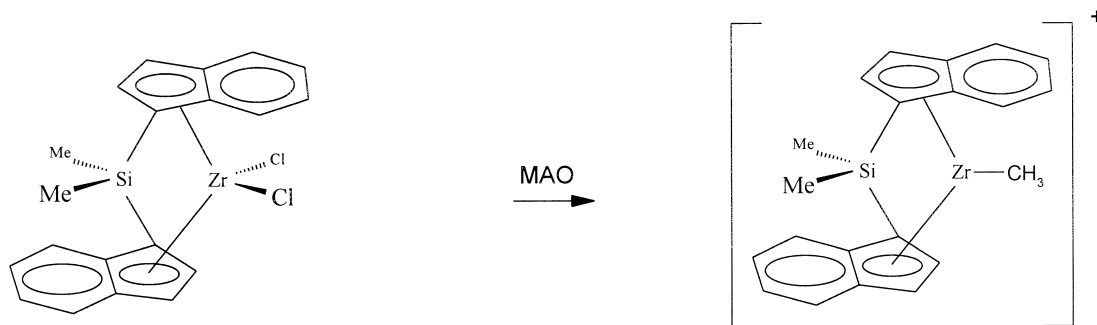
Fig. 10. Mechanism of the metallocene activation and deactivation, respectively.

the catalyst with the Cp-ring i-propyl group, the active center is strong shielded; therefore, the deactivation reaction through the TMA in a
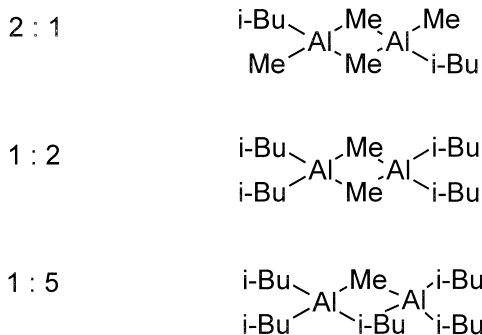
TMA : TIBA

2 : 1

1 : 2

1 : 5

Fig. 11. Dimeric aluminium compounds in a TMA/TIBA solution as function of the concentration ratio.

toluene/MAO solution is suppressed. Because of this there is no decrease in the polymerization rate with increasing amount of MAO for the Me$_2$C[3-t-BuCpFlu]ZrCl$_2$/MAO system. In the case of the Me$_2$C[3-i-PrCpFlu]ZrCl$_2$/MAO system, there is a flat decrease of the polymerization rate with increasing the amount of the cocatalyst. Here, the active center is less shielded and therefore, the deactivation reaction can occur in a smaller extent. Using the Me$_2$C[3-MeCpFlu]ZrCl$_2$/MAO system and the Me$_2$C[CpFlu]ZrCl$_2$/MAO system, the active center is no more shielded; therefore, the deactivation reaction as shown in Fig. 10 takes place after the maximum polymerization rate is reached. The first rate increasing effect of the MAO is overcompensated here through the deactivation reaction of the TMA in a toluene MAO solution.

$$\frac{1}{2}\,Al_2Me_6 \ +\frac{1}{2}\,Al_2R_6 \ \Longleftrightarrow \ \underset{H_3C}{\overset{H_3C}{\diagdown}}Al\overset{CH_3}{\underset{R}{\diagup\diagdown}}Al\overset{R}{\underset{R}{\diagup\diagdown}} \ \Longleftrightarrow \ Me_2AlR \ + \ MeAlR_2$$

deactivation through
TMA, TEA, Me$_2$AlEt

R = Et

MeAlEt$_2$
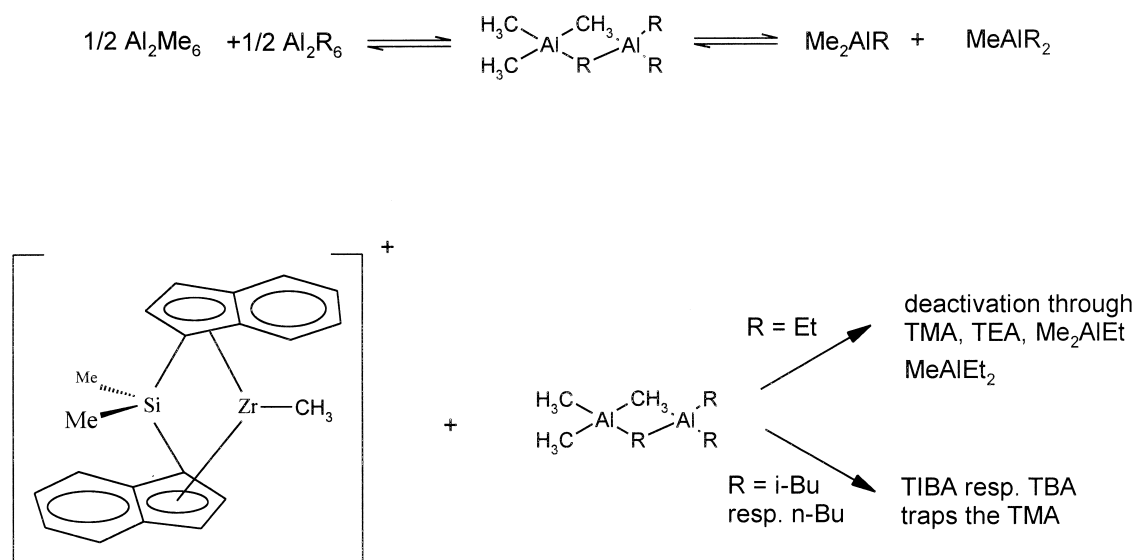
R = i-Bu
resp. n-Bu

TIBA resp. TBA
traps the TMA

Fig. 12. Mechanism of the activating and deactivating, respectively, effect of the aluminium alkyls during propylene polymerization with metallocenes.
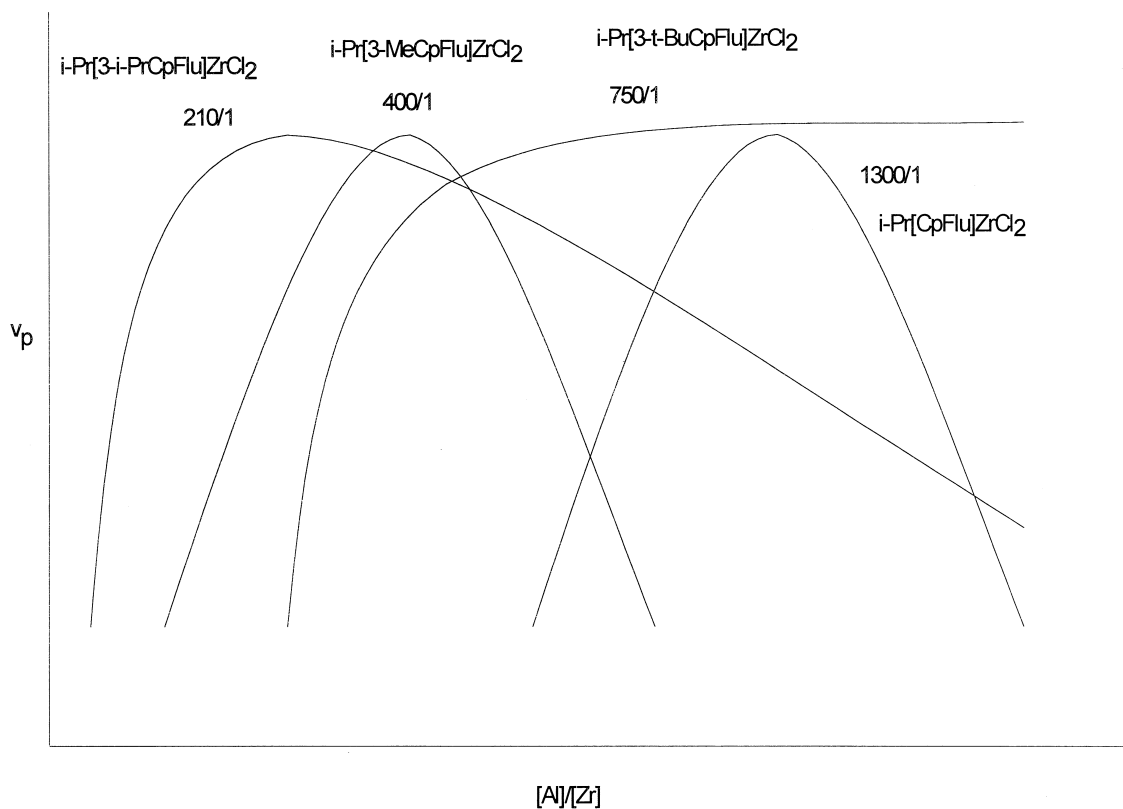

Fig. 13. Dependency of the polymerization rate on the [MAO]/[Zr]-ratio for different metallocenes (schematic).

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