[1] Institut für Anorganische Chemie, Universität Tübingen,
Auf der Morgenstelle 18, D-72076 Tübingen, Germany
[2] Institut für Anorganische und Analytische Chemie, Technische Universität Berlin,
Straße des 17. Juni 135, D-10623 Berlin, Germany

Concentration effects of methylalumoxane, zirconocene dichloride and trimethylaluminum in ethylene polymerization

Bernhard Rieger[1], Christoph Janiak[2]*

(Received 26 May 1993)

SUMMARY:

A quantitative study was carried out on the homogeneous zirconocene dichloride/methylalumoxane/trimethylaluminum (Cp_2ZrCl_2/MAO/TMA) catalyst system in ethylene polymerization. The effects of variation of the Al_{MAO}/Zr ratio, absolute Zr concentration, and addition of TMA on ethylene polymerization activity and polymer properties were investigated. The polymerization profiles for small Al_{MAO}/Zr ratios and the changes with the Zr concentration are explained with a complexation equilibrium for the active homogeneous complex and with the change to a heterogeneous catalyst upon polymer precipitation. Good polymer productivities can be achieved at Al_{MAO}/Zr < 1000 when working at Zr concentrations between 10^{-4} and 10^{-5} mol/l with addition of TMA (Al_{MAO}/Al_{TMA} ≈ 1.4).

ZUSAMMENFASSUNG:

Das homogene Katalysatorsystem Zirconocendichlorid/Methylalumoxan/Trimethylaluminium (Cp_2ZrCl_2/MAO/TMA) wurde bezüglich des Einflusses der Variation des Al_{MAO}/Zr-Verhältnisses, der absoluten Zr-Konzentration und der Addition von TMA auf die Polymerisationsaktivität von Ethylen und die Polymereigenschaften untersucht. Die Polymerisationsprofile bei kleinen Al_{MAO}/Zr-Verhältnissen und die Änderungen mit der Zr-Konzentration werden mit einem Komplexierungsgleichgewicht für den aktiven homogenen Katalysator und mit einem Wechsel zu einem heterogenen Katalysator aufgrund der Polymerabscheidung während der Polymerisation erklärt. Gute Polymerproduktivitäten werden mit Al_{MAO}/Zr < 1000 bei Zr-Konzentrationen zwischen 10^{-4} und 10^{-5} mol/l und Zugabe von TMA (Al_{MAO}/Al_{TMA} ≈ 1.4) erreicht.

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*   Correspondence author.

1 Introduction

Homogeneous, single-site metallocene/methylalumoxane catalysts are of high academic and industrial interest as a new generation of Ziegler-Natta catalysts[1,2]. This new catalyst technology is on the verge of commercialization and advantageously combines high activity with the possibility to tailor polymer properties such as molecular weight, molecular weight distribution, comonomer insertion and distribution, as well as stereoregularity of α-olefin polymers through a rational ligand design at the transition metal center.

So far, the main emphasis in research has been placed on understanding the (transition metal) ligand-polymer relationship. Little attention has been paid to the methylalumoxane (MAO) co-catalyst which is necessary for the high activity of the metallocene. A large excess of MAO is normally employed for the activation of the metallocene pre-catalyst, with Al to transition metal ratios ranging from 1 000:1 to 10000:1 and beyond[3−5]. Thus, the methylalumoxane becomes the actual cost factor in the metallocene/MAO system[6].

No explanation has been given, yet, as to the origin of such a large excess of MAO, aside from increasing the catalyst activity. The role of the methylalumoxane in the activation of the transition metal complex has also not been completely understood and can only be described as a combination of alkylation reagent for the transition metal[7], scavenger towards impurities and stabilizing agent for the metallocene cation via an assumed host-guest or crown-alumoxane complex[8].

Furthermore, effects of aluminum alkyl additions to a metallocene/MAO system have not been clearly elucidated. Chien and Wang[9] only showed that for a total Al:Zr ratio of 1 070:1 (in Cp_2ZrCl_2/MAO) up to 90% of the MAO could be replaced by trimethylaluminum (TMA) without loss in polymerization activity towards ethylene. When the same MAO-TMA replacement was, however, carried out in the system rac-Et(Ind)$_2$ZrCl$_2$/MAO, a drastic loss in polymerization activity towards propylene was observed[8].

Our intention is to correlate the Al_{MAO} : Al_{TMA} : Zr ratio and concentrations with activity and effect on polymer properties in the polymerization of ethylene. Practical implications of this study are given by attempts to lower the MAO:transition metal ratio[10] and to replace the expensive methylalumoxane co-catalyst by cheaper aluminum alkyls.

2 Experimental

2.1 Materials

Ethylene (BASF AG) was polymerization grade and used without further purification. Cp_2ZrCl_2 (98 + %, Aldrich) was applied as a toluene solution with one of the following concentrations: 1 g, 0.1 g, or 0.01 g of Cp_2ZrCl_2/100 ml solution. Methylalumoxane was purchased from Schering AG (now Witco, Bergkamen, Germany) as a 10 wt.-%-toluene solution (5.75 wt.-% aluminum, density ≈ 0.9 g/ml, average molecular weight of the MAO oligomers $900-1\,100$). Trimethylaluminum was used as a 1 M toluene solution. Toluene was refluxed over sodium metal for several hours, followed by distillation and storage under nitrogen.

All experiments were carried out with standard Schlenk and vacuum techniques under inert gas. Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC, Waters 150 chromatograph) at 140 °C in 1,2,4-trichlorobenzene.

2.2 Polymerization procedures

2.2.1 Polymerization at 6 or 10 bar

In a typical experiment a 1-L glass autoclave was charged with 490 ml of toluene, the argon atmosphere was pumped off and replaced by ethylene. When the preset reaction temperature of 80 °C or 110 °C was reached, the chosen amounts of TMA (from a 1 M toluene solution) and MAO (0.16 M in toluene) were injected, followed by a zirconocene dichloride solution ($3.4 \cdot 10^{-3}$ M in toluene). After an activation time of 2 to 3 min the autoclave was pressurized to 6 or 10 bar and after 1 h the reaction was stopped by draining the toluene/polyethylene solution-slurry into acidified water. The polymer was dried by azeotropically distilling off the toluene.

2.2.2 Polymerization at 1 bar

Method A: A 1-L round-bottom flask equipped with a gas inlet was charged with Cp_2ZrCl_2 (29 mg, 10^{-4} mol) and trimethylaluminum ($5 \cdot 10^{-2}$ mol in toluene). Toluene was added to a total volume of 300 ml, then the mixture was allowed to prereact for 20 min and was thermostatted at 60 °C. After saturating the toluene solution with ethylene, methylalumoxane was added stepwise via a canula and septum in units of 10^{-3} mol (0.64 ml of a 10%-toluene solution, corresponding to an Al_{MAO}:Zr ratio of 10:1) and the polymerization activity was followed by the ethylene uptake.

Method B: A 1-L round-bottom flask equipped with a gas inlet was charged with Cp_2ZrCl_2 (29 mg, 10^{-4} mol) and methylalumoxane ($7 \cdot 10^{-3}$ mol in toluene). Toluene was added to a total volume of 300 ml, then the mixture was allowed to activate for 20 min and was thermostated at 60 °C. After addition of the chosen amount of trimethylaluminum the polymerization was started.

3 Results and discussion

3.1 Al_{MAO}:Zr ratio

Although Cp_2ZrCl_2/MAO has been described as a polymerization catalyst in several publications, there is still a lack of knowledge concerning certain factors which influence the polymerization, one being the concentration dependence[9]. The activity of the Cp_2ZrCl_2/MAO catalyst seems to increase indefinitely with the increase of the Al:Zr ratio[4, 9, 11, 12]. A comparison of the time-activity profiles for different Al_{MAO}:Zr ratios in Fig. 1 and Tab. 1 illustrates the increase in activity with increasing MAO content. The curves

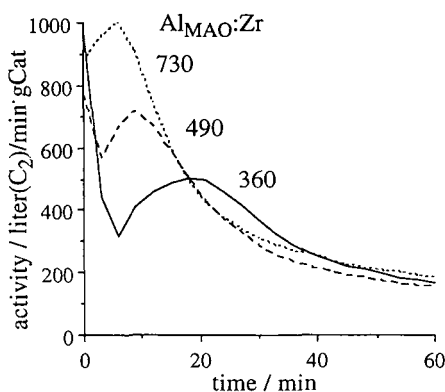Fig. 1. Polymerization profiles for different Al_{MAO}:Zr molar ratios in the ethylene polymerization with Cp_2ZrCl_2/MAO/TMA (T = 110 °C, ethylene pressure = 6 bar, 500 ml toluene, $[Cp_2ZrCl_2]$ = 10^{-5} mol/l, Al_{TMA}:Zr = 1 000, polymerization time = 1 h). (Note: TMA had to be added as a scavenger; with no TMA present, the MAO-alone productivity at e. g. the highest Al_{MAO}:Zr molar ratio given here dropped to 20%, with Al_{TMA}:Zr = 500, the productivity became 75% of the reported value; cf. section 3.3, Fig. 4).

Tab. 1. Dependence of catalyst productivity and molecular weight of polyethylene on the Al_{MAO}:Zr ratio in the ethylene polymerization with Cp_2ZrCl_2/MAO/TMA. For experimental conditions see Fig. 1.
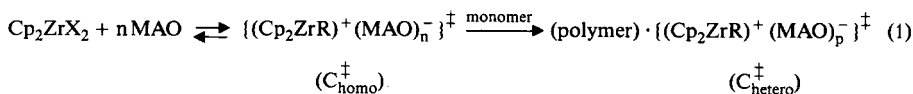
Al_{MAO}:Zr (mol:mol)	Productivity (gPE/gZr · h)	M_w	M_n	M_w/M_n
360	$7.9 \cdot 10^4$	45 900	14 500	3.2
490	$9.0 \cdot 10^4$	38 400	11 200	3.4
730	$10.8 \cdot 10^4$	44 200	13 200	3.3

show also that the activity increase occurs only within the first 20 min or even shorter time periods for higher Al_{MAO}:Zr ratios and constant Zr concentrations.

The activity maximum is followed by a steady decline, such that the higher the maximum, the steeper the decrease in activity. After about 20 min the activity profiles are the same within experimental error, regardless of the initial Al_{MAO}:Zr ratio. This observation could be explained by at first a reversible, followed by an irreversible deactivation of the catalytically active center[13]. A faster irreversible catalyst poisoning due to impurities can be accounted for by the higher gas uptake (including impurities) in a shorter time period if the catalyst is more active. Such a reversible/irreversible decay surely plays a role for the decrease in activation, but for the polymerization of ethylene we would like to offer an additional explanation here:

The polymerization is truly homogeneous only in the very beginning. Even at the reaction temperature of 110°C, a highly viscous solution with partial polymer precipitation forms rapidly, all the faster the more active the catalyst. Having the active complex embedded in a polymer matrix represents a transfer to a heterogeneous phase, i. e. a heterogeneous active complex forms and leads to a diffusion-controlled polymerization. The reaction is then controlled by diffusion processes of the monomer through the polymer matrix to the enclosed active center[14, 15]. The time-activity profiles should then only show a steady decline starting from a maximum at t = 0. This is indeed the case for very large Al_{MAO}:Zr ratios (>10000, not shown here). For the Al_{MAO}:Zr ratios of 490 and 360, resp., plotted in Fig. 1 we find, however, that after an initial period of decline the activity goes through a maximum before a steady decrease ensues. We can express and discuss this effect with the help of Eq. 1,

thereby assuming a complexation equilibrium between the zirconocene and methylalumoxane to give the homogeneous active complex $C_{homo}^{\ddagger}$.

$$Cp_2ZrX_2 + n\,MAO \rightleftharpoons \{(Cp_2ZrR)^+(MAO)_n^-\}^{\ddagger} \xrightarrow{monomer} (polymer) \cdot \{(Cp_2ZrR)^+(MAO)_p^-\}^{\ddagger} \quad (1)$$

$$(C_{homo}^{\ddagger}) \qquad\qquad\qquad\qquad (C_{hetero}^{\ddagger})$$

R = growing polymer chain, p $\ll$ n (we shall show below that in a diffusion-controlled reaction the amount of MAO needed for maximum complex activation is rather small ($Al_{MAO}:Zr < 100$)).

For very large $Al_{MAO}:Zr$ ratios the equilibrium will lie predominantly on the side of $C_{homo}^{\ddagger}$ and the result of the precipitating polymer will be a steady decline of the polymerization rate until the reaction rate of $C_{hetero}^{\ddagger}$ is reached (not taking into account irreversible deactivation processes). An important indication for the $C_{homo}^{\ddagger} \rightarrow C_{hetero}^{\ddagger}$ transition is the observed broadening of the molecular weight distributions (M_w/M_n, see values in Tab. 2) due to the diffusion control.

For small $Al_{MAO}:Zr$ ratios ($< 1\,000$), however, only a fraction of the zirconium centers are catalytically active in the form of $C_{homo}^{\ddagger}$. The precipitation of the polymer with $C_{hetero}^{\ddagger}$ attached to it will shift the equilibrium from the inactive metallocene (Cp_2ZrX_2) or an inactive zirconium-aluminum precursor complex to the active homogeneous species $C_{homo}^{\ddagger}$. In other words, as $C_{homo}^{\ddagger}$ is transferred into $C_{hetero}^{\ddagger}$ it will be replaced for some time until all of the metallocene or precursor complex is consumed and consequently the total rate (being the sum of the rate for $C_{homo}^{\ddagger}$ and $C_{hetero}^{\ddagger}$) increases and goes through a maximum. A similar behavior has been observed for the ethylene polymerization with the soluble Ziegler-Natta model catalyst $Cp_2Ti(alkyl)Cl/AlEtCl_2$ (alkyl = ethyl, propyl)[14, 16].

Concerning the effect of a variation of $Al_{MAO}:Zr$ on the polymer properties, the experiments plotted in Fig. 1, as well as other data not given here, failed to exhibit a significant trend (cf. Tab. 1).

To enhance our understanding of a diffusion-controlled rate limit and the $Al_{MAO}:Zr$ ratio necessary for this regime, we modelled the heterogeneous diffusion-controlled polymerization through a homogeneous polymerization at an ethylene atmospheric pressure of 1 bar, where the diffusion from the gas into the liquid phase becomes the rate-limiting step. We are aware of the fact that we are dealing with two different kinds of diffusion processes here (from liquid into solid and gas into liquid phase) which surely cannot be compared in their kinetics, but we are confident that the point of a maximum $Al_{MAO}:Zr$
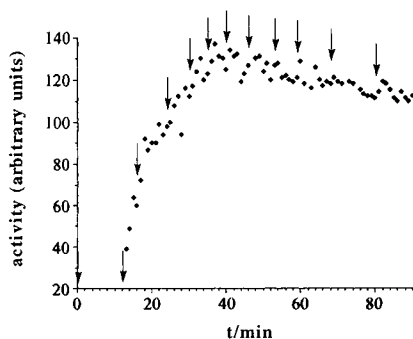
Fig. 2. Polymerization profile for the ethylene polymerization with Cp_2ZrCl_2/ MAO/TMA and a sequential increase in $Al_{MAO}:Zr$ molar ratio from 0 to 120. Each arrow marks the addition of 10 parts of Al_{MAO} (T = 60°C, ethylene pressure = 1 bar, 300 ml toluene, $[Cp_2ZrCl_2]$ = $3.3 \cdot 10^{-4}$ mol/l, molar ratio $Al_{TMA}:Zr$ = 500).

ratio, which we are going to make, is independent of the type of diffusion control involved.

A sequential addition of methylalumoxane to a zirconocene dichloride solution and monitoring of the ethylene consumption (cf. experiment 2.2.2, method A) showed an increase of activity up to an $Al_{MAO}:Zr$ ratio of about 70:1. This maximum activity could not be enhanced, only the slight but irreversible decay could be slowed down somewhat upon further addition of MAO. A typical experiment is illustrated in Fig. 2.

Initially, the scavenger properties of MAO were tried to compensate with a large excess of trimethylaluminum. Further experiments indicated, however, that essentially no TMA addition was necessary, when working carefully (cf. Tab. 2). The maximum of the polymerization rate at $Al_{MAO}:Zr \approx 70$ was not affected by additions of TMA. Effects of TMA on the productivity and polymer properties in this diffusion-controlled set-up are discussed below (Tab. 2).

The observation of a rather low $Al_{MAO}:Zr$ ratio for a maximum activation of a diffusion-controlled Cp_2ZrCl_2/MAO system has implications for the design of a heterogeneous supported metallocene catalyst[17]. Our results suggest that it will not be necessary to strive for the deposition of very high $Al_{MAO}:Zr$ ratios on a support material[18, 19].

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Tab. 2.   Ethylene polymerization productivity and polymer properties with Cp$_2$ZrCl$_2$/MAO as a function of the trimethylaluminum content at 1 bar ethylene pressure[a].

Al$_{TMA}$:Zr (mol:mol)	Al$_{TMA}$:Al$_{MAO}$ (mol:mol)	Productivity (gPE/h · gZr)	M$_w$	M$_n$	M$_w$/M$_n$
10	0.14	379	8980	2600	3.45
50	0.71	369	4250	1700	2.49
100	1.4	403	3140	1440	2.18
500	7.1	314 ± 3[b]	1340	980	1.37

[a]   60 °C, Al$_{MAO}$:Zr = 70:1, [Cp$_2$ZrCl$_2$] = 3.3 · 10^{-4} mol/l.
[b]   Average of three experiments.

3.2 Zirconium concentration

At constant Al$_{MAO}$:Zr ratio the productivity (polymer yield) critically depends on the zirconium concentration as shown in Fig. 3 and Tab. 3. The increase in productivity with decreasing concentration can be traced to a later precipitation of polymer together with the change to the diffusion-controlled rate limit. Thus, in diluted solutions the homogeneous complex with its higher activity dominates the polymerization profile.
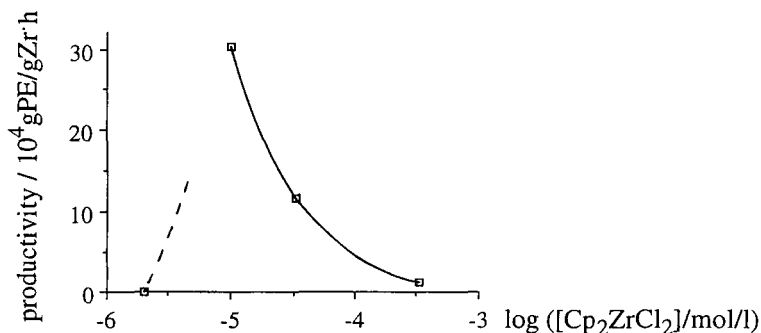

Fig. 3.   Dependence of productivity on the zirconium concentration in the ethylene polymerization with Cp$_2$ZrCl$_2$/MAO/TMA (T = 80 °C, ethylene pressure = 6 bar, 300 ml toluene, molar ratio Al$_{TMA}$:Al$_{MAO}$:Zr = 500:210:1, polymerization time = 30 min).
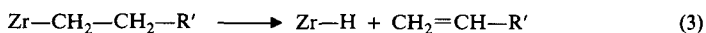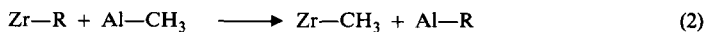
Tab. 3. Dependence of catalyst productivity and molecular weight of polyethylene on the Zr concentration in the ethylene polymerization with Cp_2ZrCl_2/MAO/TMA. For experimental conditions see Fig. 3.

[Cp$_2$ZrCl$_2$] (mol/l)	Productivity (gPE/gZr $\cdot$ h)	M$_w$	M$_n$	M$_w$/M$_n$
$33 \cdot 10^{-5}$	$1.4 \cdot 10^4$	16 000	3 400	4.7
$3.3 \cdot 10^{-5}$	$11.8 \cdot 10^4$	51 600	16 400	3.1
$1 \cdot 10^{-5}$	$30.4 \cdot 10^4$	104 200	29 400	3.5

There is, however, a limit for lowering the zirconium concentration and increasing the productivity at constant Al_{MAO}:Zr ratio. For example, a decrease from [Zr] = 10^{-5} mol/l to [Zr] = $2 \cdot 10^{-6}$ mol/l at otherwise unchanged reaction conditions leads from a good to no observable productivity. To retain a comparable productivity for the smaller Zr concentration, the Al_{MAO}:Zr ratio had to be raised to 7000. We can explain the necessary overproportional increase in methylalumoxane content again with the complex equilibrium expressed in Eq. (1). An increased dilution leads to a higher degree of dissociation for the catalytically active complex C_{homo}^{+} according to the law of mass action.

The extremely high Al_{MAO}:Zr ratios of 150000:1[3] or even 500000:1[5] for the record high productivities of 5000 kg PE/g Zr $\cdot$ h $\cdot$ bar have to be viewed in light of the very small metallocene concentrations of 10^{-7}, respectively 10^{-8} mol/l. As a consequence, employing a moderate zirconium concentration of 10^{-4} to 10^{-5} mol/l in the solution polymerization can drastically reduce the necessary amount of MAO for the activation. Taking into account the cost factor of the methylalumoxane, polymer productivities can well be optimized with Al:Zr ratios below 1000, especially with the addition of trimethylaluminum or higher aluminum alkyls as scavenger reagents (see below).

In our series of comparisons, here, the polyethylene properties are affected most by the variation in transition metal concentration such that a decrease in zirconium concentration gives rise to a large increase in molecular weight (cf. Tab. 3). We would reason this effect on the basis of the possible chain termination reactions, namely the chain transfer to aluminum[9, 20, 21] (Eq. (2)) and the β-hydride elimination[22, 23] (Eq. (3)).

$$Zr\!-\!R + Al\!-\!CH_3 \longrightarrow Zr\!-\!CH_3 + Al\!-\!R \qquad (2)$$

$$Zr\!-\!CH_2\!-\!CH_2\!-\!R' \longrightarrow Zr\!-\!H + CH_2\!=\!CH\!-\!R' \qquad (3)$$

The addition of TMA leads to a lower molecular weight of the polymer (cf. Fig. 4, Tab. 4 and Tab. 2), and TMA is a reaction partner better than MAO for the alkyl exchange between Zr and Al. The reaction in Eq. (2) is probably a bimolecular process whose rate depends in some sort on the zirconium and aluminum (TMA) concentrations, while the unimolecular process in Eq. (3) is only influenced by the zirconium concentration. In both cases, a lowering in zirconium concentration will decrease the rate for these chain termination reactions, thus, leading to an increase in molecular weight of the polymer. In a statistical interpretation of the effect one can argue that in the case of Eq. 2, the chance for a reaction between the Zr species and TMA would be less likely in more dilute solutions (at constant Al:Zr ratios).

3.3 Addition of trimethylaluminum and the Al_{TMA}:Zr ratio

Chien and Wang[9] demonstrated that in the system Cp_2ZrCl_2/MAO up to 90% of the MAO can be replaced by TMA without significant loss in polymerization activity towards ethylene (total Al:Zr = 1070). Furthermore,
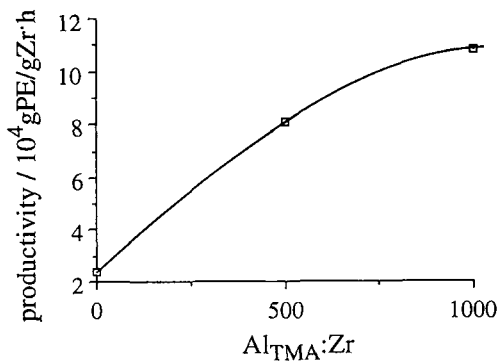

Fig. 4. Productivity as a function of the Al_{TMA}:Zr molar ratio in ethylene polymerization with Cp_2ZrCl_2/MAO/TMA (T = 110°C, ethylene pressure = 6 bar, 500 ml toluene, $[Cp_2ZrCl_2]$ = 10^{-5} mol/l, molar ratio Al_{MAO}:Zr = 730, polymerization time = 1 h).

Tab. 4. Dependence of catalyst productivity and molecular weight of polyethylene on the Al_{TMA}:Zr ratio in the ethylene polymerization with Cp_2ZrCl_2/MAO/TMA. For experimental conditions see Fig. 4.

Al_{TMA}:Zr (mol:mol)	Productivity (gPE/gZr · h)	M_w	M_n	M_w/M_n
0	$2.4 \cdot 10^4$	56400	17400	3.2
500	$8.1 \cdot 10^4$	52600	15100	3.5
1000	$10.8 \cdot 10^4$	44200	13200	3.3

they showed that for an Al_{TMA}:Al_{MAO} ratio of 100 the rate of polymerization was only 60% compared to the value for MAO alone. In an extension of this work Chien and Sugimoto[8] found that even small additions of TMA (Al_{TMA}:Al_{MAO} = 1) to the system $Et[Ind]_2ZrCl_2$/MAO cut the polymerization activity (at low pressure) towards propylene in half.

Our results indicate that for the system Cp_2ZrCl_2/MAO small additions of TMA (up to Al_{TMA}:Al_{MAO} ≈ 1.4) are still beneficial to the productivity (see also caption to Fig. 1). The plot in Fig. 4 illustrates the increase in polymer productivity by a factor of about four. We explain this result at least in part by the scavenger action of TMA which becomes more important at higher pressures with their increased gas uptake including a larger (absolute) amount of impurities.

When testing the influence of TMA at an ethylene pressure of 1 bar, we also found a decrease in productivity for a large excess of TMA over MAO (Tab. 2) concurrent to the results of Chien and Wang[9].

Addition of TMA also affects the polymer properties such that a decrease of the molecular weight with increasing TMA is observed (cf. Tab. 4 and Tab. 2), due to the action of TMA as a chain transfer agent[9, 20, 21].

Preliminary results indicate that higher aluminum alkyls, such as tris(dodecyl)aluminum (TDA) may be used as a scavenger with small MAO:Zr ratios and no side effects. When 200 equivalents of TDA (based on Zr) were added to a polymerization reaction with Cp_2ZrCl_2/MAO (Al_{MAO}:Zr = 70:1, 1 bar) no change in activity was observed and productivity as well as polymer properties were the same as for the small Al_{TMA}:Zr ratios in Tab. 2.

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