

Use of “TMA-depleted” MAO for the activation of zirconocenes in olefin polymerization

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Abstract

The behavior of two differently prepared methylaluminumoxanes (MAOs) on the activation process of $racEt(Ind)_2ZrCl_2$ for olefin polymerization was studied. Contrarily to commercial product, the two MAOs used are characterized by a low content of free trimethylaluminum (TMA). MAO-A was prepared by pumping off the TMA contained in commercial MAO, whereas MAO-B was obtained by thermal treatment of TMA with benzophenone. The different elementary steps in the zirconocene activation process depending on the amount and nature of added MAO (commercial and modified ones) were investigated by UV/visible spectroscopy. In all cases, monomethylation of $racEt(Ind)_2ZrCl_2$ rapidly takes place after addition of small amounts of MAO. Then, abstraction of the second chloride of the metallocene occurs upon addition of larger amounts of MAO ($Al/Zr < 200$) leading to the formation of highly active catalytic species for hexene polymerization. This is characterized by a bathochromic shift of the zirconocene absorption band. The role of TMA is clearly pointed out by comparing the modified MAO/zirconocene systems with the one based on commercial MAO. The influence of structure and composition of MAO on the activation process is also clearly underlined by the very different amounts of activator needed to get metallocene active species in the presence of commercial and modified cocatalysts. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Zirconocenes; TMA; MAO; UV/visible spectroscopy

1. Introduction

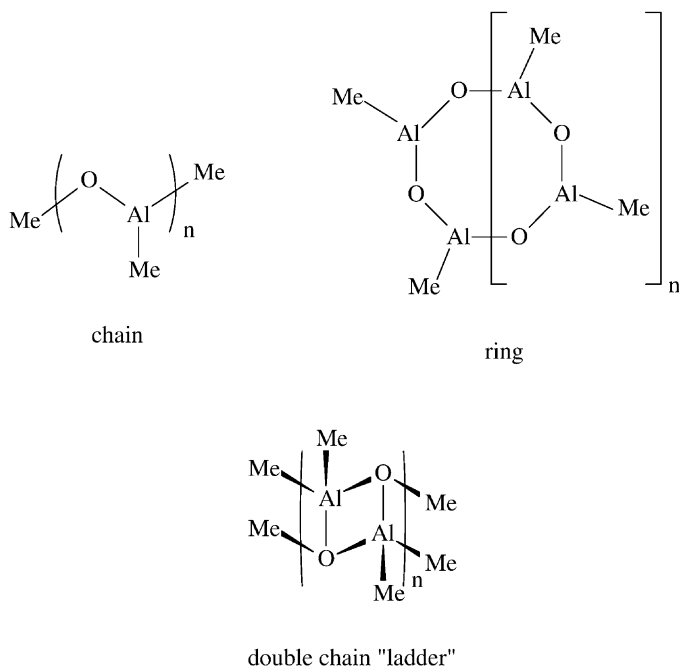
The discovery of methylaluminumoxane (MAO), a product of soft hydrolysis of trimethylaluminum (TMA), as a powerful activator for group IV metallocenes has been a decisive breakthrough in the field of olefin polymerization catalysis. It is now generally admitted that zirconocene dichloride activation by MAO occurs in two distinct steps corresponding successively to metallocene methylation and cationization by successive abstraction of the

chloride ligands. Actually, it appears that the MAO preparation mode too has a strong influence on its capacity to convert metallocene precursors into active species. Indeed, the difficulties encountered to better understand the important factors for an efficient activation are mainly due to the poor knowledge of the MAO composition and structure. Several types of macromolecular arrangements, involving linear chains, monocycles and/or various three-dimensional structures (Scheme 1) have been successively postulated [1,2].

In a very recent work, a more detailed image of MAO was proposed [3]. It is described as a cage molecule, with a general formula $Me_{6m}Al_{4m}O_{3m}$ (m

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Scheme 1. Early structure models for MAO.

equal to 3 or 4) and in which labile bridging methyl groups are the only ones reactive ($\text{Me}_{\text{bridge}}/\text{Me}_{\text{total}}$ ratio is estimated between 0.15 and 0.19).

A second difficulty is related to the presence in commercial MAO of TMA remaining from its partial hydrolysis by water, or most commonly by inorganic salt hydrates [4]. The presence of residual TMA let rise several questions. It has been suggested that TMA is responsible for the methylation of zirconocene dichloride, which corresponds to the first step of the activation process [5]. TMA has been even considered as the actual zirconocene activator [6] although this has been contradicted by other authors [7]. A "poisoning" effect of TMA has also been noted in several cases. Therefore, it was of interest to investigate the activation of metallocenes by "TMA-depleted" MAO. This was achieved by means of UV/visible spectroscopy and kinetics. Two types of "TMA-depleted" MAO were prepared. The first modified MAO was obtained from commercial MAO by removing remaining TMA, whereas the other was obtained by a non-hydrolytic procedure. Their structural characteristics and behavior towards $\text{racEt}(\text{Ind})_2\text{ZrCl}_2$ activation for 1-hexene polymerization have been investigated.

2. Experimental part

2.1. Materials

$\text{racEt}(\text{Ind})_2\text{ZrCl}_2$ and TMA (97% or 2 M in toluene) were purchased from Sigma Aldrich Chimie, Saint Quentin Fallavier, France. Methylaluminoxane (10%, w/w in toluene, TMA content 30–35% total Al) was obtained from CK Witco GmbH, Bergkam, Germany.

Toluene (Mallinckrodt Baker B.V., Deventer, Holland) was first dried over calcium hydride and distilled. Then a small amount of styrene (99%, Sigma Aldrich Chimie) and *sec*-BuLi (1.3 M in cyclohexane, Fluka for Sigma Aldrich Chimie) were added to toluene and stirred until the characteristic red color of polystyryl anion was obtained, meaning that all protonic impurities have been consumed. The desired volume of toluene was then distilled off from the polystyryl solution just before use.

2.2. Preparation of MAO-A

In a typical experiment, 20 ml of MAO (10%, w/w in toluene) were solvent dried under vacuum at room

temperature. The resulting white gel was then heated at 80 °C under vacuum for 5 h to distillate TMA. The obtained white solid residue is inflammable in contact with air and was thus kept under nitrogen in a glove box.

2.3. Preparation of MAO-B

MAO-B was synthesized as indicated in literature report [8].

2.4. Polymerization

Kinetics were followed by dilatometry recording the volume contraction of the polymerization solution in a 16 ml dilatometer ($T = 20\text{ °C}$, solvent: toluene) according to [9].

3. Results and discussion

Two “TMA-depleted” MAO were obtained by two different procedures:

- by pumping off TMA from commercial MAO (MAO-A),
- from non-hydrolytic processes involving reaction of TMA with benzophenone (MAO-B).

3.1. Preparation of “TMA-depleted” MAO from commercial MAO (MAO-A)

Commercial MAO solutions contain a high percentage of TMA (30–35%) remaining from its partial hydrolysis process. It is generally admitted that TMA in MAO solution may exist under two distinct forms: as “free” TMA mainly in a dimeric form (Al_2Me_6) and as complexed TMA, associated with MAO chains. Preparation of “TMA-depleted” MAO by pumping off TMA from commercial solutions has been reported by several groups. However, NMR spectra of the product show that elimination of TMA is not quantitative and the term “TMA-depleted” MAO, recently proposed [3], should be preferred. From a 10% (w/w) MAO solution TMA depletion was carried out by removing first the toluene, under vacuum distillation at room temperature. Then, free TMA was pumped off at 80 °C for several hours yielding a white solid. The ^1H NMR

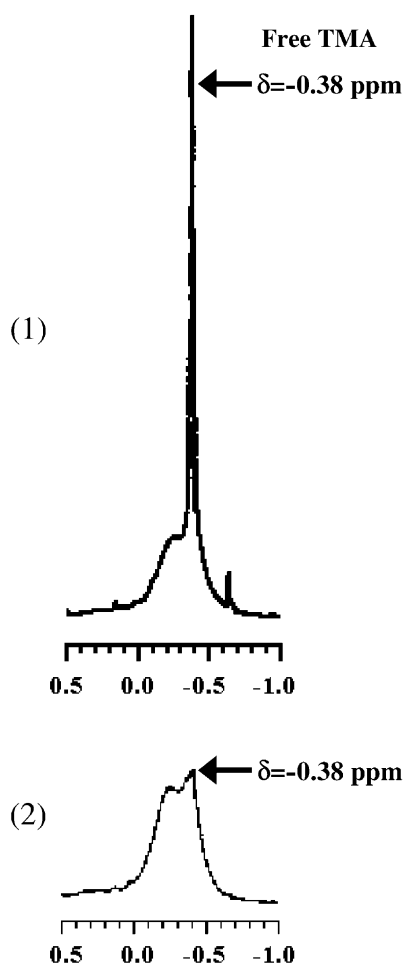


Fig. 1. ^1H NMR spectrum in toluene d_8 of commercial MAO (1) and of “TMA-depleted” MAO (2).

spectrum of the recovered MAO (Fig. 1) shows that the peak ($\delta = -0.38\text{ ppm}$) attributed to free TMA has been greatly reduced.

Although the exact structure of MAO is still not completely elucidated it has been shown that the structure can be greatly influenced by the amount of TMA present. Indeed, it was shown that addition of TMA on MAO results in disproportionation of MAO oligomers, yielding to the reduction of their molar mass [10]. In an opposite way, removal of TMA will lead to condensation of MAO chains, increasing its molar mass. This condensation process is also likely accompanied by changes in the global MAO structure.

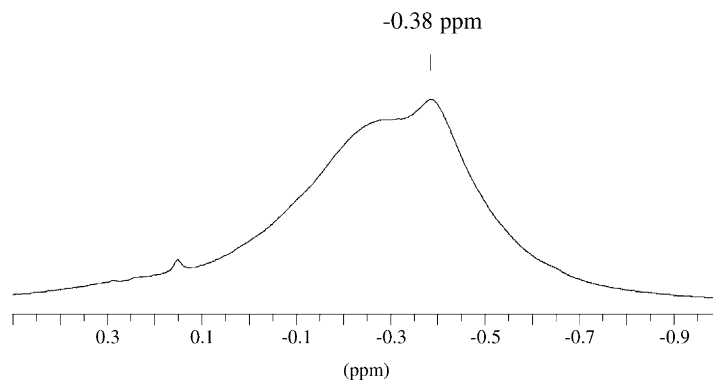


Fig. 2. ^1H NMR spectrum in toluene *d*-8 of MAO-B.

3.2. Preparation of “TMA-depleted” MAO by non-hydrolytic means

We have recently reported a detailed study of a non-hydrolytic synthetic route to MAO by the thermal treatment of benzophenone with TMA. MAO synthesized by this method contains no or very little free TMA [8b] (see Fig. 2).

3.3. Study of $\text{racEt}(\text{Ind})_2\text{ZrCl}_2$ activation with “TMA-depleted” methylaluminoxanes MAO

3.3.1. Activation by MAO-A

Although the change in MAO structure resulting from TMA removal is difficult to precisely identify, its effect on zirconocene activation can be investigated. This was performed by UV/visible spectroscopy, a technique which allows observation of zirconocene species in concentration conditions close to polymerization. Evolution, in the presence of activator molecules, of the zirconocene main absorption band which can be related to the ligand to metal charge transfer (LMCT) yields informations directly related to the activation process and to the nature of the zirconocene species [9,11–13].

Addition of small amounts of MAO-A ($0 < \text{Al/Zr} < 15$) to $\text{racEt}(\text{Ind})_2\text{ZrCl}_2$ (Fig. 3A) leads first to a hypsochromic shift of the zirconocene main absorption band from 427 nm—the absorption wavelength of $\text{racEt}(\text{Ind})_2\text{ZrCl}_2$ in toluene—to 396 nm as already observed with commercial MAO. This wavelength decrease has been explained, on the basis of molecular orbital theory, by an increase of the

electronic density onto the metal atom attributed to substitution of a chloride atom by a methyl group of MAO or of TMA contained in it.

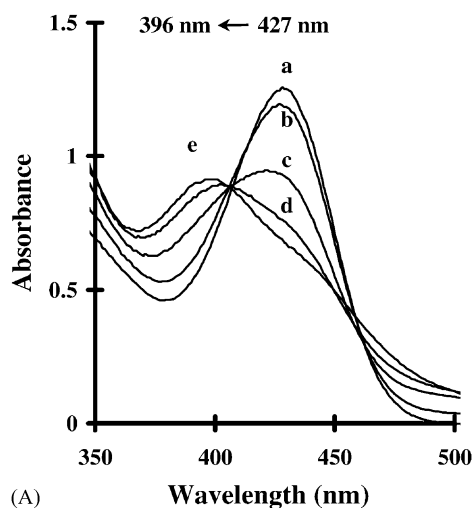
Addition of further quantities of MAO-A (up to $\text{Al/Zr} = 150$) (Fig. 3B) yields a reverse bathochromic band shift from 396 to 440 nm corresponding to a decrease of zirconium electronic density (cationization) associated with the extraction of the second chloride ligand of the metallocene. It is worth noting that the new species absorbing at 440 nm and formed at ratio $\text{Al/Zr} = 150$ are highly active towards olefin polymerization, whereas we have already shown that in similar conditions [9,11] commercial MAO yields inactive zirconocenium species, the latter system becoming active only at much higher Al/Zr ratios (>1000) (see Table 1).

Indeed, addition of larger amounts of MAO-A does not lead to any change, neither in the UV/visible zirconocene spectrum, nor in 1-hexene polymerization activity, even for very high Al/Zr ratios (up to 3000). The different behavior observed in the presence of MAO-A and commercial MAO is further discussed in the last section.

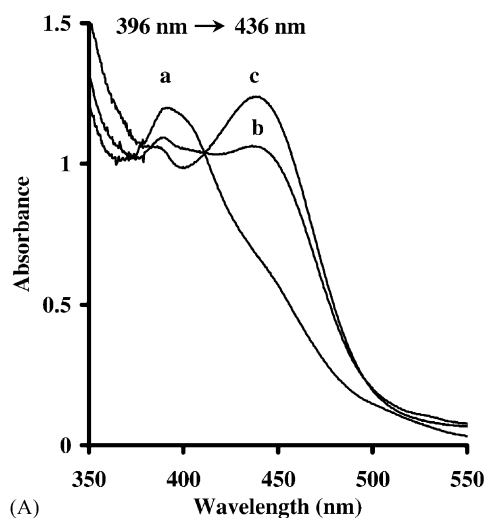
Table 1

Hexene polymerization activities of $\text{racEt}(\text{Ind})_2\text{ZrCl}_2$ combined with various MAOs at two different Al/Zr ratios

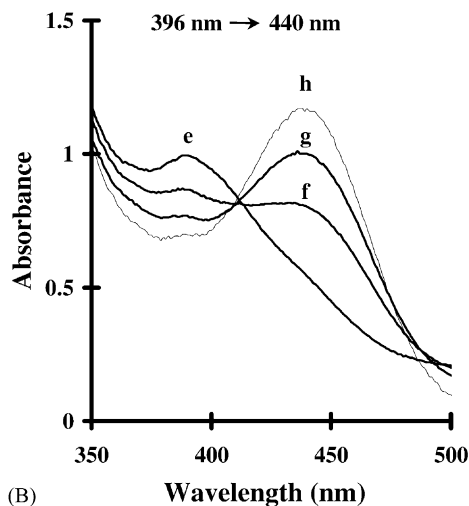
MAO type	Activity ($\text{kg}_{\text{PH}} \text{mol}_{\text{Zr}}^{-1} \text{h}^{-1}$)	
	$\text{Al/Zr} = 50$	$\text{Al/Zr} = 2000$
Commercial MAO	0	1.3
MAO-A	1.5	1.5
MAO-B	≈ 1.1	nd



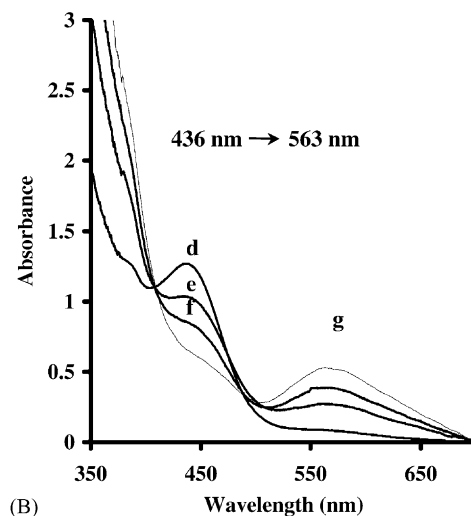
(A)



(A)



(B)



(B)

Fig. 3. UV/visible absorption spectrum of $racEt(Ind)_2ZrCl_2$ in toluene at 20 °C in the presence of increasing amounts of MAO-A. (A) Al/Zr = 0 (a), 4 (b), 8 (c), 12 (d) and 15 (e). (B) Al/Zr = 15 (e), 25 (f), 35 (g) and 200 (h).

Fig. 4. UV/visible absorption spectrum of $racEt(Ind)_2ZrCl_2$ in toluene at 20 °C in the presence of increasing amounts of MAO-B. (A) Al/Zr = 30 (a), 60 (b) and 90 (c). (B) Al/Zr = 120 (d), 450 (e), 900 (f) and 1500 (g).

3.3.2. Activation by MAO-B

A shift from 427 to 396 nm was observed on the addition of MAO-B (Al/Zr = 30) (Fig. 4A). This evolution is in agreement with the monomethylation procedure of the zirconocene dichloride as reported for commercial MAO. A reverse bathochromic shift from 396 to 436 nm is induced by further addition of MAO-B (Fig. 4B). At Al/Zr ratios of 100, the 396 nm peak conversion is completed. Moreover, the species

corresponding to this new band, at 436 nm, were found very active towards 1-hexene polymerization (as also found in the case of zirconocene activation by TMA-depleted MAO-A).

Contrary to the latter, further addition of MAO-B led to the formation of a new absorption band located at around 563 nm. For a Al/Zr ratio of 300 the transformation is complete after 1 h. It is almost instantaneous at Al/Zr = 1500. These new species, not observed

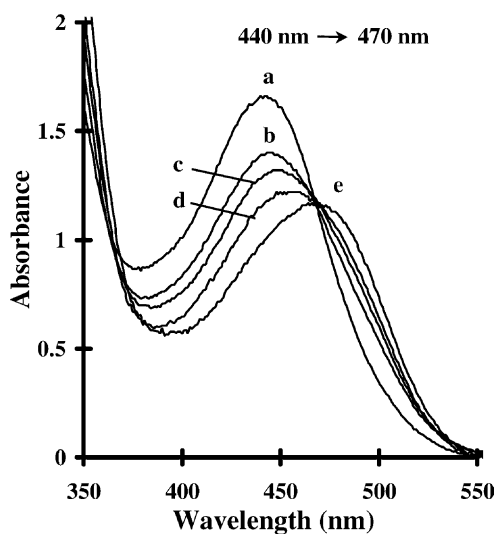


Fig. 5. UV/visible absorption spectrum of species absorbing at 440 nm resulting from addition of “TMA-free” MAO ($\text{Al/Zr} = 300$) on $\text{racEt}(\text{Ind})_2\text{ZrCl}_2$ in toluene at 20°C in the presence of increasing amounts of TMA. $\text{TMA/Zr} = 0$ (a), 90 (b), 360 (c), 780 (d) and 1000 (e).

with previous MAO preparations can be attributed to the degradation of catalytic system.

3.4. Effect of TMA onto species located at 440 nm

To further understand the specific role of TMA in zirconocene activation, complementary experiments were performed. After reaction of MAO-A with $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ at an Al/Zr ratio of 300, leading to polymerization active species ($\lambda_{\text{max}} = 440\text{ nm}$), increasing amounts of TMA was added to the system. As expected, a bathochromic shift from 440 to 470 nm (Fig. 5) similar to the one found with commercial MAO at high Al/Zr ratio, was observed [11].

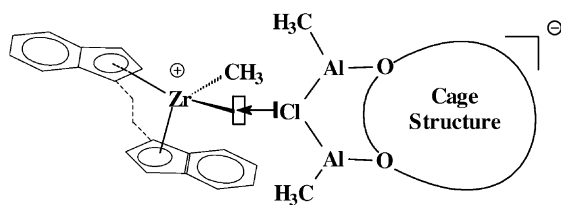
The same shift was observed upon addition of TMA onto inactive species absorbing at 440 nm formed with commercial MAO. Nevertheless, in this latter case very large quantities of TMA were required to obtain the bathochromic shift of the 440 nm absorption band.

4. General discussion

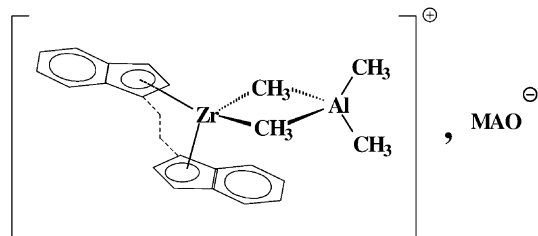
Activation of $\text{racEt}(\text{Ind})_2\text{ZrCl}_2$ by “TMA-depleted” MAO occurs in two main steps, as deduced from

UV/visible spectroscopy observations. In the first step, corresponding to addition of small amounts of “TMA-depleted” MAO ($\text{Al/Zr} < 30$), $\text{racEt}(\text{Ind})_2\text{ZrCl}_2$ is monomethylated, i.e. one chloride ligand is substituted by one methyl group to yield $\text{racEt}(\text{Ind})_2\text{ZrClMe}$. Same behavior was observed after addition of small amounts of commercial MAO on $\text{racEt}(\text{Ind})_2\text{ZrCl}_2$ [9,11]. It is worth noting that during this stage, MAO does not need the presence of TMA to methylate dichlorozirconocene. Nevertheless, this is not a proof that MAO is the only methylating agent in commercial solutions, since addition of TMA alone on $\text{racEt}(\text{Ind})_2\text{ZrCl}_2$ leads to the same hypsochromic shift from 427 to 396 nm, in agreement with zirconocene methylation. The few remaining TMA, probably present in an associated form, may be also responsible of the methylation in MAO-A. Structure of MAO formed by non-hydrolytic means (MAO-B) is still not clear, but some TMA used in the preparation may remain associated with MAO. As with MAO-A, the latter could induce zirconocene methylation. At least, it can be concluded that the free form of TMA (Al_2Me_6) present in commercial MAO solutions is not required to methylate dichlorozirconocene.

The effective activation of metallocene occurs in second step. Addition of “TMA-depleted” MAO (MAO-A and -B) at Al/Zr ratios of about 100–200 yields new species absorbing at around 440 nm. The latter species are highly active towards olefin polymerization. Interestingly, although the same spectroscopic behavior is observed after addition of commercial MAO on $\text{racEt}(\text{Ind})_2\text{ZrCl}_2$, the species absorbing at 440 nm are totally inactive towards hexene polymerization. These differences point out that MAO structure plays an important role in the zirconocene activation process. It has been recently shown that MAO extracted chloride groups of zirconocene inhibits the activity of species absorbing at 440 nm [11,12]. According to Ystenes et al. [3], only labile bridging methyl groups from MAO-cage are able to exchange with chloride ligands. This exchange yields chlorinated MAO (MAO-Cl) inefficient to further activate metallocene. This was explained by a strong interaction between free electron pair of MAO bridging chloride group and the vacant coordination site of the electron deficient zirconocene. A hypothetical structure showing cation-like methylzirconocene



Scheme 2. Hypothetical structures of species absorbing at 440 nm resulting from activation by commercial MAO.



Scheme 3. Hypothetical structure of the species absorbing at 470 nm.

and MAO-Cl counter anion (Scheme 2) may be thus postulated.

On the basis of this work and previous reports [3,11,12], we may conclude that *rac*-ethylene bisindenylzirconocenium species absorbing at 440 nm can be either inactive when formed with commercial MAO or active when they result from the use of TMA-depleted MAO. Indeed, the low amount of TMA in the latter systems might allow an increase of the number of reactive bridging methyl groups in MAO. Conversely, in the presence of TMA, the active methyl bridges of MAO would be partly displaced, yielding a much less efficient MAO structure.

Presence of TMA is clearly responsible for the formation of metallocenium species absorbing at 470 nm. As already described [11,12], a complexed structure between TMA and cationic zirconocene, as depicted in Scheme 3, is suggested in agreement with literature proposals [14,15]. With respect to molecular orbital theory separation of the ion pair by TMA, would reduce the electron density around zirconium and would explain the observed bathochromic shift.

5. Conclusion

In this paper, we attempted to further understand the distinct roles of MAO and TMA in the zirconocene activation process. Action of two different MAOs on *rac*Et(Ind)₂ZrCl₂ was studied. These MAOs offer the same property: absence of free TMA in their composition, contrarily to commercial MAO that contains high percentage of remaining TMA.

The use of these TMA-depleted MAO offers the possibility to activate zirconocene at rather low Al/Zr ratios in homogeneous conditions (Al/Zr ≈ 50–200), thus underlining the poisoning role of TMA in MAO in the activation process of metallocenes.

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