

Influence of X ligand nature in the activation process of $racEt(Ind)_2ZrX_2$ by methylaluminoxane

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Abstract

The activation process by methylaluminoxane (MAO) of various zirconocene precursors of the type $racEt(Ind)_2ZrX_2$, with different extractable X ligands (X = Cl, Me, NMe₂, CH₂Ph), was investigated both by means of UV–VIS spectroscopy and through hex-1-ene polymerization kinetics. The different elementary steps yielding olefin polymerization active species, i.e. methylation and cationization of the transition metal could be readily discriminated. Unlike $racEt(Ind)_2ZrCl_2$ precursor for which high amount of MAO (Al/Zr = 2000) is required to form catalytic species active towards olefin polymerization, the complete activation of other $racEt(Ind)_2ZrX_2$ tested (with X = Me, NMe₂, CH₂Ph) is readily achieved at relatively low Al/Zr ratios (Al/Zr = 40–50). The corresponding zirconocenium species exhibit different catalytic activity according to the nature of the extracted X ligand, showing the important role of the formed [MAO-X][−] counter-anion in the activation process and more particularly, its ability to still coordinate with the metal center and compete with the incoming olefin. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

In our course of elucidating the elementary steps of zirconocene activation by methylaluminoxane (MAO) for olefin polymerization, we recently stressed the negative role of chloride-extracted ligands on the formation of active metallocenium species [1].

We have shown that the different elementary steps of the activation process can be readily discriminated by analysis of zirconocene UV–VIS spectrum changes as a function of the MAO concentration and structure. Indeed, on the basis of molecular orbital theory, change in the ligand to metal charge transfer

(LMCT) zirconocene absorption band gives very useful information on the metal electronic density modifications [1–5].

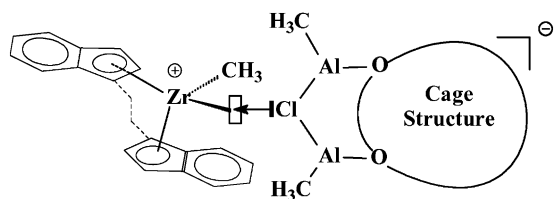
Rytter et al. have recently shown that MAO possesses a cage-like structure [6] with bridging methyl groups, which are directly involved in the cationization pathway; during this process, exchange between MAO bridging methyl groups and zirconocene chloride ligands yields a chlorinated MAO which was found not able any more to activate dimethylated zirconocene for olefin polymerization as initial MAO does.

In the case of $racEt(Ind)_2ZrCl_2$ activation by MAO investigated by UV–VIS spectroscopy [1,2], monomethylation of the zirconocene dichloride was shown to occur at very low Al/Zr ratio (Al/Zr = 5–20). The addition of higher amount of MAO up to Al/Zr = 150 was required to extract the second chloride ligand

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Scheme 1. Hypothetical structures of the species absorbing at 440 nm issued from the reaction between $racEt(Ind)_2ZrCl_2$ and MAO (Al/Zr = 150).

and yield an electronic deficient (“cation-like”) zirconocene species with $[MAO-Cl]^-$ as counter-anion. The corresponding species, distinctly characterized by UV–VIS spectroscopy ($\lambda_{max} = 440$ nm) is totally inactive for hex-1-ene polymerization. The inactivity was explained by a persistent interaction between the cationic metal center and chloride ligands, although trapped by the MAO. This impedes the olefin coordination and consequently, its insertion into the metal–carbon bond (Scheme 1).

Actually, the major consequence of this process is the need of MAO in large excess (Al/Zr = 3000) to suppress the direct interaction between the electrophilic cationic metal centers and the $[MAO-Cl]^-$ counter-anion and yield zirconocenium species active towards olefin polymerization. The latter which exhibit an absorption band at 470 nm were identified as hetero-bimetallic complexes between TMA and zirconocenium species, i.e. $[racEt(Ind)_2Zr(\mu-Me)_2AlMe_2]^+$ in agreement with previous proposals [5–9].

The fact that zirconocene dichloride systems are only active at high Al/Zr ratios (typically Al/Zr > 2000) led us to investigate the use of other zirconocene precursors. In particular, our study was extended to zirconocenes $racEt(Ind)_2ZrX_2$, bearing various extractable X ligands other than chloride. Indeed, literature already reveals that the activation of $racEt(Ind)_2ZrX_2$ with dimethylamino- [10–12] and benzyl- [13] as X groups requires lesser amounts of MAO to yield active species, compared to the zirconocene dichloride precursor. The elementary reactions involved during the activation of these different zirconocene derivatives by MAO was investigated by UV–VIS spectroscopy and compared to the $racEt(Ind)_2ZrCl_2/MAO$ catalytic system. The aim of this study was to determine the influence and role of the X ligands during the different activation steps

leading to the formation of zirconocene active species for olefin polymerization.

2. Experimental

2.1. Materials

The $racEt(Ind)_2ZrCl_2$, 1,2-bisindenylethane (99%), $PhCH_2MgCl$ (1.0 M in diethyl ether) and trimethylaluminum (TMA) (97% or 2 M in toluene) were purchased from SAFC, Saint Quentin Fallavier, France. $B(C_6F_5)_3$ (minimum 97%), $[C_6H_5N(CH_3)_2H]^+ [B(C_6F_5)_4]^-$, and $Zr(NMe_2)_4$ were purchased from Strem Chemicals, Inc., Bischheim, France. All zirconocenes and boron derivatives were kept in a glove box under nitrogen. Methylaluminoxane (10 wt.% in toluene, containing 30–35% TMA; CK Witco GmbH, Bergkam, Germany) and TMA were used as received, following conventional safety procedures.

2.1.1. Purification procedures

Toluene (Mallinckrodt Baker B.V., Deventer, Holland) was first dried over calcium hydride. Then a small amount of styrene (99%, SAFC) and $sec-BuLi$ (1.3 M in cyclohexane, Fluka-SAFC) were added onto the freshly distilled toluene which was stirred until the characteristic red color of polystyryl anion was obtained, meaning that all moisture and protonic impurities have been consumed. The desired volume of toluene was distilled under inert atmosphere before use. For zirconocene synthesis, a last purification by distillation of toluene over sodium mirror was done.

Diethyl ether (Baker) was dried over Na/benzophenone. Hexane (Baker) was dried over CaH_2 and distilled over Na/benzophenone. All solvents were stored in glass apparatus fitted with PTFE stopcocks.

2.1.2. Zirconocene synthesis

The $racEt(Ind)_2ZrMe_2$ [14], $racEt(Ind)_2Zr(NMe_2)_2$ [10], and $racEt(Ind)_2Zr(CH_2Ph)_2$ [13] were synthesized following literature procedure.

2.2. Instrumentation

UV–VIS absorption spectra were recorded on a Varian Cary 3E UV–VIS spectrometer in a quartz cell (0.5 cm pathlength) attached to the glass reactor fitted with PTFE stopcocks.

Table 1
Influence of X ligands of *racEt(Ind)₂ZrX₂*/activator systems on hex-1-ene polymerization activity

X ligand	Activator	Activator/Zr ratio (Al/Zr for MAO)	Maximum (nm)	Activity (kg Ph mol _(Zr) ⁻¹ h ⁻¹)
-Cl	MAO	150	440	0
	MAO	2000	470	1290
-Me	MAO	150	439	1150
	MAO	2000	470	1190
	[HNMe ₂ Ph] ⁺ [B(C ₆ F ₅) ₃] ⁻	1	421	980
-NMe ₂	MAO	40	435	27
	MAO	2000	470	30
-CH ₂ Ph	MAO	50	432	940
	MAO	2000	470	970

2.3. Polymerization

Kinetics were followed by dilatometry recording the volume contraction of the polymerization solution in a 16 ml dilatometer ($T = 20^{\circ}\text{C}$; solvent: toluene) according to [1].

3. Results and discussion

3.1. UV–VIS study of *racEt(Ind)₂ZrMe₂* activation

Activation by MAO of *racEt(Ind)₂ZrMe₂* — characterized by an absorption band located at 367 nm — was investigated both by UV–VIS spectroscopy and through hex-1-ene polymerization kinetics. Unlike *racEt(Ind)₂ZrCl₂*, the maximal activation of *racEt(Ind)₂ZrMe₂* towards olefin polymerization is already achieved at relatively low Al/Zr ratios (Al/Zr \leq 150) for which rapid polymerization of hex-1-ene already takes place (see Table 1). The activation step is characterized by a bathochromic shift of the zirconocene LMCT main absorption band from 367 to 439 nm (Fig. 1A). On the basis of the molecular orbital theory, it corresponds to a decrease of the electronic density on the metal which may be attributed to the abstraction of one methyl group of *racEt(Ind)₂ZrMe₂* by MAO. Direct NMR characterization of the active species is difficult due to the still large excess of MAO, but the formation, during this process of zirconocenium type species can be admitted, regarding to spectroscopic data of zirconocene activation by non-coordinating anions ([B(C₆F₅)₄]⁻ type) [14–17].

Addition of larger amounts of MAO (Al/Zr = 2000) to these active species leads to a second bathochromic shift of the absorption band from 439 to 470 nm (Fig. 1B). The formation of species absorbing at this wavelength was already reported in the case of *racEt(Ind)₂ZrCl₂* activated by MAO at very high Al/Zr ratios (>1000). They were attributed to the formation of a hetero-bimetallic complex between TMA (contained in MAO) and the zirconocene, [*racEt(Ind)₂Zr*(μ -Me)₂AlMe₂]⁺ (Scheme 2).

The catalytic activity towards hex-1-ene polymerization of species absorbing at 439 and 470 nm was found almost identical (see Table 1). This important feature will be discussed in the final section.

3.2. Activation of *racEt(Ind)₂Zr(NMe₂)₂*

The activation of *racEt(Ind)₂Zr(NMe₂)₂* by MAO was examined by UV–VIS spectroscopy, following the procedure described for the dimethyl derivative. The addition of small amounts of MAO (Al/Zr < 15) onto *racEt(Ind)₂Zr(NMe₂)₂* ($\lambda_{\text{max}} = 464$ nm) leads first to a hypsochromic shift of the zirconocene main absorption band to 367 nm, in line with UV–VIS spectroscopic data obtained with dimethylated zirconocene. The new absorption band location (367 nm) is consistent with the substitution of the two NMe₂ ligands by two methyl groups. This is in agreement also with Kim and coworkers' NMR observations [10–12]. The direct derivatization of *racEt(Ind)₂Zr(NMe₂)₂* into *racEt(Ind)₂ZrMe₂* is illustrated by the presence of an isosbestic point on the UV–VIS spectra (Fig. 2), the transformation being complete for Al/Zr = 10.

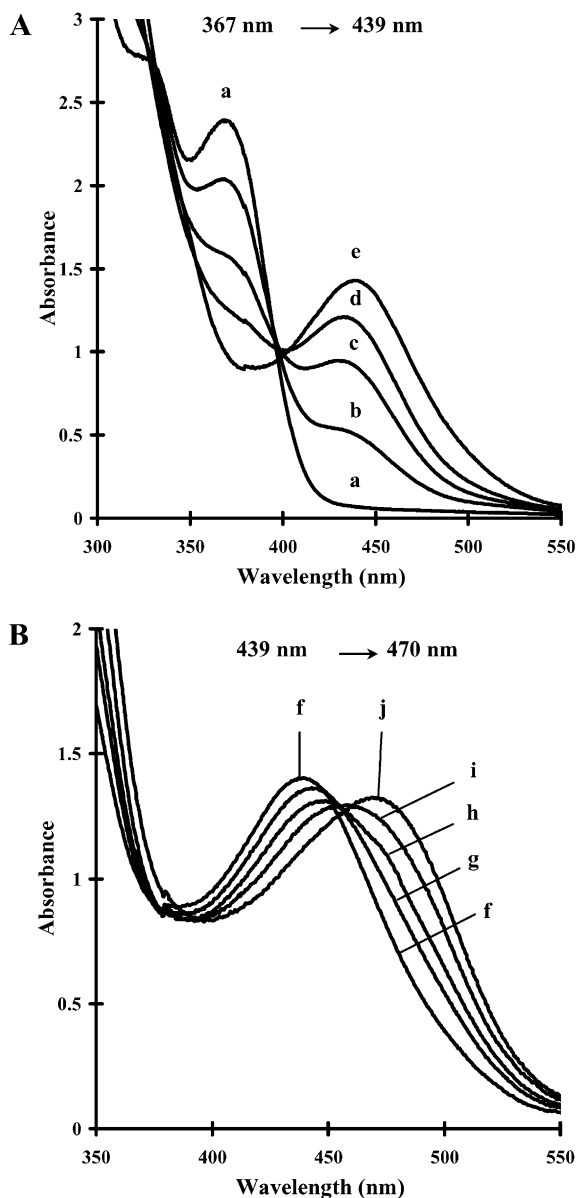
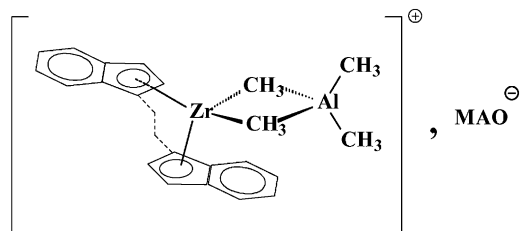


Fig. 1. UV–VIS absorption spectra of $racEt(Ind)_2ZrMe_2$ in toluene at 20°C in the presence of increasing amounts of MAO — (A): (a) Al/Zr = 0; (b) Al/Zr = 40; (c) Al/Zr = 80; (d) Al/Zr = 120; (e) Al/Zr = 150; (B): (f) Al/Zr = 300; (g) Al/Zr = 800; (h) Al/Zr = 1400; (i) Al/Zr = 2000; (j) Al/Zr = 3000.

UV–VIS investigation shows that dimethylation of $racEt(Ind)_2Zr(NMe_2)_2$ can be readily achieved by addition of TMA [11,12]. Indeed, the hypsochromic shift of the main absorption band from 464 to



Scheme 2. Hypothetical structures of the species absorbing at 470 nm.

367 nm as well as the presence of one isosbestic point shows that TMA, as MAO, is able to transform bis(dimethylamino)zirconocene into dimethylated species at a ratio Al/Zr = 5 (Fig. 3). The lower amounts of aluminic compounds (MAO or TMA) required to dimethylate the zirconocene precursor indicates that dimethylamino groups are much more easily extractable ligands than the chloride ones.

As expected, addition of higher amounts of MAO leads to a bathochromic shift of the absorption band from 367 to 435 nm (Fig. 4A), attributed to abstraction of one of the methyl ligand. Interestingly, this is achieved at Al/Zr ratios close to 40, a value even lower than the one found with $racEt(Ind)_2ZrMe_2$.

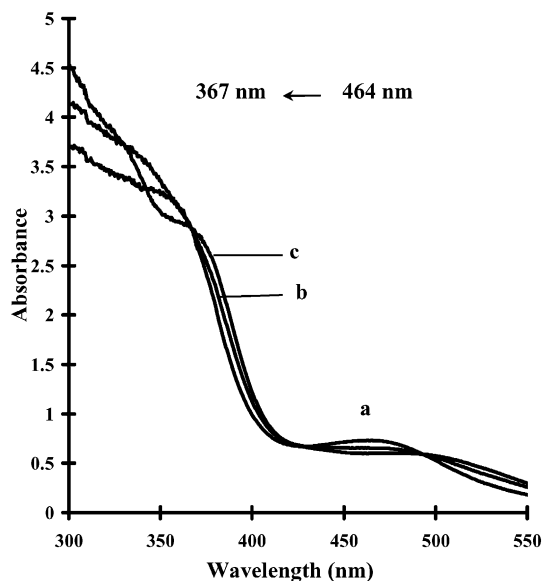


Fig. 2. UV–VIS absorption spectra of $racEt(Ind)_2Zr(NMe_2)_2$ in toluene at 20°C in the presence of small amounts of MAO: (a) Al/Zr = 0; (b) Al/Zr = 4; (c) Al/Zr = 10.

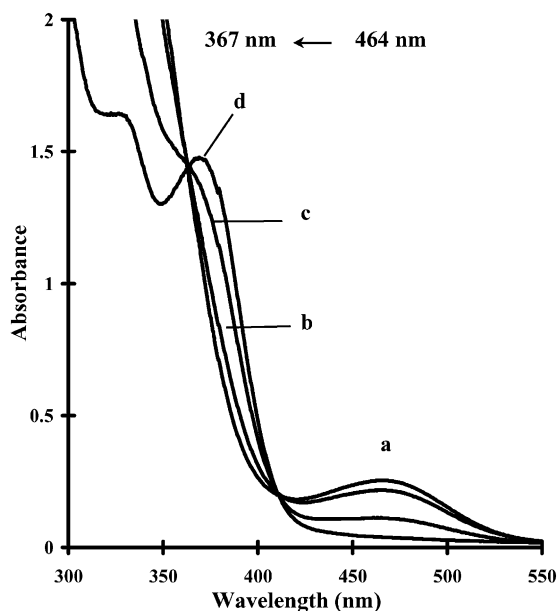


Fig. 3. UV–VIS absorption spectra of $racEt(Ind)_2Zr(NMe_2)_2$ in toluene at 20°C in the presence of increasing amounts of TMA: (a) Al/Zr = 0; (b) Al/Zr = 1.25; (c) Al/Zr = 2.5; (d) Al/Zr = 5.

The addition of larger amounts of MAO (until Al/Zr = 2000) is again accompanied by a second bathochromic shift from 435 to 470 nm (see Fig. 4B), likely due to a TMA complexation onto the cationic site, as already discussed for the dimethyl- and dichlorozirconocene derivatives. Interestingly, the two species absorbing at 435 and 470 nm exhibit the same catalytic activity towards hex-1-ene polymerization (Fig. 5) as previously found for the system $racEt(Ind)_2ZrMe_2/MAO$. Assuming from spectroscopic data that conversion of the 435 nm species into the 470 nm one is complete (total disappearance of the 435 nm band with presence of an isosbestic point), these results suggest that the two species exhibit almost the same intrinsic reactivities. The overall activity of this system is however much lower — by a factor of 50 — than the one observed with dichloro- and dimethylzirconocene precursors.

3.3. Activation of $racEt(Ind)_2Zr(CH_2Ph)_2$

The activation of $racEt(Ind)_2Zr(CH_2Ph)_2$ ($\lambda_{max} = 403$ nm) by MAO was then investigated in a similar

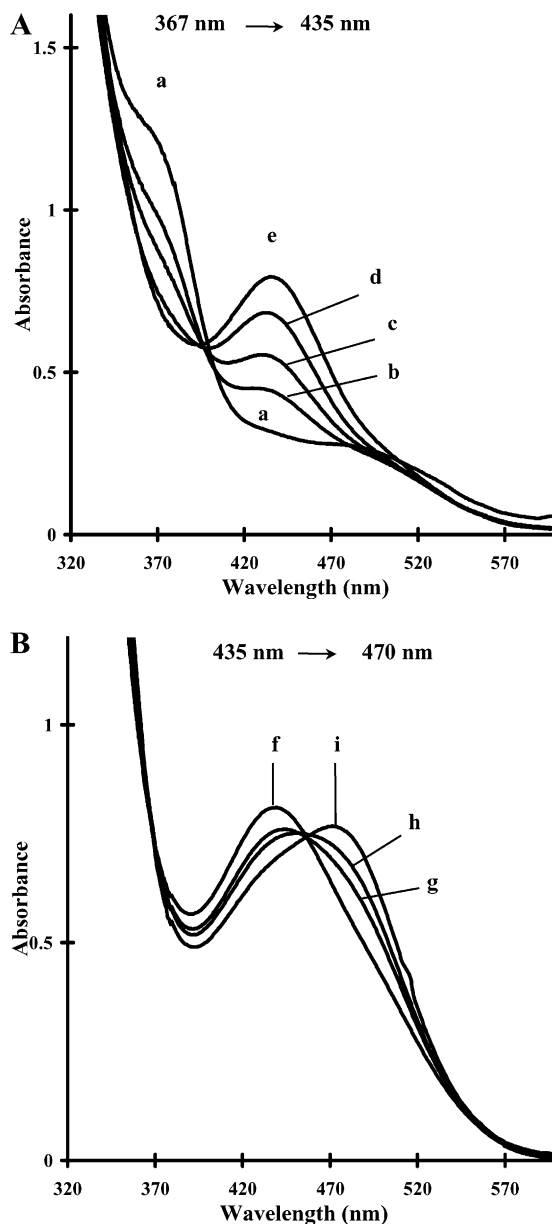


Fig. 4. UV–VIS absorption spectra of $racEt(Ind)_2Zr(NMe_2)_2$ in toluene at 20°C in the presence of increasing amounts of MAO — (A): (a) Al/Zr = 15; (b) Al/Zr = 20; (c) Al/Zr = 25; (d) Al/Zr = 30; (e) Al/Zr = 40; (B): (f) Al/Zr = 150; (g) Al/Zr = 300; (h) Al/Zr = 500; (i) Al/Zr = 1200.

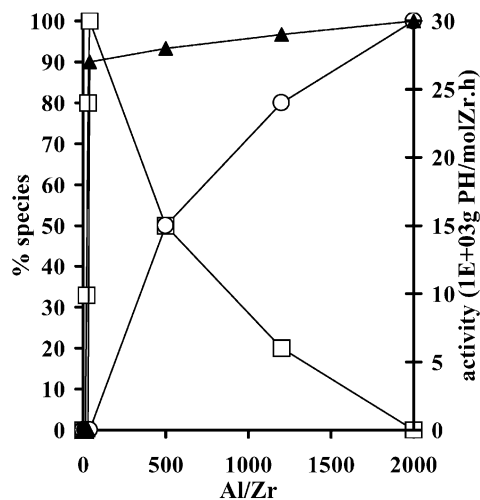


Fig. 5. Evolution of the catalytic activity of $\text{racEt}(\text{Ind})_2\text{Zr}(\text{NMe})_2$ for hex-1-ene polymerization with increasing $[\text{MAO}]/[\text{Zr}]$ ratios in toluene at 20°C (▲); comparison with the percentage of the active species at 435 nm (□) and at 470 nm (○).

way. The addition of small amounts of MAO ($\text{Al}/\text{Zr} < 15$) is first accompanied by a hypsochromic shift of the main absorption band from 403 to 390 nm in agreement with the formation of a monomethylated species. Similarly, addition of TMA on $\text{racEt}(\text{Ind})_2\text{Zr}(\text{CH}_2\text{Ph})_2$ ($\text{Al}/\text{Zr} < 15$) yields also monomethylated zirconocene. In both cases, it is very difficult to observe an isosbestic point because of the close location of the initial and final absorption bands.

The addition of much larger amounts of TMA ($\text{Al}/\text{Zr} = 2000\text{--}3000$) is required to achieve the complete dimethylation of the zirconocene.

Contrarily to the TMA effect, further addition of MAO ($15 < \text{Al}/\text{Zr} < 50$), yields a bathochromic shift of the UV band. The new species exhibit a main absorption band located at 432 nm (Fig. 6), in agreement with direct abstraction of one alkyl ligand (methyl or benzyl) instead of dimethylation. Such species were found already active towards hex-1-ene polymerization (Table 1). Again, the addition of higher amounts of MAO ($\text{Al}/\text{Zr} = 1500$) leads to a second bathochromic shift of the main absorption band from 432 to 470 nm, indicating the formation of cationic species complexed by TMA contained in MAO. Modification of the active species did not yield any significant

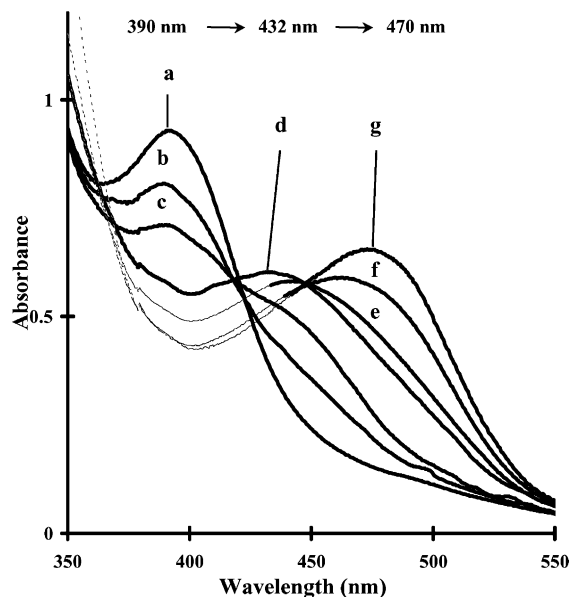


Fig. 6. UV-VIS absorption spectra of $\text{racEt}(\text{Ind})_2\text{Zr}(\text{CH}_2\text{Ph})_2$ in toluene at 20°C in the presence of increasing amounts of MAO: (a) $\text{Al}/\text{Zr} = 15$; (b) $\text{Al}/\text{Zr} = 30$; (c) $\text{Al}/\text{Zr} = 45$; (d) $\text{Al}/\text{Zr} = 50$; (e) $\text{Al}/\text{Zr} = 60$; (f) $\text{Al}/\text{Zr} = 150$; (g) $\text{Al}/\text{Zr} = 1500$.

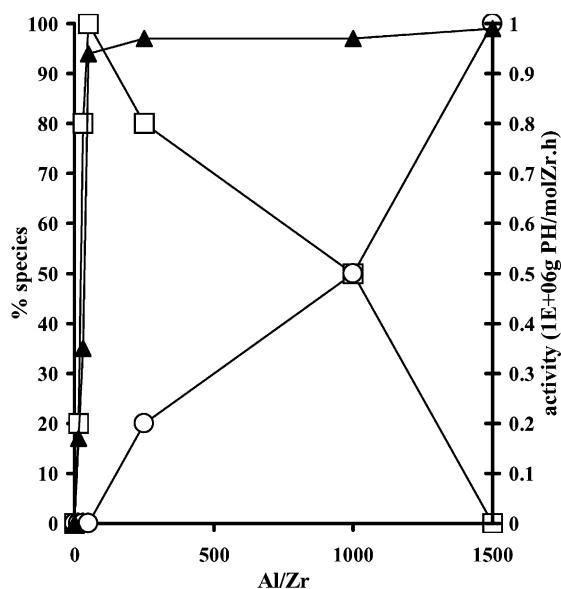
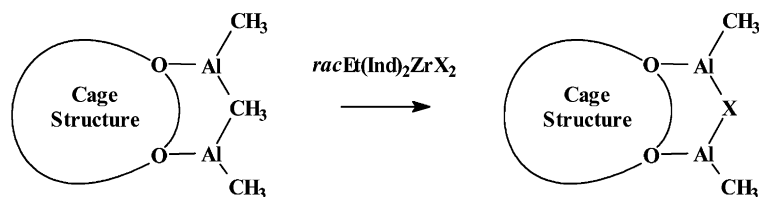


Fig. 7. Evolution of the catalytic activity of $\text{racEt}(\text{Ind})_2\text{Zr}(\text{CH}_2\text{Ph})_2$ for hex-1-ene polymerization with increasing $[\text{MAO}]/[\text{Zr}]$ ratios in toluene at 20°C (▲); comparison with the percentage of the active species at 432 nm (□) and at 470 nm (○).



Scheme 3. Schematic representation of MAO showing the substitution of one bridging methyl group by X ligand extracted from $\text{racEt}(\text{Ind})_2\text{ZrX}_2$ (X = Cl, NMe₂, CH₂Ph).

variation of the activity, as already observed with $\text{racEt}(\text{Ind})_2\text{Zr}(\text{NMe}_2)_2$. Evolution of polymerization activities with the proportion of species located at 432 and 470 nm, depending on Al/Zr ratio, is presented in Fig. 7.

3.4. General discussion

The general characteristics of the various catalytic systems investigated in this study and in previous ones [1] are summarized in Table 1. It can be noticed that, except for $\text{racEt}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}$ catalytic system, species exhibiting an absorption band in the range 420–440 nm, which form at rather low Al/Zr ratio = 50–150, are already highly active towards hex-1-ene polymerization. Their activity is in line with cationization of zirconocene precursor after alkylation as well as with the accessibility of the electro-deficient center to the incoming olefin monomer. However, the catalytic activity of the various species absorbing in this wavelength range could not be correlated more precisely to the location of their maximum of absorption.

The lack of reactivity of “intermediate” species absorbing at 440 nm in the case of $\text{racEt}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}$ catalytic system at Al/Zr ratios close to 150 [1] has been interpreted by back complexation of the chloride of [MAO-Cl]⁻ counter-anion onto the vacant site of the transition metal. This interaction would impede the olefin double-bond coordination on the zirconocene.

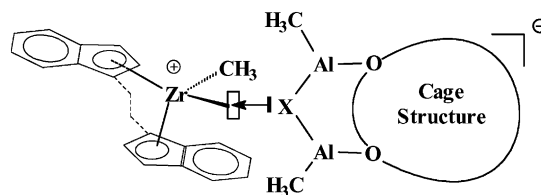
Since substitution of both dimethylamino ligands by methyl groups occurs prior to cationization, a quite similar structure can be considered for active species issued from the reaction of $\text{racEt}(\text{Ind})_2\text{Zr}(\text{NMe}_2)_2$ and $\text{racEt}(\text{Ind})_2\text{ZrMe}_2$ with MAO. In fact, the two species exhibit slightly different wavelengths. Lesser amount

of MAO is necessary to activate dimethylaminozirconocene compared to dimethylzirconocene. These results suggest that X ligands even extracted during the first alkylating steps are still interacting with the electron-deficient zirconocene species. The much lower catalytic activity observed for species issued from the dimethylamino-precursor is consistent with this hypothesis and may be interpreted by coordination of MAO-extracted dimethylamino groups to the metal vacant site through nitrogen electron pair. In the case of $\text{racEt}(\text{Ind})_2\text{ZrMe}_2$ as precursor, the extracted methyl ligands do not yield any modification in the structure and reactivity of the MAO counter-anion, thus allowing zirconium coordination site available for olefin (Scheme 3).

Similarly, kinetic data show that the extracted benzyl groups from $\text{racEt}(\text{Ind})_2\text{Zr}(\text{CH}_2\text{Ph})_2$ do not hinder the coordination for the incoming monomer. This last system yields high polymerization activity at low Al/Zr ratio.

4. Conclusions

In conclusion, the results reported in this paper point out the importance of the nature of extractable X ligands. The latter play a crucial role in the two



Scheme 4. Hypothetical structures of the species absorbing at around 440 nm (X = Me, Cl, NMe₂, CH₂Ph).

elementary steps of metallocene activation by MAO, i.e. alkylation and cationization which can be readily discriminated by means of UV–VIS spectroscopy. In agreement with recent literature [6], alkylation of the zirconocene precursor is accompanied by the replacement of MAO reactive bridging methyl groups by extracted X ligands, modifying the MAO structure and efficiency. This has a direct consequence on the cationization step yielding active species. Competition between MAO-extracted X groups of various coordinating ability and olefin coordination on metal vacant site is a key factor for catalytic activity of the zirconocenium species formed. A schematic representation of the structure of these species is shown in Scheme 4.

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