



## Novel aluminum based cocatalysts for metallocene catalyzed olefin polymerization

Incoronata Tritto<sup>a,\*</sup>, Laura Boggioni<sup>a</sup>, Maria Carmela Sacchi<sup>a</sup>, Tiziano Dall'Occo<sup>b</sup>

<sup>a</sup> *Istituto per lo Studio delle Macromolecole, CNR, Via E. Bassini 15, 20133 Milano, Italy*

<sup>b</sup> *Basell Italia S.p.A., Centro Ricerche G. Natta, P.le G. Donagani 12, 44100 Ferrara, Italy*

Received 24 October 2002; received in revised form 23 January 2003; accepted 8 February 2003  
Dedicated to Professor Renato Ugo on the occasion of his 65th birthday

### Abstract

The ethylene polymerization activity of *rac*-Et(indenyl)<sub>2</sub>ZrCl<sub>2</sub>/AlR<sub>3</sub>/modifier was studied. Modifiers were added to  $\beta$ -branched trialkylaluminum Al(*i*-Bu)<sub>3</sub> (TIBA), and Al(*i*-Oct)<sub>3</sub> (TIOA), and to their aluminoxanes, TIBAO and TIOAO, respectively, with the aim of obtaining new cocatalysts that operate at low aluminum/transition metal ratios. The modifiers selected contain hetero-atoms and aryl or alkyl groups bearing electron withdrawing substituents or sterically encumbered groups: C<sub>6</sub>F<sub>5</sub>OH, C<sub>6</sub>Cl<sub>5</sub>OH, C<sub>6</sub>F<sub>4</sub>(OH)<sub>2</sub>, C<sub>6</sub>F<sub>5</sub>NH<sub>2</sub>, 2,5-(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>OH, (CF<sub>3</sub>)<sub>2</sub>CHOH. The in situ reaction between aluminum compounds and modifiers such as C<sub>6</sub>F<sub>5</sub>OH yields new modified aluminum alkyl and aluminoxane cocatalysts bearing one alkoxy or aryloxy group. The simultaneous effect of electron withdrawing substituents on the aryloxy group and of steric hindrance due to  $\beta$ -alkyl substituted alkyls on aluminum leads to good activation of metallocenes at Al/Zr molar ratios as low as 200/1, in conditions in which methylaluminoxane and  $\beta$ -branched alkylaluminoxanes are inactive. NMR studies of the reactions between C<sub>5</sub>Me<sub>5</sub>ZrCl<sub>2</sub> with TIOA, TIOA/C<sub>6</sub>F<sub>5</sub>OH, TIOAO and TIOAO/C<sub>6</sub>F<sub>5</sub>OH demonstrated that in contrast to TIOAO-C<sub>6</sub>F<sub>5</sub>OH, TIOA-C<sub>6</sub>F<sub>5</sub>OH allows the formation of an active alkylated ion pair, thus qualitatively allowing us to understand the polymerization activity of C<sub>5</sub>Me<sub>5</sub>ZrCl<sub>2</sub> based systems.

© 2003 Elsevier Science B.V. All rights reserved.

**Keywords:** Aluminum alkyls; Aluminoxanes; Metallocenes; Olefin polymerization; NMR

### 1. Introduction

One of the most exciting advances in the area of organo transition metal catalyzed olefin polymerization has been the development of homogeneous single-center catalysts [1]. The recent advances originate from the discoveries of metallocenes [2,3] for stereoselective olefin polymerization and of methyl-

aluminoxane (MAO), a hydrolysis product of trimethylaluminum, as a very effective cocatalyst for metallocene catalyzed polymerization [4]. Traditional aluminum alkyls are unable to activate metallocenes for  $\alpha$ -olefin polymerization. Although MAO yields very high catalytic activities, it has several drawbacks such as the high Al/Mt ratios necessary to achieve good catalytic activities, and a solution instability that increases with time. Despite this interest, there are only few reports in the literature on the use of aluminum based cocatalysts different from MAO [5]. It was reported that branched  $\beta$ -alkyl substituted

\* Corresponding author. Tel.: +39-02-23699370;

fax: +39-02-2362-946.

E-mail address: [i.tritto@ismac.cnr.it](mailto:i.tritto@ismac.cnr.it) (I. Tritto).

aluminoxanes, prepared in situ from hydrolysis of the parent aluminum alkyls, exhibit remarkable catalytic activities for ethylene polymerization catalyzed by racemic ansa metallocenes [6–8].

Yang et al. [9] and Ewen and Elder [10] independently discovered that tris(perfluoroaryl)borane in combination with metallocenes yields highly active catalysts for olefin polymerization. Now it appears to be generally accepted that the active catalyst is a metal-alkylated cation in the presence of a labile stabilizing anion [11]. Methylaluminoxane has the ability to create very active sites by alkylating the metallocene and by stabilizing the metallocene cation as a bulky non-coordinating anion. This was shown by our studies of the reactions between metallocenes and aluminoxanes by low temperature  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy [12–14].

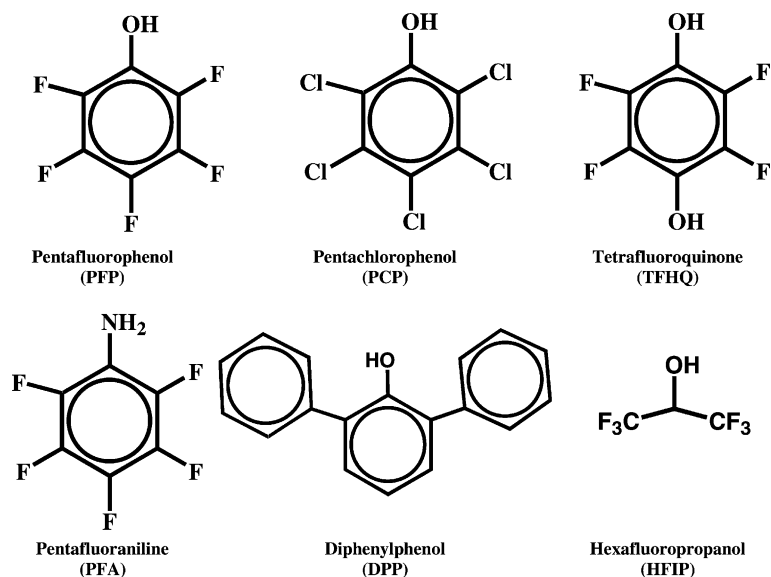
Sterically congested perfluoroarylaluminum derivatives [15–18] such as  $\text{Al}(\text{C}_6\text{F}_5)_3$  [15] and  $[\text{Ph}_3\text{C}]^+[\text{Al}(\text{C}_6\text{F}_5)_4]^-$  [16] are effective cocatalysts for activating metallocene and yield highly efficient olefin polymerization catalysts. Also the tritylaluminum  $[\text{Ph}_3\text{C}]^+[\text{Al}(\text{OC}_6\text{F}_5)_4]^-$  activates  $\text{Cp}'_2\text{ZrMe}_2$  ( $\text{Cp}' = \text{C}_5\text{H}_5$  (Cp) and substituted Cp) for ethylene polymerization [17].

The aim of the research work described herein is the obtaining of new cocatalysts which could replace MAO by promoting efficient olefin polymerization at

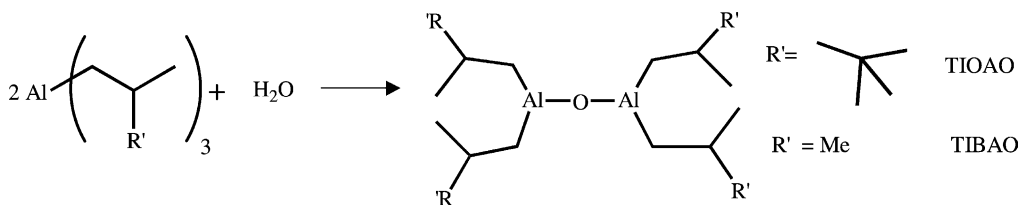
low Al/Mt molar ratios. Our approach consists of reacting compounds, containing hetero-atoms (N, O) having one reactive hydrogen and aryl or alkyl groups with electron withdrawing (F, Cl) or with steric encumbered substituents (Scheme 1), with aluminum alkyls and alkyaluminoxane. On the basis of previous results on new  $\beta$ -alkylsubstituted aluminoxane the selected  $\beta$ -branched trialkylaluminum are  $\text{Al}(i\text{-Bu})_3$  (TIBA),  $\text{Al}(i\text{-Oct})_3$  (TIOA) and the  $\beta$ -branched aluminoxanes are TIBAO and TIOAO [19,20].

The TIBAO and TIOAO cocatalysts are prepared in situ at the Al/H<sub>2</sub>O ratio of 2, the mole ratio at which they give the highest catalytic activity. Scheme 2 is only a schematic sketch of TIBAO and TIOAO [19–21], since they may be present in various more complex structures [22].

We sought a screening on the simultaneous effect of electron withdrawing  $-\text{N}-\text{R}$  or  $-\text{O}-\text{R}$  substituents and of  $\beta$ -alkylsubstituted alkyls on aluminum which could allow us to identify novel effective cocatalysts. Electronwithdrawing groups on arylboranes, arylborates or aluminates are known to enhance Lewis acidity and cocatalytic activity of this class of compounds. Groups having suitable steric hindrance should allow, after reaction with metallocene, the formation of active separated ion pairs. An exceedingly high steric hindrance is expected to restrict the approach with sterically



Scheme 1.



Scheme 2. Modifiers utilized in presence TIOA, TIOAO, TIBA and TIBAO.

hindered metallocenes and thus yield low polymerization activity. We tested them for ethylene polymerization with an ansa metallocene and performed NMR reaction studies on a selected model system to reveal their ability of acting as weakly coordinating anions.

## 2. Experimental

All manipulations were performed under dry nitrogen atmosphere by using a glove-box or standard Schlenk techniques. Materials: MAO, Al(*i*-Bu)<sub>3</sub>, were all purchased from WITCO GmbH. Al(*i*-Oct)<sub>3</sub>, TIBAO and TIOAO were synthesized as already reported [20]. For the NMR studies 30% solutions of MAO in toluene (Witco) were used after removing all volatiles and drying the resulting powder in vacuum (12 h, room temperature, 0.1 mmHg) *rac*-Et(indenyl)<sub>2</sub>ZrCl<sub>2</sub> was purchased from WITCO GmbH. Toluene and toluene-d<sub>8</sub> were extensively dried and distilled in nitrogen from sodium and sodium benzophenone ketyl, respectively. Modifiers were purchased from Aldrich and dried in vacuum and then dissolved in dried toluene, the solution was kept over molecular sieves.

### 2.1. NMR analysis

The samples for NMR analysis were prepared and studied by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy as already described [12,21].

### 2.2. Polymerization

Ethylene polymerization was performed in a 250 ml thoroughly dried round bottom flask. Toluene, aluminum derivative and modifier toluene solution (or suspension) (total volume 100 ml) were introduced.

Ethylene pressure was set at 1 atm and equilibration was allowed (for 15 min) and kept constant during the polymerization runs by continuously feeding ethylene. The temperature was increased to 55 °C. The metallocene (4 μmol), which was prealkylated by mixing metallocene and aluminum alkyl (TIBA or TIOA) in a ratio of 50/1 in a 10 ml Schlenk flask in toluene solution and then left to react for 10 min at room temperature, was introduced. The total pressure was maintained constant. After 1 h polymerization at 55 °C, the reactor was degassed, the polymer was recovered by filtration and dried in vacuum at 70 °C.

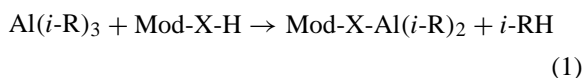
### 2.3. Molar mass measurements

Intrinsic viscosity of polymers was measured in tetrahydronaphthalene at 135 °C. Molar mass distribution was measured using a Waters GPCV 2000 high-temperature gel permeation chromatography (GPC) equipped with refractive index and a viscosity detector (differential viscometer). Columns 3TSK gel GMHXL-HT + 2F (2.10 μm). Measurements were taken in *o*-dichlorobenzene at 145 °C.

## 3. Results and discussion

### 3.1. Polymerization

The new aluminum based cocatalysts have been generated in situ and used without isolation by reacting aluminum alkyls and/or aluminoxanes and the modifiers (Mod-X-H, X = N or O) in Scheme 1 by using Al/Mod-X-H molar ratio greater than 5/1. The active hydrogen could react with the aluminum alkyls according to the following general equation.



Indeed, it is reported that O–H proton in pentafluorophenol reacts rapidly at room temperature in pentane with trialkylaluminum derivatives, including triisobutylaluminum, according to Eq. (1) to yield  $C_6F_5O-Al(i-Bu)_2$  [23].

The in situ generation of  $C_6F_5O-Al(i-Oct)_2$  has been verified by NMR spectroscopy, the  $^1H$  NMR signal of  $C_6F_5OH$  observed in toluene at 3.8 ppm disappeared in the spectrum of  $Al(i-Oct)_3/C_6F_5OH$  mixture at Al/PFP molar ratio of 5/1. We assume that only one alkyl has been substituted since the condition in which three equivalents of  $C_6F_5OH$  completely substitute the methyl of  $AlMe_3$  to yield  $Al(OC_6F_5)_3$ , are reported to be 12 h in toluene to reflux.  $Al(OC_6F_5)_3$  is reportedly not able to activate a number of bridged dimethylzirconocenes [24].

Great care has been taken in order to avoid adventitious moisture, which would immediately cause the formation of  $\beta$ -substituted aluminoxane extremely active cocatalysts for olefin polymerization catalyzed by metallocenes.

The efficacy of the modified aluminum alkyls and aluminoxanes as olefin polymerization initiators was tested for ethylene polymerizations. We have selected to test  $rac-Et(indenyl)_2ZrCl_2$ , the most studied and easily available ansa metallocene, for the ethylene polymerization activity screening in the presence of aluminum alkyls-modifiers mixtures. The metallocene dichloride has been prealkylated by using an aluminumtrialkyl/Zr molar ratio of 50/1 before injecting it in the polymerization medium. The modified aluminum reagents could be less effective in alkylating the metallocene dichloride than the trialkylaluminum

thus masking the results of assays of their ability in abstracting an alkide or halide from metallocene and in acting as weakly coordinating anions [12].

We have chosen for the screening of the new cocatalysts  $Al_{tot}/Zr$  molar ratios as low as 200 in which the aluminoxanes (MAO, TIBAO, TIOAO) potentially produced by reaction of adventitious water are inactive, under our experimental conditions, as shown in Table 1, while the amount of metallocene was suitable to keep an [Al] concentration high enough to scavenge all possible impurities. Initially we have explored the conditions for the screening of the new cocatalysts by varying the ratio between aluminum compound and pentafluorophenol. Results obtained at various  $Al_{tot}/PFP$  (Table 1) showed that the modified cocatalyst is able to activate  $rac-Et(indenyl)_2ZrCl_2$  for ethylene polymerization at a low Al/Zr molar ratio and under conditions in which MAO or the  $Al(i-Oct)_3/H_2O$  mixture are not good activators. Since the polymerization activity did not vary in the Al/Mod-X-H ratio interval between 3 and 20, polymerization tests for all the other modifiers were performed at the more convenient molar ratio Al/modifier of 20 and  $Al_{tot}/Zr$  of 200.

Results of ethylene polymerization by using the mixtures of TIOA and the whole range of modifiers along with polymer characterization are reported in Table 2 and Fig. 1. Interestingly all the aromatic modifiers containing an electron withdrawing substituent when combined with TIOA activate  $rac-Et(Indenyl)_2ZrCl_2$  for ethylene polymerization. The polymerization activity increases in the order:



Table 1  
Polymerisation activity of ethylene obtained with  $rac-Et(indenyl)_2ZrCl_2$  and different cocatalyst<sup>a</sup>

$Al_{tot}/Zr$	$Al_{tot}/PFP$	Activity (kg pol/mol Zr h)	Cocatalyst	$M_w (\times 10^{-3})$ (g/mol)	$M_w/M_n$
500	–	258	MAO	221	3.43
200	–	–	MAO	–	–
200	–	–	TIOA	–	–
200	3	264	TIOA	–	–
200	10	257	TIOA	–	–
200	20	296	TIOA	240	4.25
200	–	7.5	TIOAO <sup>b</sup>	–	–
200	20	194	TIOAO	–	–

<sup>a</sup> Polymerization conditions:  $[Zr] = 0.04$  mmol/l, solvent = toluene,  $T = 55^\circ C$ ,  $t = 1$  h,  $pC_2 = 1$  atm, prealkylation ratio: Al/Zr = 50/1 molar ratio, prealkylation time = 15 min.

<sup>b</sup> TIOAO obtained from in situ reaction between TIOA and  $H_2O$  at molar ratio TIOA/ $H_2O$  = 2.

Table 2

Polymerisation activity of ethylene,<sup>a</sup> molecular weight ( $M_w$ ) and intrinsic viscosity of polyethylene obtained with *rac*-Et(indenyl)<sub>2</sub>ZrCl<sub>2</sub> and TIOA/TIOAO + modifiers

Modifier	Aluminium alkyl derivative	Activity (kg pol/mol Zr h)	$M_w$ ( $\times 10^{-3}$ ) (g/mol)	$M_w/M_n$	$[\eta]$ (dl/g)
PFP	TIOA	296	240	4.25	1.81
PFP	TIOAO <sup>b</sup>	194	–	–	2.02
PCP	TIOA	158	185	3.62	1.82
PCP	TIOAO	238	246	4.22	2.28
TFHQ	TIOA	197	206	4.09	2.01
TFHQ	TIOAO	269	247	4.14	2.25
PFA	TIOA	60	141	3.24	1.84
PFA	TIOAO	191	170	3.22	1.73
DPP	TIOA	13	–	–	2.02
DPP	TIOAO	208	312	5.01	2.48
HFIP	TIOA	–	–	–	–
HFIP	TIOAO	134	155	3.33	1.65

<sup>a</sup> Polymerization conditions:  $[Zr] = 0.04$  mmol/l,  $Al_{tot}/Zr = 200$ ,  $Al_{tot}/modifier = 20$ , solvent = toluene,  $T = 55^\circ C$ ,  $t = 1$  h,  $pC_2 = 1$  atm, prealkylation ratio:  $Al/Zr = 50/1$  molar ratio, prealkylation time = 15 min.

<sup>b</sup> TIOAO obtained from in situ reaction between TIOA and H<sub>2</sub>O at molar ratio TIOA/H<sub>2</sub>O = 2.

The non-aromatic HFIP is not able to give an active modified cocatalyst. The order of the polymerization activity observed seems to be due to the electronwithdrawing effect of the substituents (pentafluorophenoxy derivative being more active than the pentachlorophenoxy one). The low performance of pentafluoroaniline could be due to the nature of the hetero-atom or to the presence of two

active hydrogens which could lead to the formation of  $-Al-N(R)-Al-$  species. Finally, the diphenylphenoxyaluminum derivative has some beneficial effect on the polymerization activity, while we found that the unsubstituted phenoxy-di-*i*-octylaluminum reagent does not act as activator. Such an effect could arise from the size or from the electronic effect of the phenyl substituent.

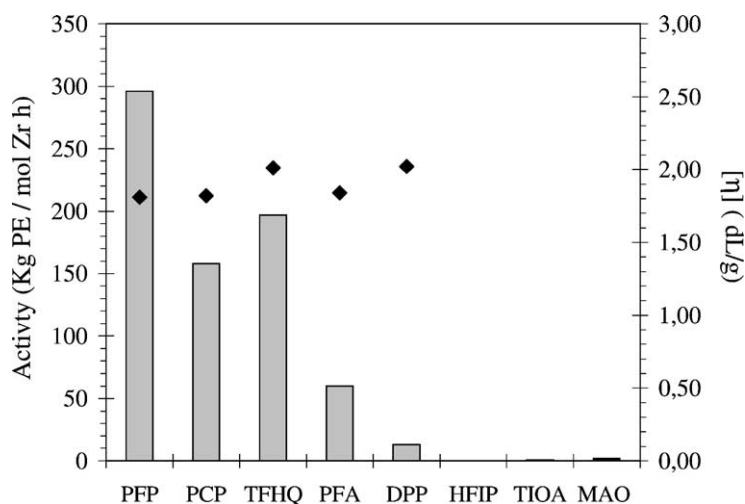


Fig. 1. Polymerisation activity of ethylene and intrinsic viscosity ( $\blacklozenge$ ) of polyethylene obtained with *rac*-Et(indenyl)<sub>2</sub>ZrCl<sub>2</sub> in presence of TIOA, MAO and TIOA/modifiers (see Tables 1 and 2).

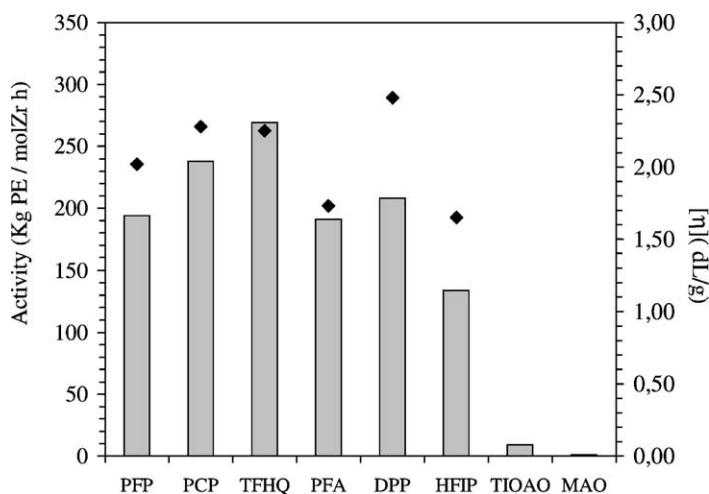


Fig. 2. Polymerisation activity of ethylene and intrinsic viscosity (◆) of polyethylene obtained with *rac*-Et(indenyl)<sub>2</sub>ZrCl<sub>2</sub> in presence of TIOAO, MAO and TIOAO/modifiers (see Table 2).

Ethylene polymerization results with TIOAO/modifiers are reported in Fig. 2 and Table 2. In the presence of TIOAO, all the modifiers give a relatively high comparable catalytic activity. It is worthwhile remembering that the TIOAO alone is almost inactive under the same polymerization conditions (Al/Zr molar ratio of 200 and 1 atm ethylene pressure). The least active being the HFIP modified oxane, HFIP modified TIOA was not effective in initiating the ethylene

polymerization. The values of intrinsic viscosity are different from those obtained with TIOA/modifiers. The order of the polymerization activity does not seem to follow the electron withdrawing capacity of aromatic substituents.

The complexity of the activating effects is also evident from the comparison of ethylene polymerization results in the presence of TIBA and TIBAO (Table 3). Pentafluorophenol confirms to have the most beneficial

Table 3

Polymerisation activity of ethylene,<sup>a</sup> molecular weight ( $M_w$ ) and intrinsic viscosity of polyethylene obtained with *rac*-Et(indenyl)<sub>2</sub>ZrCl<sub>2</sub> and TIBA/TIBAO + modifiers

Modifier	Aluminium alkyl derivative	Activity (kg pol/mol Zr h)	$M_w$ ( $\times 10^{-3}$ ) (g/mol)	$M_w/M_n$
PFP	TIBA	163	–	–
PFP	TIBAO <sup>b</sup>	4	–	–
PCP	TIBA	78	127	3.80
PCP	TIBAO	61	112	6.73
TFHQ	TIBA	7	–	–
TFHQ	TIBAO	75	134	3.72
PFA	TIBA	–	–	–
PFA	TIBAO	–	–	–
DPP	TIBA	3	–	–
DPP	TIBAO	182	189	4.16
HFIP	TIBA	–	–	–
HFIP	TIBAO	–	–	–

<sup>a</sup> Polymerization conditions: [Zr] = 0.04 mmol/l, Al<sub>tot</sub>/Zr = 200, Al<sub>tot</sub>/modifier = 20, solvent = toluene,  $T = 55$  °C,  $t = 1$  h,  $p_{C_2} = 1$  atm, prealkylation ratio: Al/Zr = 50/1 molar ratio, prealkylation time = 15 min.

<sup>b</sup> TIBAO obtained from in situ reaction between TIBA and H<sub>2</sub>O at molar ratio TIBA/H<sub>2</sub>O = 2.

effect when added to a trialkylaluminum, while it is almost ineffective when added to TIBAO. In contrast with the good activities obtained when using TIOAO/modifiers, the addition of modifiers to TIBAO does not yield good activities with the exception of DPP. This may reflect the fact that, as is reported in the literature [5c] and as we found in our experience, TIBAO likely due to the high reactivity of isobutyl alkyl derivative with water under some conditions can give the inactive polyaluminumoxane.

Values of intrinsic viscosity are similar for all the TIOA and TIOAO based cocatalytic systems, similarity in the molecular masses (MM) are clear from data obtained from SEC (Tables 1 and 2 and Figs. 1 and 2). Polydispersities are rather broad, but not unusual for polyethylene which soon tends to precipitate when prepared under the present conditions see data for PE obtained with MAO (Table 1). Minor, but significant dependence of molar masses on the modifier and on the aluminum alkyl or on the aluminoxane derivative is observed: (i) the MM of PE obtained in the presence of the modified aluminoxane being in general higher than those of PE obtained in the presence of the aluminum alkyl/modifiers mixtures; (ii) MM slightly depends on the type of modifier, e.g. MM of PE obtained by activating the catalyst precursor with TFHQ/TIOA or TFHQ/TIOAO are both

greater than those PE obtained by aluminum alkyl derivative modified with PFA. This confirms that the reaction between aluminum compounds has produced novel aluminum derivatives bearing one alkoxy or aryloxy group [25], which act as initiators rather than having formed TIBAO or TIOAO because of moisture impurities in the reaction medium.

### 3.2. NMR reaction studies

NMR reaction studies of metallocenes with various cocatalysts are a very valuable tool for revealing the activation and decomposition reactions between metallocenes and cocatalysts which affect the cocatalytic activity [11,21,26,27]. Our previous NMR studies of reactions between  $\text{Cp}_2\text{ZrCl}_2$  and  $\text{Cp}_2^*\text{ZrCl}_2$  ( $\text{Cp} = \text{C}_5\text{H}_5$ ,  $\text{Cp}^* = \text{Me}_5\text{C}_5$ ) with TIOA, TIBA, TIOAO, and TIBAO accounted for the trend of polymerization activity of these systems and demonstrated the importance of the stability of Zr-alkyl bond on the catalytic activity [21].

Thus,  $\text{Cp}_2^*\text{ZrCl}_2$  has been used as metallocene model in NMR experiments because the  $^1\text{H}$  and  $^{13}\text{C}$  signals of  $\text{Cp}^*$  in alkylated and ionic species are known in literature and in our previous experiments with the  $\beta$ -branched alkylaluminum compounds of the present study ( $\text{Al}/\text{Zr} = 10$ ) [21]. We have selected

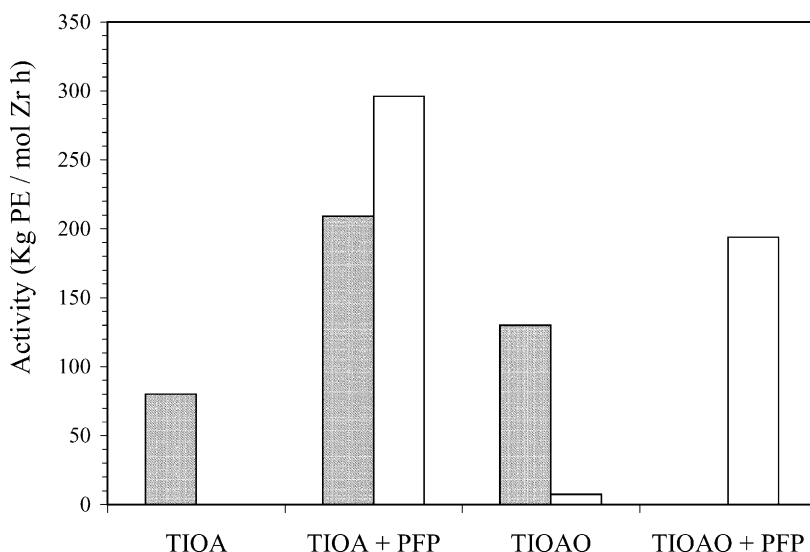


Fig. 3. Polymerisation activity of ethylene in presence of  $\text{Cp}_2^*\text{ZrCl}_2$  (■),  $\text{rac-Et}(\text{indenyl})_2\text{ZrCl}_2$  (□) and different cocatalysts.



Table 4  
 $\text{Cp}_2^*\text{ZrCl}_2$  reaction products at 313 K<sup>a</sup>

Cocatalyst	<sup>13</sup> C NMR (ppm) <sup>b</sup> Cp*	Zirconocene complex <sup>c</sup>	mol%
TIOA	120.72	$\text{Cp}_2^*\text{Zr}(i\text{-Oct})^{\delta+} \text{ClA}^{\delta-}$ (Alk-IP 1)	16
	124.44	$\text{Cp}_2^*\text{ZrCl}^+ \text{ClA}^-$ (Cl-IP)	84
TIOA + PFP	120.49	$\text{Cp}_2^*\text{Zr}(i\text{-Oct})^{\delta+} \text{ClA}^{\delta-}$ (Alk-IP 2)	15
	124.18	$\text{Cp}_2^*\text{ZrCl}^+ \text{ClA}^-$ (Cl-IP)	85
TIOAO <sup>d</sup>	120.29	$\text{Cp}_2^*\text{Zr}(i\text{-Oct})^{\delta+} \text{ClA}^{\delta-}$ (Alk-IP 2)	11
	120.58	$\text{Cp}_2^*\text{Zr}(i\text{-Oct})^{\delta+} \text{ClA}^{\delta-}$ (Alk-IP 1)	30
	123.94	$\text{Cp}_2^*\text{ZrCl}^+ \text{ClA}^-$ (Cl-IP)	59
TIOAO <sup>d</sup> + PFP	123.49	$\text{Cp}_2^*\text{ZrCl}_2$ (NC)	100

<sup>a</sup> Solvent: toluene- $d_8$ ,  $[\text{Zr}] = 0.07 \text{ M}$ ;  $[\text{Al}]/[\text{Zr}] = 10$ .

<sup>b</sup> <sup>13</sup>C NMR spectra was recorded in toluene- $d_8$  on a Bruker AM 270 spectrometer. Chemical shifts are referenced to <sup>13</sup>C NMR signal (20.52 ppm) of the deuterated toluene- $d_8$  solvent.

<sup>c</sup> A: cocatalyst.

<sup>d</sup> TIOAO obtained from in situ reaction between TIOA and H<sub>2</sub>O at molar ratio TIOA/H<sub>2</sub>O = 2.

pentafluorophenol among the modifiers as the one which yields modified aluminium alkyls with interesting cocatalytic activities. NMR studies of reactions between  $\text{Cp}_2^*\text{ZrCl}_2$  with PFP/TIOA and PFP/TIOAO have been performed in conditions similar to those used in previous studies without modifiers [21]. These NMR reaction studies have been accompanied by polymerization experiments by activating  $\text{Cp}_2^*\text{ZrCl}_2$  under conditions like those used for activating *rac*-Et(indenyl)<sub>2</sub>ZrCl<sub>2</sub> and reported in Tables 2 and 3. The comparison of polymerization activities in Fig. 3 already shows how the cocatalytic efficiency of initiators also depends on metallocene ligands. TIOA–PFP yields the best activities with both metallocenes, in contrast TIOAO–PFP is unable to initiate ethylene polymerization with  $\text{Cp}_2^*\text{ZrCl}_2$ . These polymerization data are accounted for by results of NMR studies of reactions between  $\text{Cp}_2^*\text{ZrCl}_2$  and PFP modified cocatalysts. In Table 4 the reaction products, observed by NMR, due to the effects of the addition of PFP modifier to  $\text{Cp}_2^*\text{ZrCl}_2$ /TIOA and to the higher active  $\text{Cp}_2^*\text{ZrCl}_2$ /TIOAO are compared. Identification of the reaction products has been made taking into account that under similar conditions (i) both AlMe<sub>3</sub>, TIOA, and TIOAO only monoalkylate both  $\text{Cp}_2^*\text{ZrCl}_2$  and  $\text{Cp}_2^*\text{ZrCl}_2$  [21]; (ii) aluminumalkyls tends to give chlorine rather than alkyl abstraction [14,28]; (iii) TIOA forms the alkylated ion pair (Alk-IP 1) and TIOAO two alkylated ion pairs (Alk-IP 1) and (Alk-IP 2), which have slight differences in Cp chemical shifts [21].

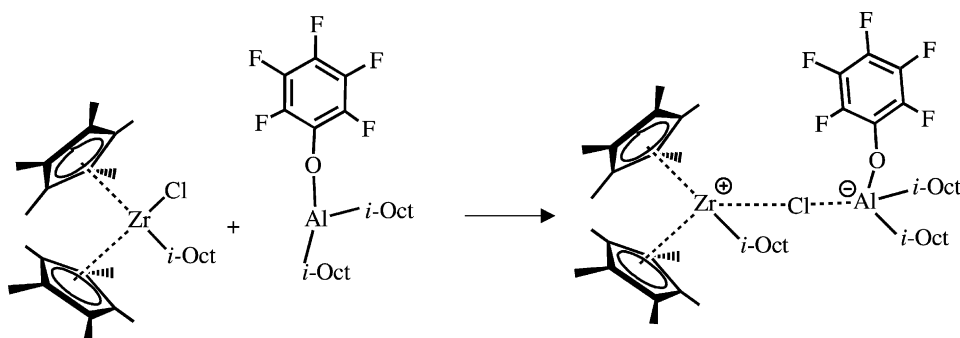
TIOA–PFP allows the formation of an alkylated ion pair (Alk-IP 2)<sup>1</sup> corresponding to the more active one of the two species we observed in the system in the presence of TIOAO.<sup>2</sup> Such a species is present in higher amount (15 mol%) in TIOA–PFP than in TIOAO (11 mol%) based systems. Surprisingly the TIOAO–PFP is not able to alkylate and yield alkylated ion pairs with  $\text{Cp}_2^*\text{ZrCl}_2$  in agreement with the no activating effect observed in the polymerization experiments. We see that, although that the Al/Zr ratio of 10 used for the NMR experiments is low with respect to Al<sub>tot</sub>/Zr = 200 used in the polymerization experiments, the difference in polymerization activities can be qualitatively related to the alkylated ion pairs present in the reactions in NMR tube.

Finally, since the polymerization activity of these catalytic systems does not vary by using Al/modifier ratios between 3 and 20 (Table 1) we propose that equilibrium in Scheme 3 represents the catalytically active ion pair formation.

<sup>1</sup> It is worthwhile noting that the difference in Cp\* chemical shifts between Cl-IP and Alk-IP2 in TIOA + PFP and in TIOAO is about 3.67 ppm in both.

<sup>2</sup> It is difficult on the basis of these data to elucidate the nature of the two ion pairs (Alk-IP 1) and (Alk-IP 2). Unpublished results of our laboratory from in situ NMR studies performed by adding <sup>13</sup>C enriched ethylene to the two systems under NMR conditions indicated that while  $\text{Cp}_2^*\text{ZrCl}_2$ /TIOA gives only oligomers,  $\text{Cp}_2^*\text{ZrCl}_2$ /TIOAO is able to polymerize ethylene. Simultaneously to polymer formation there is a decrease in intensity of the Cp signal of the alkylated ion pair (Alk-IP 2), which seems to be the most active of the two species.





Scheme 3.

#### 4. Conclusions

To summarize we have tested the efficiency for ethylene polymerization of *rac*-Et(indenyl)<sub>2</sub>ZrCl<sub>2</sub>/AlR<sub>3</sub>/modifier. Novel cocatalysts have been prepared in situ from the reaction of  $\beta$ -branched trialkylaluminum Al(*i*-Bu)<sub>3</sub>, and Al(*i*-Oct)<sub>3</sub> and of their  $\beta$ -branched aluminoxanes, with several organic compounds having hydroxyl or amine groups, and bearing electronwithdrawing or sterically hindered substituents on the alkyl or aryl groups. We have found that they can activate *rac*-Et(indenyl)<sub>2</sub>ZrCl<sub>2</sub> at low aluminum/transition metal ratios (Al/Zr = 200/1) under conditions in which we do not observe catalytic activities with alkylaluminoxanes of this study. Polymer molecular weights are comparable to those obtained with MAO. Significant polymerization activity are obtained especially for hydroxylated aromatic compounds having fluorine substituents which yield interesting non-aluminoxane cocatalysts when reacting C<sub>6</sub>F<sub>5</sub>OH with Al(*i*-Oct)<sub>3</sub> to yield the active C<sub>6</sub>F<sub>5</sub>O-Al(*i*-Oct)<sub>2</sub> [25].<sup>3</sup> NMR studies

<sup>3</sup> In the course of this work we have found patents which described the use of reagents or additives containing electron-rich heteroatoms and hydrocarbyl substituents to polymethylalumoxane. Compositions formed by use of such reagents or additives [29] are reported to have allowed enhanced solution stability and in some cases enhanced cocatalytic efficiency. A catalyst system for the polymerization of olefins in which the cocatalyst is a composition which predominantly includes aryloxyaluminoxane [–O(OR)Al–]<sub>n</sub> is described [30]. R is an unsubstituted or substituted aryl, such as a phenyl group, which contains at least one suitable electron withdrawing group such as fluoro. Very high Al/Zr molar ratios (3.14 × 10<sup>5</sup>) are used when the aluminum compound is isobutylaluminoxane.

performed on the reactions between Cp<sup>\*</sup><sub>2</sub>ZrCl<sub>2</sub> and the most active cocatalyst obtained from C<sub>6</sub>F<sub>5</sub>OH with Al(*i*-Oct)<sub>3</sub> confirm the ability of C<sub>6</sub>F<sub>5</sub>O-Al(*i*-Oct)<sub>2</sub> to form active ion pairs. The use of isotopically enriched aluminium alkyls would allow to monitor NMR reactions at higher Al/Zr ratios, that is, in conditions closer to polymerization experiments [31], although it is worth noting that the activity of these catalytic systems does not vary by using Al/modifier ratios between 3 and 20. Thus, the excess of aluminumalkyl used acts as mere scavenger at Al/modifier ratio of 20.

However, in order to find a rationale of the complex catalytic features observed a thorough study of each cocatalytic system would be required. The combination of <sup>13</sup>C, <sup>19</sup>F NMR spectroscopy is expected to give detailed information. Indeed, each of these cocatalytic systems depending on the relative modifier metallocene steric hindrance could irreversibly yield byproducts which are inactive for polymerization, for example, by more or less facile F or X-Ar abstraction or exchanges.

#### Acknowledgements

The authors are grateful to the late Prof. Umberto Giannini for having inspired this work and his very helpful and valuable advice. They would also like to thank Giulio Zannoni, for his NMR assistance and Alberto Giacometti Schieronni for SEC measurements. Dr. L. Boggioni would like to thank MONTELL (now BASSELL) for a fellowship.

## References

- [1] L. Resconi, L. Cavallo, A. Fait, F. Piemontesi, *Chem. Rev.* 100 (2000) 1253.
- [2] W. Kaminsky, K. Külper, H.H. Brintzinger, F.R.W.P. Wild, *Angew. Chem. Int. Ed. Engl.* 24 (1985) 507.
- [3] J.A. Ewen, *J. Am. Chem. Soc.* 106 (1984) 6355.
- [4] H. Sinn, W. Kaminsky, *Adv. Organometal Chem.* 18 (1980) 99.
- [5] W. Kaminsky, M. Miri, H.J. Sinn, R. Woldt, *Makromol. Chem., Rapid Commun.* 4 (1983) 417.
- [6] T. Dall'Occo, M. Galimberti, L. Resconi, E. Albizzati, G. Pennini, WO 96/02580 to Montell Technology B.V. (1996).
- [7] L. Resconi, M. Galimberti, F. Piemontesi, F. Guglielmi, E. Albizzati, EP 0575875 to Montell Technology B.V. (1993).
- [8] L. Resconi, T. Dall'Occo, U. Giannini, in: J. Scheirs, W. Kaminsky (Eds.), *Metallocenes-Based Polyolefins. Preparation, Properties and Technology*, Wiley, Chichester, 2000, p. 69.
- [9] X. Yang, C.L. Stern, T.J. Marks, *Angew. Chem. Int. Ed. Engl.* 31 (1992) 1375.
- [10] J.A. Ewen, M.J. Elder, *Eur. Patent Appl.* 0,427,697 (1991).
- [11] E.Y. Chen, T.J. Marks, *Chem. Rev.* 100 (2000) 1391.
- [12] I. Tritto, R. Donetti, M.C. Sacchi, P. Locatelli, G. Zannoni, *Macromolecules* 30 (1997) 1247.
- [13] I. Tritto, M.C. Sacchi, P. Locatelli, S.X. Li, *Macromol. Symp.* 89 (1995) 289.
- [14] I. Tritto, S.X. Li, M.C. Sacchi, G. Zannoni, *Macromolecules* 26 (1993) 7111.
- [15] P. Biagini, G. Lugli, L. Abis, P. Andreussi, US Patent 5,602,269 to Enichem (1997).
- [16] Y. Sun, M.V. Metz, C.L. Stern, T.J. Marks, *Organometallics* 19 (2000) 1625.
- [17] Y.X. Chen, M.V. Metz, L.T. Li, C.L. Stern, T.J. Marks, *J. Am. Chem. Soc.* 120 (1998) 6287.
- [18] Y.X. Chen, C.L. Stern, S.T. Yang, T.J. Marks, *J. Am. Chem. Soc.* 118 (1996) 12451.
- [19] L. Resconi, U. Giannini, E. Albizzati, US Patent 5,126,303 to Himont (1992).
- [20] T. Dall'Occo, M. Galimberti, I. Camurati, M. Destro, O. Fusco, D. Brita, in: W. Kaminsky (Ed.), *Metalorganic Catalysts for Synthesis and Polymerization*, Springer, Berlin, 1999, p. 142.
- [21] I. Tritto, D. Zucchi, M. Destro, M.C. Sacchi, T. Dall'Occo, M. Galimberti, *J. Mol. Catal. A: Chem.* 160 (2000) 107.
- [22] C.J. Harlan, S.G. Bott, A.R. Barron, *J. Am. Chem. Soc.* 117 (1995) 6465.
- [23] D.G. Hendershot, R. Kumar, M. Barber, J.P. Oliver, *Organometallics* 10 (1991) 1917.
- [24] D. Chakraborty, E.Y.-X. Chen, *Macromolecules* 35 (2002) 13.
- [25] S.J. Obrey, A.R. Barron, Reaction of  $\text{Ph}_3\text{COH}$  and  $\text{AlMe}_3$  is reported to yield  $[\text{Me}_2\text{Al}(m\text{-OCPh}_3)]_2$  and not MAO, *J. Chem. Soc., Dalton Trans* 17 (2001) 2456.
- [26] S. Beck, H.H. Brintzinger, *Inorg. Chim. Acta* 270 (1998) 376.
- [27] S. Beck, M.H. Prosen, H.H. Brintzinger, *J. Mol. Catal. A: Chem.* 128 (1998) 41.
- [28] I. Tritto, M.C. Sacchi, P. Locatelli, F. Forlini, in: R. Blom, A. Follestad, E. Rytter, M. Tilset, M. Ystenes (Eds.), *Organometallic Catalysts and Olefin Polymerization*, Springer, Berlin, 2001, p. 253.
- [29] N.H. Tran, S.D.L. Devenport, D.B. Malpass, C.S. Rabbit, US Patent 5,329,032 to Akzo Chemicals (1994).
- [30] T.J. Marks, X. Yang, S.B. Mirviss, US Patent 5,939,346 to Akzo Nobel (1999).
- [31] D.E. Babushkin, N.V. Semikolenova, V.A. Zakharov, E.P. Talsi, *Makromol. Chem. Phys.* 201 (2000) 558.