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Investigation of the Reaction Between Benzophenone and Trimethylaluminium: A Source of Novel Aluminic Activator for Single-site Olefin Polymerization Catalysts

Thomas Dalet, Henri Cramail, Alain Deffieux*

Summary: The reaction between benzophenone and TMA was investigated in details at 20 °C for different TMA/benzophenone (r) ratios. For $r = 2$, a heterodimer μ-(1,1-diphenylethoxy)-μ-methyl-tetramethyldialuminium (**B**) is only formed. The latter was found able to activate MeDIP(2,6-iPrPh)$_2$FeCl$_2$ catalyst towards ethylene polymerization. Such catalytic system leads to the formation of high molar mass polyethylene with a broad molar mass distribution, without the presence of oligomers, that is attributed to a strong reduction of the transfer reaction to TMA.

Keywords: catalysts; iron catalyst; MAO; polyethylene (PE)

Introduction

An important breakthrough in the field of polyolefins was the discovery in the 80's of methylaluminoxane (MAO) as an effective activator of metallocene derivatives and, later on, of post-metallocene complexes. The MAO commonly used in such reactions is formed by soft hydrolysis of trimethylaluminium (TMA) and presents an ill-defined cage-like structure. It has to be added in large excess with respect to the transition metal (typically Al/Met > 3000, in homogeneous conditions) to yield high catalytic activity.[1] These limitations have triggered a series of studies undertaken with the goal to develop novel routes to MAO or to found substitutes that could be more efficient towards transition metal derivatives activation.

Several patents[2,3,4] describe the synthesis of MAO by non-hydrolytic routes based on the reaction of TMA with either oxygen-containing compounds such as phenyl boronic acid, trialkylboroxine or organic compounds having a carbonyl function such as ketones, esters, acids, etc... These pathways result in the formation first of aluminium alcoholates and then of oligomeric Al-O compounds (MAO-like). Shifting the reaction towards the formation of alumoxane structures generally requires the presence of catalytic amounts of commercial MAO.[5]

In this paper, we examine the reaction of TMA with benzophenone at different ratios of the reactants and at different temperatures, without the use of any additional commercial MAO as catalyst. The various aluminum alkoxide mixtures obtained in these reactions were then tested as activators of MeDIP(2,6-iPrPh)$_2$FeCl$_2$ for ethylene polymerization.

Experimental Section

Reagents

Toluene (Baker) was purified by distilling over polystyryl lithium. 2 M solution of trimethylaluminum (TMA) in toluene and MAO as 10 wt % solution in toluene (Schering, A.G.; Germany) were used as such. 2,6-bis{1-[2,6(diisopropylphenyl)-imino]ethylpyridine iron dichloride [Me

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Laboratoire de Chimie des Polymères Organiques, ENSCPB-CNRS-Université Bordeaux-1 (UMR 5629), 16, Avenue Pey-Berland, 33607 Pessac Cedex, France

DIP(2,6-iPr Ph)$_2$FeCl$_2$] was synthesized as reported in literature.[6]

Typical Reaction Between TMA and Benzophenone

In a 100 mL round bottom flask fitted with a reflux condenser, 5.3 g (29.3×10^{-3} moles) of benzophenone was taken under nitrogen atmosphere. 20 mL of dry toluene was then added and the mixture was stirred for the complete dissolution of benzophenone and let at 0 °C. 18.6 mL of 2 M TMA solution (38.1×10^{-3} moles) in toluene was then added drop-wise over a period of 10 minutes. The solution became yellow and was then maintained at room temperature (20 °C) until discoloration.

Ethylene Polymerization

100 mL of dry toluene was first transferred into a Schlenk tube (previously flame dried under vacuum) having a magnetic stirrer and was then connected to the one atmosphere ethylene gas outlet using a rubber tube. Ethylene was bubbled through the Schlenk tube for half an hour to remove dissolved N_2. 0.8 mL of the aluminic alkoxide (**B**) was then introduced into the Schlenk tube using a syringe. The polymerization was initiated at 30 °C by the addition of required amount of catalyst in toluene using a syringe. The polymerization was terminated after 1 h by the addition of 5 mL of methanol. The Schlenk tube was then disconnected from the ethylene outlet and the polymer was precipitated by the addition of methanol containing 2 % HCl. The precipitated polymer was filtered, washed and dried to constant weight.

Analysis

^{1}H NMR spectra were recorded on a 200 MHz Bruker spectrometer in CDCl$_3$ at room temperature. Molar mass (M_w) and molar mass distribution (I_p) were determined using Waters GPC 2000CV instrument equipped with an online viscometer and a refractive index detector at 150 °C in 1,2,4-trichlorobenzene as the solvent at a flow rate of 1 mL/min.

Results and Discussion

Elementary Reaction Between Benzophenone and TMA: Mechanism Investigation

We first investigated the synthesis of aluminium alkoxides of the type ($R^1R^2R^3COAlR_2{}^4$) and checked their capacity to activate single-site catalysts towards olefin polymerization. To that purpose, we revisited in details the reaction between benzophenone (BZ) and TMA, already described in the literature.[7] The effect of the TMA/BZ ratio (r) on the reaction products was first analyzed at 20 °C in toluene. TMA was added onto a benzophenone solution in stoichiometric conditions and the reaction mixture let for 48 hours until the solution becomes colourless. After toluene removal, a white solid was obtained and analyzed by ^{1}H NMR spectroscopy (Figure 1). The peak assignments indicate that TMA and benzophenone are totally consumed during the reaction and is consistent with the formation of the mono-alcoholate compound, $Ph_2C(Me)OAlMe_2$.

Further characterization of the main reaction product carried out by electronic impact reveals that this derivative is stabilized in a dimeric structure $(Ph_2C(Me)OAlMe_2)_2$, (**A**), as illustrated in Figure 2. The formation of such a homo dimer is in agreement with the ability of the aluminium atoms to get coordination number higher than 3.

The effect of the ratio (r) on the structure of the reaction products was then investigated. To that purpose, increasing amounts of TMA were added ($r > 1$) into the benzophenone in solution. The ^{1}H NMR spectrum of the white solid recovered after 48 hours reaction at 20 °C for $r = 2$ is given in Figure 3.

The chemical shifts and assignments of the peaks observed indicate a total consumption of benzophenone and the absence of free TMA. The integrations of the aromatic protons (7.3–7.4 ppm) and of those located at 2.2 ppm, attributed to a methyl group, are in agreement with the

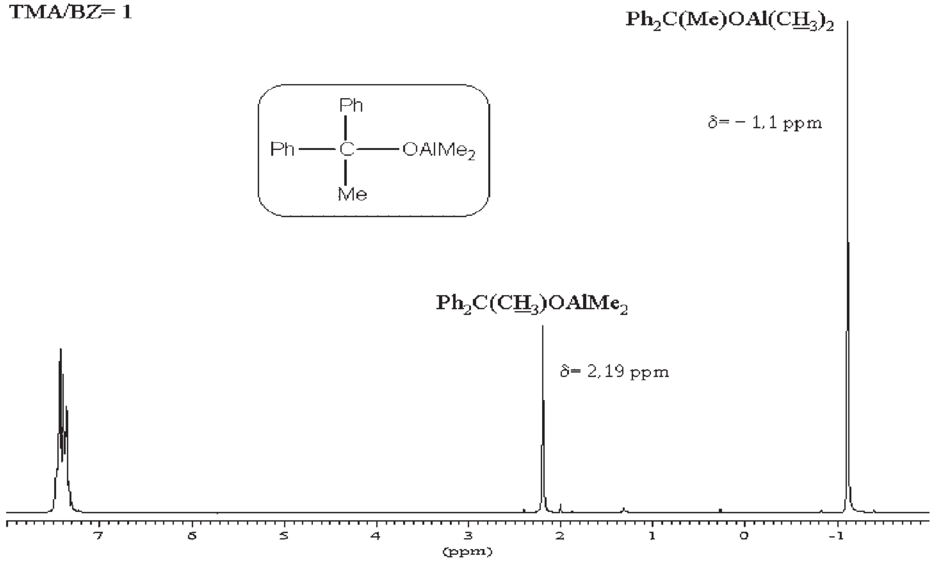


Figure 1.
^1H NMR spectrum in $CDCl_3$ of $Ph_2C(Me)OAlMe_2$ obtained for TMA/Bz = 1, at 20°C.

monomethylation of benzophenone, yielding $Ph_2C(Me)OAlMe_2$. Nevertheless, the integration of the large peak located in between –1.8 and 0 ppm, assigned to methyl groups linked to aluminium atoms, reveals an excess of three methyl groups per $Ph_2C(Me)OAlMe_2$ molecule. Therefore, the interaction between $Ph_2C(Me)OAlMe_2$ and TMA leading to the hetero dimer μ-(1,1-diphenylethoxy)-μ-methyl-tetramethyldialuminium (**B**) was speculated.

The reaction between TMA and benzopheneone was then carried out at r ratios higher than 2. In all the cases, (**B**) is the only product formed together with un-reacted TMA. In the cases of r ratios comprised in between 1 and 2, a mixture of (**A**) and (**B**) is obtained, with the proportion given in Table 1.

We further explored the mechanism of (**A**) and (**B**) formation by means of NMR spectroscopy. As already indicated, (**A**) is the thermodynamic product obtained for TMA/BZ ratio, r = 1, after 48 hours. Interestingly, an analysis by ^1H NMR of the reaction product after 30′ reaction shows the presence together of un-reacted benzophenone, (**A**) and (**B**). It is worth

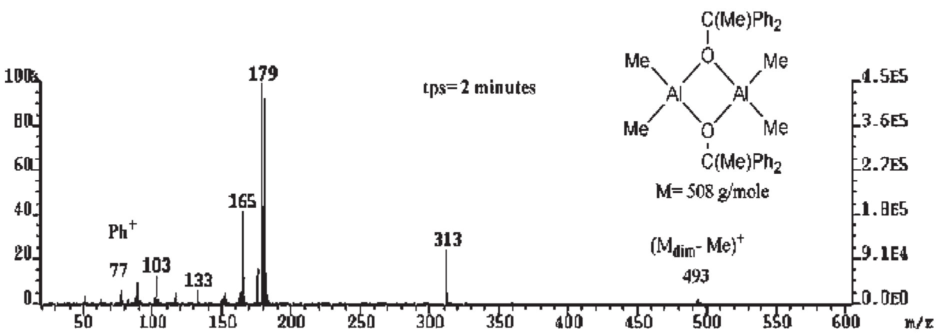


Figure 2.
Mass spectrum from electronic impact of species obtained for TMA/BZ = 1.

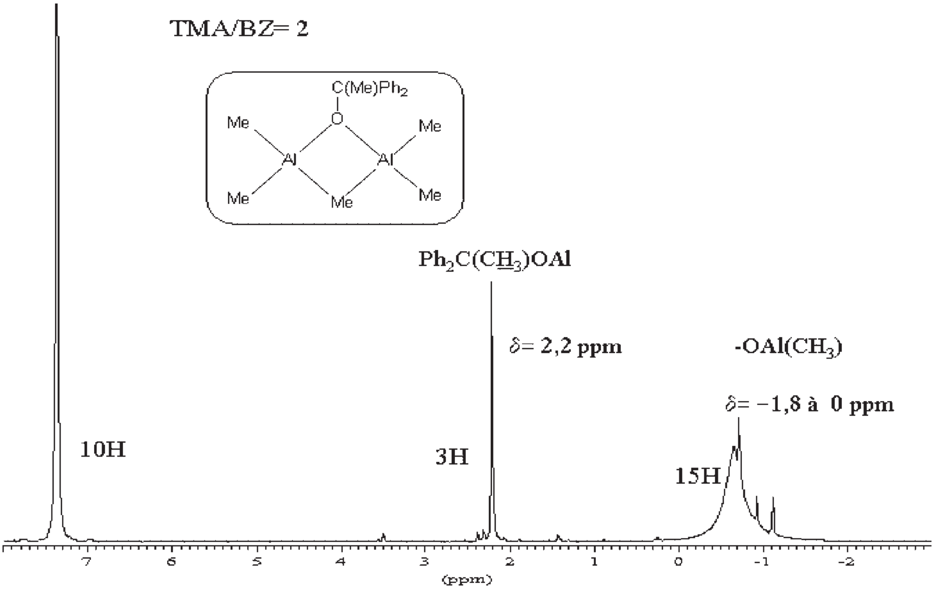


Figure 3.
^{1}H NMR spectrum in $CDCl_3$ of the reaction product obtained for TMA/Bz = 2, at 20 °C.

noting that no free TMA remains in the solution. A following of the NMR spectra with time reveals that the (**A**)/(**B**) ratio increases till the total disappearance of (**B**) and of benzophenone. These data show that (**B**) can be considered as an "intermediary" compound in the formation of (**A**). To further understand the formation of (**A**) and (**B**), a series of complementary reactions were carried out that allowed us to check the following:

(i) the addition of an excess of TMA onto (**A**) has no specific effect (no reaction),
(ii) the reaction of (**B**) and benzophenone at the stoichiometric ratio is complete and yields (**A**) as the only product formed.

Table 1.
Relative proportions of compounds (A) and (B) as a function of r = TMA/BZ.

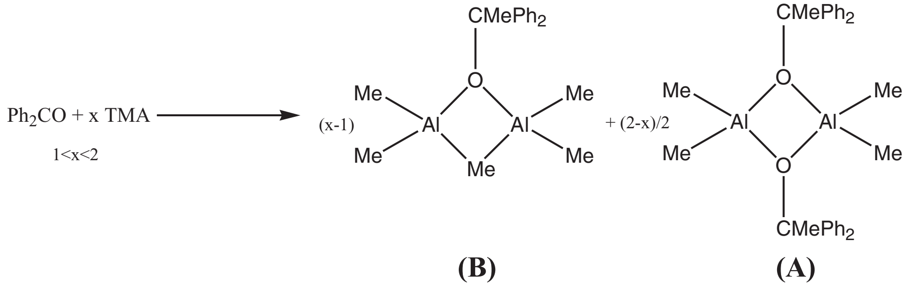
TMA/BZ (r)	% (A)	% (B)
1	100	0
1.24	61	39
1.33	51	49
1.45	40	60
1.58	31	69
1.79	11	89
2	0	100

All these data led us to the conclusion that the reaction of benzophenone with TMA first yields (**B**), the latter then reacting with remaining benzophenone to give (**A**). As (**A**) does not react with TMA, it can not produce (**B**). A synthetic scheme of the reaction between TMA and benzophenone is shown in Scheme 1:

The effect of the reaction temperature was also investigated. The reaction products obtained at 60 °C are identical to those obtained at 20 °C. Higher temperatures (80 °C to 130 °C) lead to the formation of 2,2-diphenyl propane (C-methylated product) together with an aluminium alkoxide product, insoluble in toluene. It is worth noting that the same reaction products may be formed at lower temperature by adding a slight amount of commercial MAO. In this last case, the aluminum alkoxide product remains soluble in toluene.

Ethylene Polymerization in The Presence of MeDIP(2,6-iPrPh$_2$)FeCl$_2$/(A) or (B) Catalytic System

The ability of (**A**) and (**B**) to activate single-site iron derivatives towards ethylene



Scheme 1.
Reaction of benzophenone and TMA at 20 °C.

Table 2.
Ethylene polymerization in the presence of MeDIP(2,6-iPrPh$_2$)FeCl$_2$/(B); 0,8*10^{-6} mol$_{Fe}$, 30 °C, 50mL de toluène, P$_{Et}$ = 1 Bar.

[(B)]/[Fer]	Activity KgPE/ (mol$_{Fe}$ · h · Bar)	Mw (g/mol)	Ip
100	356	166000	5,3
200	473	183000	11,3
300	952	180000	22,8
400	1080	298000	large
500	1284	453000	large
1000	2175	nd	large

polymerization was investigated. Polymerization experiments in the presence of the homo dimer (**A**) as an activator of the iron catalyst were unsuccessful. This result is not surprising since (**A**) does not contain neither TMA nor MAO moieties and is a weaker Lewis acid.

Conversely, (**B**) was found enable to activate MeDIP(2,6-iPrPh$_2$)FeCl$_2$. Data of ethylene polymerization carried out in the presence of (**B**) are collected in Table 2.

As it may be observed, the catalytic activity and the PE molar mass (see also Figure 4) increase with the [(**B**)]/[Fe] ratio. A rather narrow PE molar mass distribution is obtained atl ratio [(**B**)]/[Fe] = 100. Above this value, a broadening of the SEC trace is observed but the presence of a second population of low molar mass fraction (oligomer) is not observed, contrarily to experiments where MAO or TMA as used as activators.

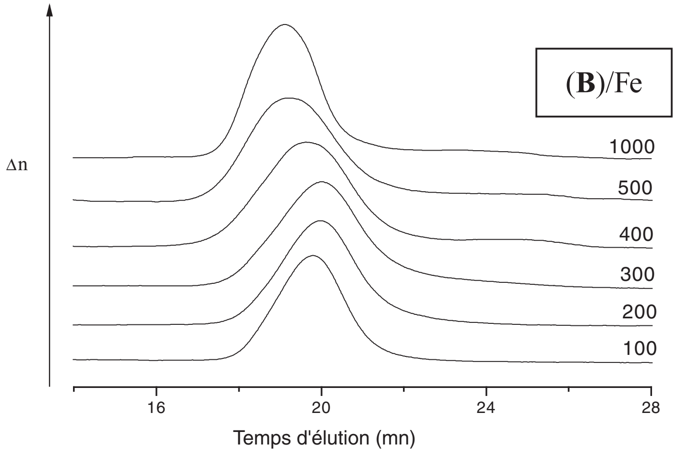
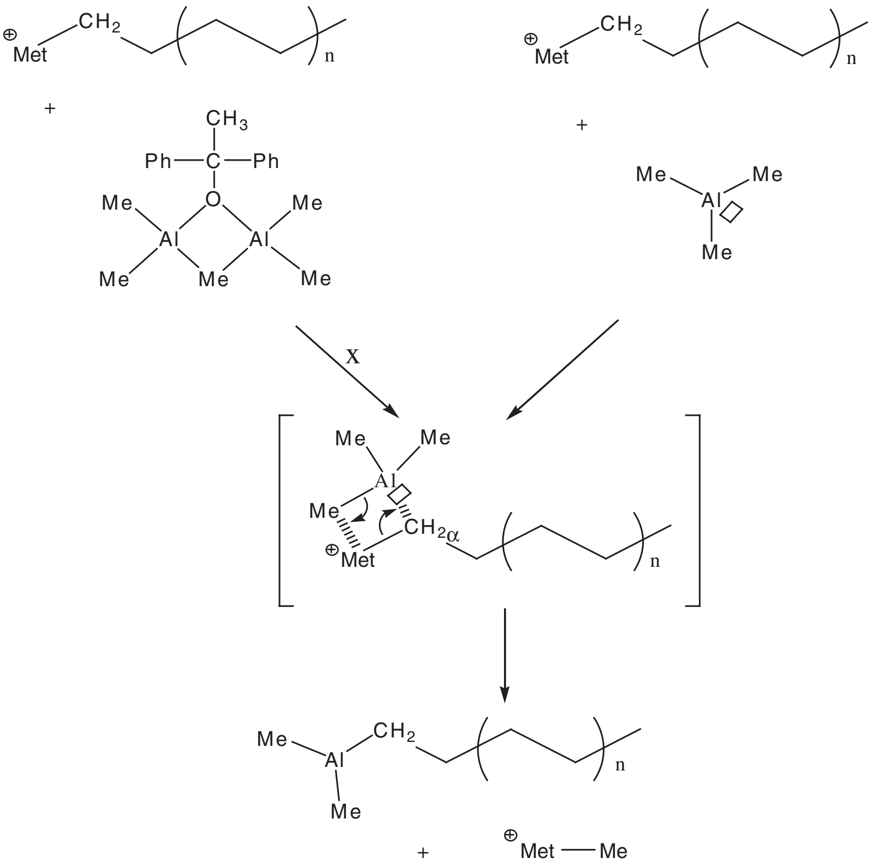


Figure 4.
SEC traces of PE obtained at different (**B**)/MeDIP(2,6-iPrPh$_2$)FeCl$_2$ ratios.



Scheme 2.
transfer mechanism to TMA in ethylene polymerization catalyzed by transition metal derivatives.

As already indicated, the ability of (**B**) to activate the Fe catalyst may be attributed to the presence of a TMA unit in its structure. However, as the TMA group is trapped within the hetero complex (**B**), its capacity to generate transfer reactions, as generally observed when it is used as a single activator (see Scheme 2), dramatically decreases. This is a significant difference compared to literature data.

This study shows that complexed aluminic alkoxide with TMA molecule (**B**) can activate iron-based complexes towards ethylene polymerization at the place of commercial MAO. The catalytic activity is in the same range of what is expected with commercial MAO but the drastic reduction of transfer reaction to aluminium leads PE with a rather broad but unimodal molar mass distribution, free of a PE low molar mass fraction.

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