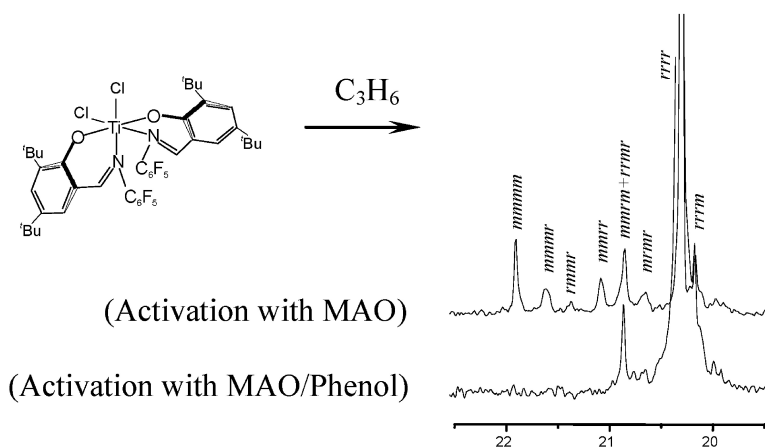


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## Improving the Performance of Methylalumoxane: A Facile and Efficient Method to Trap “Free” Trimethylaluminum

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Methylalumoxane (MAO) has been the first highly effective activator of metallocene catalysts.<sup>1,2</sup> Although the details of its oligomeric structure in solution are still under debate, it is generally accepted that the delocalized anion formed upon activation of  $L_2MX_2$  precursors ( $X = \text{halide, alkyl, or aryl}$ ) is a much weaker Lewis base than, e.g. mononuclear  $AlR_2X_2^-$  anions deriving from  $AlR_3$ , and as such, it is much less prone to associate with  $L_2MR^+$  active cations in the form of a strong ion couple hindering monomer attack.<sup>2</sup> As a matter of fact, all known alternatives to MAO consist in “poorly coordinating” anions (typically, borates); however, the sensitivity of such systems to impurities is generally higher, or their chemistry in the presence of scavengers is more complicated.<sup>2</sup> This explains why MAO remains the elective choice for activating metallocene<sup>3</sup> and “post-metallocene”<sup>4</sup> catalysts, at least in laboratory practice.

In turn, MAO has two main weak points:<sup>2</sup> (i) for optimum performance, it needs to be used in large excess relative to the transition metal species (a convincing explanation for this is still pending); (ii) MAO solutions always contain “free” trimethylaluminum (TMA) in equilibrium with the oligomeric part. TMA is a reducing agent; with transition metal complexes it easily forms Me-bridged dinuclear species which are believed to be catalytically inactive and promotes chain transfer to the point that with some catalysts this results in the formation of oligomers rather than of high polymers.

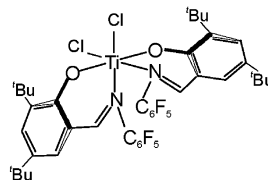
The most-used strategy to remove “free” TMA from MAO solutions is to evaporate these to dryness, until a free-flowing white powder (“solid MAO”) is left.<sup>2,5–7</sup> This procedure is tedious and potentially hazardous, because in some cases the distillate is a concentrated hydrocarbon solution of TMA. Moreover, “solid MAO” is poorly soluble in common polymerization media, and once in solution it can regenerate TMA to some extent.

More recently, it has been found that synthesizing MAO by nonhydrolytic means can lead to MAO solutions with much less “free” TMA.<sup>2,8</sup> In particular, a nonhydrolytic MAO in toluene is now commercially available from Akzo-Nobel (“PMAO-IP”);<sup>9</sup> however, according to the manufacturer, the residual content of TMA is still as high as ca. 0.10 mol (TMA)/mol (Al).

In this communication, we report on a facile and effective third route, which consists in the addition to MAO of a proper amount of a sterically hindered phenol, such as 2,6-di-*tert*-butylphenol (*t*-Bu<sub>2</sub>Ph-OH) or its 4-Me-substituted homologue. Modification of Al-trialkyls, and in particular of Al(isobutyl)<sub>3</sub> (TIBAl), by reaction with the quoted phenols in 1:1 to 1:2 mol ratio has long been known<sup>10</sup> to be an effective means to decrease the reactivity of the former. The resulting alkyl-Al-phenoxides have been described as “noninteracting scrubbing agents”, mainly for use with metallocene (and related) catalysts in combination with boron compounds.<sup>10b–d</sup>

Surprisingly, less attention has been paid to the same approach with MAO. The only related example we are aware of in the scientific literature involves 6-*tert*-butyl-2-(1,1-dimethylhept-6-

Chart 1



enyl)-4-methylphenol, used as a comonomer in ethene and propene polymerization promoted by  $C_2$ -symmetric *ansa*-zirconocenes in combination with MAO, with the aim to incorporate the phenol functionality into the polyethylene and polypropylene backbone.<sup>11</sup> A few patents,<sup>12</sup> on the other hand, claim the addition of (sterically hindered) phenols or other Lewis bases to MAO, in some cases with improved results in the activation of certain metallocene<sup>12c</sup> and “constrained-geometry”<sup>12a</sup> catalysts.

We investigated by <sup>1</sup>H NMR the reaction of *t*-Bu<sub>2</sub>Ph-OH with MAO in benzene-*d*<sub>6</sub> at 25 °C. Our source of MAO was a commercial solution in toluene (Crompton, 10% w/w), containing ca. 20% of the Al in the form of “free” TMA; this gives a sharp singlet at  $\delta = -0.36$  ppm (downfield of TMS), overlapped with the very broad resonance of the methyl protons of MAO centered at around  $\delta = -0.2$  ppm. The spectra of systems with *t*-Bu<sub>2</sub>Ph-OH/Al mol ratio up to 0.2 revealed the presence of Me<sub>2</sub>Al-O-Ph(*t*-Bu)<sub>2</sub>, with the *tert*-butyl protons resonating at  $\delta = 1.40$  ppm and the Me groups on Al (in fast exchange with those of TMA<sup>10a</sup>) at  $\delta = -0.41$  ppm. Further addition of *t*-Bu<sub>2</sub>Ph-OH resulted in the formation of MeAl(O-Ph(*t*-Bu)<sub>2</sub>)<sub>2</sub>, characterized by two singlets at  $\delta = 1.51$  ppm (*tert*-butyl protons) and  $\delta = -0.33$  ppm (methyl protons on Al). Peak integration by full simulation showed that in all cases the resonance of MAO was unaffected, which in turn indicates that *t*-Bu<sub>2</sub>Ph-OH reacts primarily with “free” TMA.

At *t*-Bu<sub>2</sub>Ph-OH/Al mol ratio > 0.4, the resonances of unreacted *t*-Bu<sub>2</sub>Ph-OH appeared (*tert*-butyl protons at  $\delta = 1.31$  ppm, alcoholic proton at  $\delta = 4.88$  ppm), with only a very slight, asymptotic tendency to fade out. We attribute this to a slow reaction of *t*-Bu<sub>2</sub>Ph-OH with part of the Al–Me bonds of MAO or with TMA molecules progressively released from it. This is consistent with a corresponding decrease of the resonance of MAO (at *t*-Bu<sub>2</sub>Ph-OH/Al mol ratio = 0.5, to a limit of ca. 90% of the original value, reached after 3 h at 25 °C; at 50 °C, the same limit within the experimental error was attained after ca. 1 h).

We have tested “TMA-free” MAO/*t*-Bu<sub>2</sub>Ph-OH in the activation of two Column 4 metal complexes representative of very well-known classes of propene polymerization catalysts. *rac*-Me<sub>2</sub>Si(1-Indenyl)<sub>2</sub>ZrCl<sub>2</sub> (**1**) is the archetype of all modern  $C_2$ -symmetric isotactic-selective *ansa*-zirconocenes.<sup>3</sup> The recently disclosed Ti complex **2** (Chart 1), instead, produces syndiotactic polypropylene in a living manner after activation with “solid MAO”;<sup>5</sup> according to the literature, the living character of this and other bis(phenoximine)Ti catalysts<sup>6</sup> is lost when using standard MAO solutions.

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**Table 1.** Results of Propene Polymerization in Toluene at 25 °C Promoted by **1**, **2**, and Different MAO-Based Activators<sup>a</sup>

entry	catalyst/activator <sup>b</sup>	[Al]/[M]	$R_p$ <sup>b</sup>	$M_n$ , kDa	$M_w/M_n$
1	<b>1</b> /MAO	$8.0 \times 10^3$	$9.4 \times 10^3$	34	2.2
2	<b>1</b> /MAO/ <sup>t</sup> Bu <sub>2</sub> Ph-OH	$8.0 \times 10^3$	$2.1 \times 10^4$	47	2.1
3	<b>1</b> /PMAO-IP	$8.0 \times 10^3$	$1.3 \times 10^4$	50	2.0
4	<b>1</b> /MAO	$8.0 \times 10^2$	$2.3 \times 10^3$	44	2.0
5	<b>1</b> /MAO/ <sup>t</sup> Bu <sub>2</sub> Ph-OH	$8.0 \times 10^2$	$2.1 \times 10^3$	50	2.0
6	<b>1</b> /MAO/ <sup>t</sup> Bu <sub>2</sub> Ph-OH <sup>c</sup>	$8.0 \times 10^3$	$1.2 \times 10^4$	53	1.8
7	<b>2</b> /MAO	$1.65 \times 10^2$	1.0	34	2.3
8	<b>2</b> /MAO/ <sup>t</sup> Bu <sub>2</sub> Ph-OH	$1.65 \times 10^2$	3.1	105	1.3
9	<b>2</b> /PMAO-IP	$1.65 \times 10^2$	1.0	84	4.1

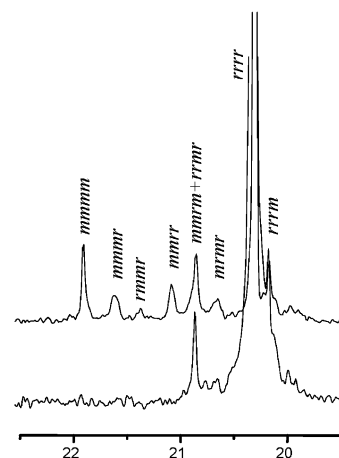
<sup>a</sup> For experimental conditions, see Supporting Information. <sup>b</sup> In kg (PP)/(mol (M)·[C<sub>3</sub>H<sub>6</sub>]·h). <sup>c</sup> <sup>t</sup>Bu<sub>2</sub>Ph-OH/Al mol ratio = 0.3 instead of 0.5.

In Table 1, we compare the performance of **1** and **2** in propene polymerization, when activated by MAO in toluene with and without added <sup>t</sup>Bu<sub>2</sub>Ph-OH. We used a <sup>t</sup>Bu<sub>2</sub>Ph-OH/Al mol ratio of 0.5 (corresponding to slightly more than 2 mol of <sup>t</sup>Bu<sub>2</sub>Ph-OH per mol of “free” TMA in our MAO), because MeAl-(O-Ph(<sup>t</sup>Bu)<sub>2</sub>)<sub>2</sub> is reported to be a stable species, whereas Me<sub>2</sub>Al-O-Ph(<sup>t</sup>Bu)<sub>2</sub> disproportionates to the former and TMA.<sup>10a</sup> Data for catalyst activation by PMAO-IP are also given for comparison.

Let us comment on the results. At the very high [Al] needed for maximum activity,<sup>13</sup> the productivity of **1**/MAO/<sup>t</sup>Bu<sub>2</sub>Ph-OH and the average molecular mass of the polypropylene obtained with it were substantially higher than for **1**/MAO (compare entries 1 and 2). The increase in polymer molecular mass is easily explained in terms of a corresponding decrease in chain transfer to “free” TMA; that in catalyst productivity can be tentatively traced to a lower amount of nonpropagating dinuclear M-(*u*-Me)-Al species. At lower [Al], on the other hand, the two systems gave similar results (entries 4 and 5), possibly due to the higher effect of impurities on the residual amount of “free” TMA (which is by far the most reactive scavenger<sup>10b</sup>). In relative sense, the picture did not change at 50 °C, although the absolute productivities were generally higher (e.g.,  $2.9 \times 10^4$  and  $5.0 \times 10^4$  kg (PP)/(mol (M)·[C<sub>3</sub>H<sub>6</sub>]·h) for **1**/MAO and **1**/MAO/<sup>t</sup>Bu<sub>2</sub>Ph-OH).

Interestingly, compared with **1**/MAO/<sup>t</sup>Bu<sub>2</sub>Ph-OH at a <sup>t</sup>Bu<sub>2</sub>Ph-OH/Al mol ratio = 0.5 (entry 2), lower productivities but virtually identical polymer  $M_n$  and  $M_w$  values were obtained both with **1**/PMAO-IP (entry 3), and with **1**/MAO/<sup>t</sup>Bu<sub>2</sub>Ph-OH at a <sup>t</sup>Bu<sub>2</sub>Ph-OH/Al mol ratio = 0.3 (entry 6), which clearly calls for the presence of residual “free” TMA in the latter two cases, and indicates that this affects catalyst activity more than chain transfer.

Even more relevant was the impact of <sup>t</sup>Bu<sub>2</sub>Ph-OH addition on the catalytic performance of **2**/MAO. Syndiotactic polypropylene prepared with **2**/MAO/<sup>t</sup>Bu<sub>2</sub>Ph-OH (entry 8) is practically monodisperse (which is consistent with a living catalyst character) and highly stereoregular ( $[rrrr] = 95.6\%$ ,  $[rrrm] = [rrmr] = 2.2\%$ ). With **2**/MAO (entry 7) and **2**/PMAO-IP (entry 9), instead, we obtained more complicated and almost identical polymers showing at the <sup>13</sup>C NMR analysis (Figure 1), along with the major syndiotactic part, a predominantly isotactic (ca. 6 wt %) and an atactic (ca. 25 wt %) part, the latter separable by extraction with boiling diethyl ether; correspondingly, the molecular mass distribution was rather broad ( $M_w/M_n > 2$ ). The presence of nonsyndiotactic byproducts in syndiotactic polypropylene produced with MAO-activated bis(phenoxyimine)/Ti catalysts has never been mentioned explicitly in the literature but can be seen on inspection of published <sup>13</sup>C NMR spectra, even for polymers prepared with “solid MAO”.<sup>6</sup> On the other hand, it has been reported that TIBAl reduces the phenoxyimine ligands, with the in situ formation of phenoxyamine species which can be catalytically active.<sup>14</sup> Our tentative interpreta-



**Figure 1.** Methyl region of the 50.3 MHz <sup>13</sup>C NMR spectra (in tetrachloroethane-1,2-*d*<sub>2</sub> at 125 °C) of polypropylene samples prepared with **2**/MAO (upper trace; Table 1, entry 7) and with **2**/MAO/<sup>t</sup>Bu<sub>2</sub>Ph-OH (lower trace; Table 1, entry 8), with resonance assignment. The  $\delta$  scale is in ppm downfield of TMS.

tion is that “free” TMA also interacts somehow with the ligands of **2**, although to a lower extent than TIBAl.

In conclusion, we have shown that the controlled addition of a sterically hindered phenol such as <sup>t</sup>Bu<sub>2</sub>Ph-OH to MAO solutions is a facile and highly effective way to trap “free” TMA. The resulting MAO/<sup>t</sup>Bu<sub>2</sub>Ph-OH reaction product activated equally well the dichloro-precursors of a metallocene and a “post-metallocene” catalyst, and its use in propene polymerization (even in the presence of excess free phenol) ended up with a higher catalyst productivity, polymer stereoregularity, and/or average molecular mass compared with MAO alone and with PMAO-IP as well. We are currently investigating the effect of <sup>t</sup>Bu<sub>2</sub>Ph-OH addition on the polymerization kinetics.

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**Supporting Information Available:** Experimental section; <sup>1</sup>H NMR spectra of MAO/<sup>t</sup>Bu<sub>2</sub>Ph-OH (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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