Study on the Role of Methylalumoxane in Homogeneous Olefin Polymerization

Homogeneous olefin polymerization by group 4 metallocenes–methylalumoxane systems has been the object of intensive studies, and some remarkable results have recently been achieved.[1,2] Despite its uniqueness as cocatalyst, methylalumoxane (MAO) still remains a "black box" whose structure is postulated as being an oligomeric (cyclic or linear) chain of [Al(Me)O] units.[3] Sinn and co-workers showed by ebullioscopy studies in THF that MAO, even after distillation in the presence of cumene, still retains some unreacted, strongly bound $AlMe_3$ (TMA).[4] The presence of residual TMA in MAO can also be detected by GPC.[5]

We confirm this result by ^1H NMR and present some data on dialkylzirconocene–TMA ethylene polymerization, which, by comparison with previous data obtained in our laboratories,[6] show that TMA might be the actual cocatalyst in MAO-based systems.

The proton spectrum of a MAO sample in toluene-d_8 shows two main resonances (Figure 1, top), one very broad at −0.21 ppm and another one slightly broad at −0.36 ppm. When a solid MAO sample is heated in vacuo for several hours at 100–120 °C, the resonance at −0.36 ppm decreases in intensity, as TMA is liberated.[7] By comparison with an authentic sample (Figure 1, bottom), this peak is assigned to free TMA (as the dimer Al_2Me_6). This assignment is confirmed by low-temperature NMR (Figure 2).[8] TMA therefore remains in the reaction product. Under our experimental conditions the equilibrium shown in eq 1 must occur in toluene solution.

$$\text{MAO}\cdot n\text{TMA} \rightleftharpoons \text{MAO}\cdot(n-m)\text{TMA} + (m/2)(\text{TMA})_2 \quad (1)$$

Even if the peaks of MAO and TMA are partially overlapped, the molar ratio of the two compounds can be evaluated, thus giving the amount of free TMA in toluene solution as being 3.5 (±1)%.[9] We attribute the slight broadening of the line at −0.36 ppm to be due to the reversible adduct formation between MAO and TMA in solution (coalescence of the two peaks is observed at 90 °C).

Giannetti had shown[6] that the activity of the Cp_2ZrR_2–MAO system for ethylene polymerization depends on R and increases in the order R = Me < Ph < CH_2Ph < CH_2SiMe_3.

We found that, *substituting TMA for MAO, the polymerization activity follows the same order* (Table I), although the activity is much lower. Furthermore, the system ethylenebis(indenyl)zirconium dichloride–TMA produces isotactic polypropylene, with an activity of about 300 g_{PP}/g_{Zr}.h and with *exactly the same microstructure* as the one produced in the presence of MAO.[10] Zirconocene–trialkylaluminum systems have been previously reported to be inactive (or weakly active after aging) toward ethylene polymerization and to be unable to polymerize propylene.[3]

The lower molecular weights of polyethylene samples obtained with TMA compared to those obtained with MAO (Table I) can be ascribed to the ability of TMA to act as a chain-transfer agent. This is confirmed by ^{13}C NMR analysis of the polypropylene sample prepared with TMA as cocatalyst, which clearly shows the presence of isobutyl end groups (only traces of vinylidene end groups, due to β-H elimination, can be detected).

Interestingly, Lasserre and Derouault from IR, Raman, and cryoscopic studies proposed that the product of the partial hydrolysis of TMA in benzene solution (O/Al up to 0.5) is made of small alumina aggregates, surrounded by O_2AlMe and $OAlMe_2$ groups, and residual TMA.[11] In the case of MAO (O/Al = 1), the presence of small alumina aggregates is even more likely.

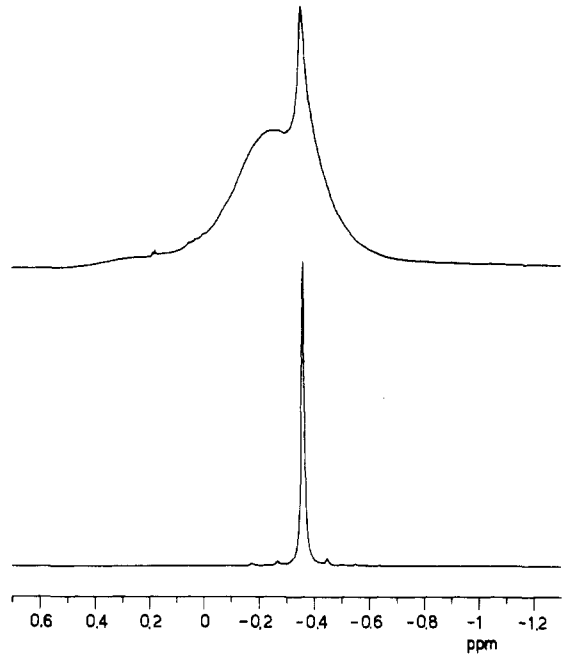

Figure 1. ^1H NMR of (top) methylalumoxane and (bottom) trimethylaluminum in toluene-d_8 at 295 K. Referenced to the central line of residual CHD_2 at 2.086 ppm.

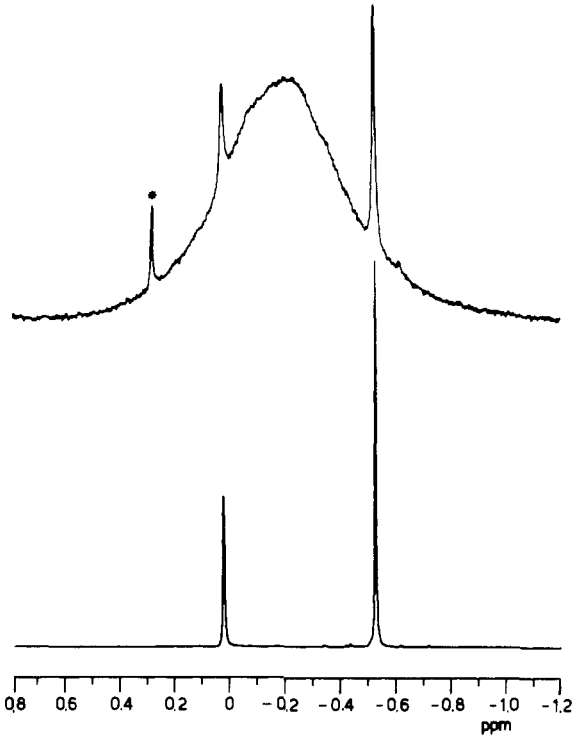

Figure 2. ^1H NMR of (top) methylalumoxane and (bottom) trimethylaluminum in toluene-d_8 at 203 K. Referenced to the central line of residual CHD_2 at 2.086 ppm. An asterisk indicates CH_4 impurity.

As a working hypothesis, we propose that the actual cocatalyst in the metallocene–MAO system is actually TMA itself, with MAO acting as a soluble carrier–activator of the ion pair formed upon reaction of the metallocene with TMA.[12] Further studies to better address this point are in progress in our laboratories.

The effect of different alkylaluminums on ethylene polymerization will be reported in a future paper.

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Table I
Ethylene Polymerization with Cp_2ZrR_2 and $AlMe_3$[a]

zirconocene	polymer yield, g	productivity, $g_{PE}/g_{Zr}\cdot h$		viscosity,[b] dL/g	
		this work	ref 6	this work	ref 6
Cp_2ZrMe_2	6.0	16 700	321 000	2.6	4.5
Cp_2ZrPh_2	5.2	21 700	948 300	3.3	5.0
$Cp_2Zr(CH_2Ph)_2$	7.6	33 600	1 155 100	2.7	4.0
$Cp_2Zr(CH_2SiMe_3)_2$	21.9	95 200	1 700 600	3.6	4.4

[a] Conditions: toluene, 400 mL; ethylene, 4 atm, $AlMe_3$, 2 mmol, Cp_2ZrR_2, 1 mg, 50 °C, 1 h. [b] In tetrahydronaphthalene at 135 °C.

Experimental Section. All operations and manipulations were carried out under dry nitrogen atmosphere.

Toluene (Carlo Erba) was purified by refluxing over $Al\textit{i}Bu_3$ and subsequent distillation under nitrogen. Polymerization grade ethylene was further purified from traces of water by passing over 3–4-Å activated molecular sieves. $AlMe_3$ (Fluka) was used as received, after checking its purity by titration (against pyridine to the phenazine end point), which was >98%, and by ^1H NMR, from which no Al–OMe was detectable. All ^1H NMR spectra were run on a Bruker AM300 spectrometer in toluene-d_8 as solvent. Proton chemical shifts are referred to the middle peak at 2.086 ppm of the quintet of residual $-CHD_2$ in the solvent.

Cp_2ZrMe_2,[13] Cp_2ZrPh_2,[13] $Cp_2Zr(CH_2Ph)_2$,[14] $Cp_2Zr(CH_2SiMe_3)_2$,[15] and ethylenebis(indenyl)zirconium dichloride[16] were synthesized by known procedures.

MAO was prepared from $FeSO_4\cdot 7H_2O$ and $AlMe_3$, using a slight modification of a reported method:[17] $FeSO_4\cdot 7H_2O$ (24 g) and toluene (150 mL) were placed in a 500-mL, four-neck round-bottomed flask equipped with magnetic stirrer, dropping funnel, reflux condenser connected to a gas flowmeter, and thermometer. A total of 50 mL of neat $AlMe_3$ (Caution! extremely flammable) was placed in the dropping funnel, and both the flask and the reflux condenser were cooled to −10 °C with an *n*-heptane–dry ice recirculating mixture. $AlMe_3$ was added to the vigorously stirred suspension in about 5 min, keeping the reaction temperature below 10 °C. Then the flask was slowly warmed up to 80 °C over 3 h and stirred at this temperature until 22.4 L of gas was evolved (total reaction time 4 h). After filtration and washing of the residue with 50 mL of toluene, a clear, faintly pink solution is obtained. After removal of volatiles [60 °C (0.1 mmHg), 4 h], 15.7 g of a glassy, white solid was obtained; yield 53% as Al(Me)O with respect to $AlMe_3$. ⟨MW⟩ = 900.[18]

Polymerizations. In a 1-L glass autoclave (Büchi), washed with a diluted solution of $AlEt_3$ in *n*-hexane and dried at 50 °C in vacuo was placed 350 mL of toluene under monomer stream. A 50-mL toluene solution containing 2 mmol of $AlMe_3$ and 1 mg of the dialkylzirconocene was injected, and the monomer pressure raised to 4 bar: stirring, 1100 rpm; polymerization temperature, 50 °C, 1 h. Polymerizations were quenched by rapidly venting the monomer and adding CH_3OH. The polymers were washed with CH_3OH–HCl and then CH_3OH and dried in vacuo.

Propylene polymerizations were performed as follows.

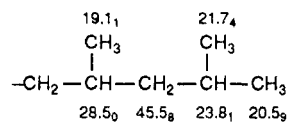
Sample A. In the autoclave thermostated at 25 °C were subsequently charged 200 mL of toluene, 100 mL of propylene, 18 mL of a 1 M solution of $AlMe_3$ in toluene, and 4.4 mg of ethylenebis(indenyl)zirconium dichloride dissolved in 10 mL of toluene: polymerization time, 17 h. After venting of the monomer, coagulation of the polymer with CH_3OH–HCl, washing with CH_3OH, filtration, and drying, 4.74 g of white powdery polypropylene was obtained. $\bar{M}_w$ = 29 100; $\bar{M}_w/\bar{M}_n$ = 4.5; T_m = 134.2 °C.

Sample B (Comparison Experiment). Sample B was prepared in a similar manner as sample A, except that MAO (550 mg) was used as cocatalyst instead of TMA, together with 1 mg of ethylenebis(indenyl)zirconium dichloride: polymerization time, 4 h; yield, 39 g. $\bar{M}_w$ = 46 000; $\bar{M}_w/\bar{M}_n$ = 3.8; T_m = 140.8 °C.

^{13}C NMR Analysis of Polypropylene Samples. For peak assignments and nomenclature, see ref 10. HMDS scale. Pentad composition (% area; partial peak overlapping prevents a more precise measurement). Sample A: mmmm, 89.8; mmmr, 4.7; mmrr, 3.7; mmrm + rmrr, traces; rrrm, traces; mrrm, 1.0. Sample B: mmmm, 87.4; mmmr, 5.3; mmrr, 4.1; mmrm + rmrr, traces; rrrm, traces; mrrm, 1.4.

Regioinversions (head-to-tail–tail-to-head, % area of the misplaced methyl group). Sample A: meso, 0.45; racemic, 0.15. Sample B: meso, 0.32; racemic, 0.20.

End group analysis: sample A shows a series of peaks at 45.5_8, 28.5_0, 23.8_1, 21.7_4, 20.5_9, and 19.1_1 ppm, that are absent in sample B. By comparison with published works,[19] these peaks are readily assigned to isobutyl end groups, according to



The fact that the polymer chain is isobutyl-terminated *on both ends* is a direct evidence for chain transfer to aluminum, which is therefore the cause for the lower molecular weight of sample A (TMA cocatalyst) compared to sample B (MAO cocatalyst).

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