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Role of Trimethylaluminum on the Zirconocene–Methylaluminoxane-Catalyzed Polymerization of Ethylene[†]

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Introduction

Homogeneous catalysts based on group IV metallocene–methylaluminoxane (MAO) systems have been the subject of intensive research in recent years.[1] They are also currently attracting significant commercial attention.[2] In spite of many advances, the role of cocatalyst continues to be intriguing. A question that still awaits a satisfactory answer is the precise role of free trimethylaluminum (TMA) associated with MAO on the activity and the kinetic profile of the catalyst.

MAO, whose structure is postulated as a mixture of linear and cyclic oligomers of $[Al(Me)O]_n$ units, is prepared by controlled hydrolysis of TMA with hydrated metal salts. Depending on the nature of salt used and the reaction conditions, MAO with widely differing activities as cocatalysts in polymerization of ethylene is formed.[3] Sinn and co-workers proposed that MAO forms an adduct with three molecules of TMA which even after distillation in the presence of cumene or complexation with tetrahydrofuran retained one molecule of strongly associated TMA.[4]

There have been only a few attempts in the literature to examine the role of associated TMA on the nature of catalysis. Resconi and co-workers showed that TMA alone can initiate ethylene polymerization with various zirconocenes.[5] However, activities and molecular weights were much lower. The activities could be substantially enhanced by using sterically hindered zirconocene and triisobutylaluminum.[6] Giannetti and co-workers studied the effect of free TMA on polymer productivity and the molecular weight of ethylene polymerization using $(Ind)_2Zr(CH_3)_2$ and $Cp_2Zr(CH_2C_6H_5)_2$ and MAO at $[Al]/[Zr] = 16\,600$ and at 50 °C.[3] The ratio of free TMA to MAO varied between 0 and 1.2. Catalyst activity was found to decrease with increasing [TMA]/[MAO] ratios. Molecular weights of the polyethylene obtained with $Cp_2Zr(CH_2C_6H_5)_2$ strongly decreased with increasing TMA whereas it was invariant when $(Ind)_2Zr(CH_3)_2$ was used. Ethylene polymerization with Cp_2ZrCl_2/MAO was investigated by progressively replacing MAO with TMA at $[Al]/[Zr] = 1970$.[7] The ratio of $[Al]_{TMA}$ to $[Al]_{MAO}$ was varied between 0 and 1000. With increasing addition of free TMA to MAO, both catalyst productivity and molecular weight decreased. The kinetic profile of the catalyst was not substantially altered up to a $[TMA]/[MAO] \leq 10$. At $[TMA]/[MAO] = 100$, the rate profile changed from a decay to a buildup curve. The interaction of Cp_2ZrCl_2 with MAO has been studied by Cam and Giannini using ^1H NMR spectroscopy.[8] They concluded that, at $[Al]/[Zr] > 15$, Cp_2ZrCl_2 is completely monoalkylated by the TMA present in MAO.

In the course of a program of research in homogeneous catalyst for ethylene polymerization we have found that addition of TMA to MAO under specified conditions leads to a dramatic increase in catalyst productivity as well as catalyst lifetime. This paper reports the results of this study.

Experimental Section

All operations were carried out under dry nitrogen using standard benchtop inert atmosphere techniques.

Material. Toluene (LOBA-AR grade) was purified by refluxing over sodium wire and subsequent distillation under nitrogen. Polymerization grade ethylene was obtained from the C_2–C_3 gas cracker unit of Indian Petrochemical Corp. Limited at Nagothane (O_2 = 3 ppm, moisture = 4 ppm). TMA (Schering-A.G., Germany) and zirconocene (Aldrich Chemicals) were used as received. A sterically hindered aryl oxide substituted alkylaluminum $[AlMe(BHT)_2]$ was prepared from TMA and 2,6-di-*tert*-butyl-*p*-cresol as per literature procedure and characterized by melting point, ^1H NMR, and methyl/aluminum ratio.[9]

MAO (Schering-A.G., Germany), 5.5% wt Al in toluene solution (average molecular weight = 850) was found to have a [methyl]/[aluminum] ([Me/Al]) ratio of 1.22:1. Toluene was distilled off at 30 °C/0.5 mmHg which resulted in a glassy solid. The [Me]/[Al] ratio of the solid was 1.20:1. The solid was analyzed for free TMA by NMR in toluene-d_8 and was found to be 12%.[5] A stock solution of solid MAO in toluene was prepared and used for further study.

Polymerization. Ethylene polymerization was conducted at atmospheric pressure and at 70 °C in a jacketed reaction cell connected to a 1-L gas buret. The desired amount of TMA was first added followed by MAO to 30 mL of dry toluene saturated with ethylene. The reaction was initiated by addition of zirconocene solution. The temperature was maintained constant both in the reaction cell and in the gas buret by circulating water through the jacket. Consumed ethylene was measured as a function of time. The reaction was terminated by addition of acidified methanol, filtered, and dried under vacuum to a constant weight.

Analysis. The aluminum content was estimated by EDTA titration. The methyl content was determined by estimating the amount of methane evolved upon hydrolysis using a gas buret. NMR analysis was performed on a Bruker AC-200 spectrometer. Intrinsic viscosities of the polymers were measured at 135 °C using decalin as solvent.

Results and Discussion

Polymerization of ethylene was carried out with three different catalyst systems, namely, Cp_2ZrCl_2/TMA (I), Cp_2ZrCl_2/MAO (II), and Cp_2ZrCl_2/MAO + TMA (III) in toluene at 70 °C. For the sake of comparison, $AlMe(BHT)_2$ was also used instead of MAO. TMA was added to a toluene solution of $AlMe(BHT)_2$ just prior to addition of Cp_2ZrCl_2. The zirconocene concentration ranged from 1.15×10^{-5} to 1.15×10^{-7} mol/L. Three ratios of $[Al]_{total}/[Zr]$ were studied which in the case of TMA and MAO were 10^3, 10^4, and 10^5. In the case of experiments with MAO + TMA, $[Al]_{total}/[Zr]$ varied from 1676 to 167 600. However, the free TMA added to MAO, by itself, contributed to an [Al]/[Zr] of 10^3, 10^4, and 10^5, which is essentially similar to the ratio used when TMA alone was used as cocatalyst.

The results are shown in Table I and are graphically plotted in Figures 1–3.

The Cp_2ZrCl_2/TMA system shows relatively poor catalyst productivity and low initial rates of polymerization. Both the rate and catalyst productivity increased with increasing [Al]/[Zr] ratio. The Cp_2ZrCl_2/MAO system shows a similar behavior except that absolute magnitudes of both the rate and catalyst productivity are higher. Addition of TMA causes a dramatic increase in catalyst productivity (entries 7–9).

The changes in the kinetic profile of the polymerization (Figures 1 and 2) upon addition of TMA to MAO are more

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Table I
Ethylene Polymerization Using Zirconocene–Organoaluminum Compounds[a]

entry no.	Al compd	[Me]/[Al]	10^2[Al]$_{\text{total}}$	10^7[Zr]	[Al]$_{\text{total}}$/[Zr]	time (min)	10^{-2}Rp ($M \cdot s^{-1}$)	productivity of [kg of PE/(g of Zr·h)]	[η][b] ($dL \cdot g^{-1}$)
1	TMA	3.00	1.15	115.00	1000	120	0.55	3.94	1.59
2	TMA	3.00	1.15	11.50	10000	120	2.50	7.21	1.41
3	TMA	3.00	1.15	1.15	100000	120	5.65	13.22	
4	MAO	1.22	1.15	115.00	1000	9	12.87	4.72[c]	1.18
5	MAO	1.22	1.15	11.50	10000	30	68.24	20.51[d]	2.31
6	MAO	1.22	1.15	1.15	100000	60	89.81	136.20	2.67
7	MAO + TMA	2.20	1.15 + 0.78	115.00	1676	50	20.65	14.52[e]	1.57
8	MAO + TMA	2.20	1.15 + 0.78	11.50	16760	120	52.14	77.85	1.69
9	MAO + TMA	2.20	1.15 + 0.78	1.15	167600	120	62.87	205.31	2.50
10	$AlMe(BHT)_2$ + TMA	2.20	1.15 + 0.78	115.00	1676	120	2.04	3.24	1.48
11	$AlMe(BHT)_2$ + TMA	2.20	1.15 + 0.78	11.50	16760	120	7.50	6.57	1.66

[a] Polymerization conditions: temperature, 70 °C; toluene = 30 mL; $P_{C_2H_4}$ = 1 atm. [b] In decalin at 135 °C. [c] Reaction ceased after 9 min. [d] Reaction ceased after 30 min. [e] Reaction ceased after 50 min.

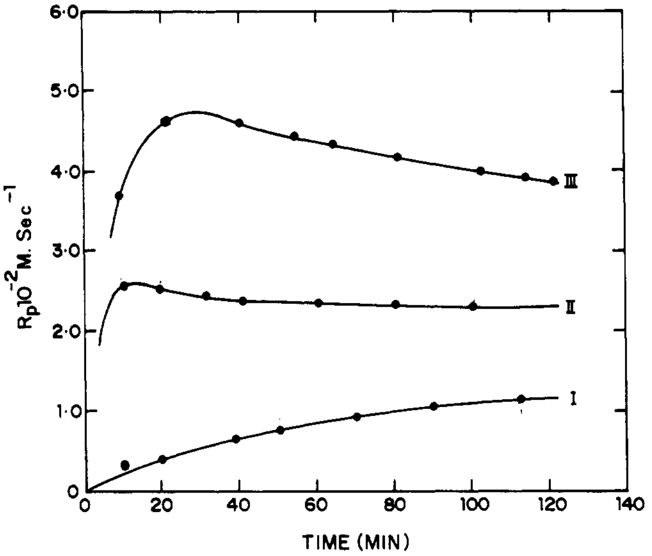

Figure 1. Polymerization of ethylene using zirconocene–trimethylaluminum catalyst: (I) [Al]$_{\text{TMA}}$/[Zr] = 10^3; (II) [Al]$_{\text{TMA}}$/[Zr] = 10^4; (III) [Al]$_{\text{TMA}}$/[Zr] = 10^5.

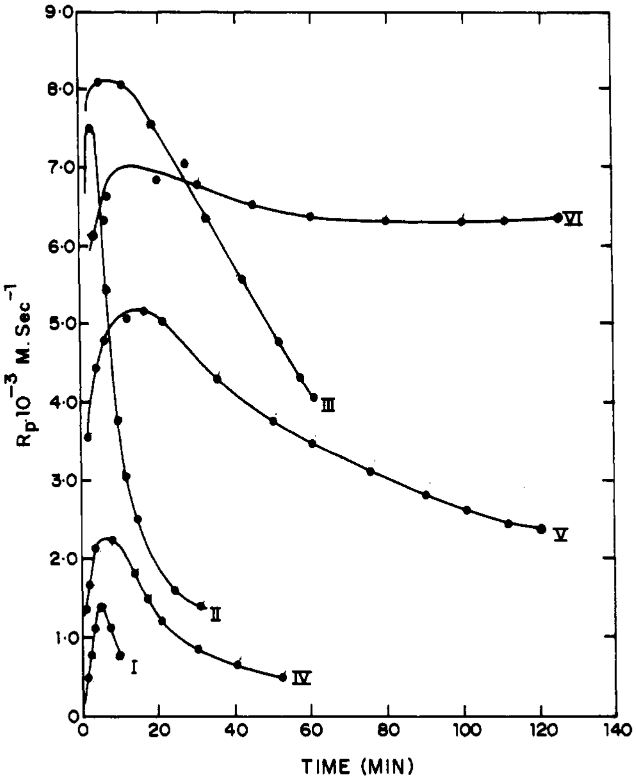

Figure 2. Polymerization of ethylene using zirconocene–MAO and zirconocene–MAO + TMA catalysts: (I) [Al]$_{\text{MAO}}$/[Zr] = 10^3; (II) [Al]$_{\text{MAO}}$/[Zr] = 10^4; (III) [Al]$_{\text{MAO}}$/[Zr] = 10^5; (IV) [Al]$_{\text{total}}$/[Zr] = 1676; (V) [Al]$_{\text{total}}$/[Zr] = 16 760; (VI) [Al]$_{\text{total}}$/[Zr] = 167 600.

revealing of the subtle yet substantive role played by TMA. TMA alone with Cp_2ZrCl_2 shows a steady-state buildup type kinetic curve, especially at a [Al]/[Zr] ratio of 10^3 and 10^4. The onset of a moderate rate decay is evident at [Al]/[Zr] = 10^5 (Figure 1). MAO alone shows a decay type kinetic curve, the rate of decay being faster at lower [Al]/[Zr] ratios (Figure 2). The peak rate is achieved within 5–10 min, and therefore rapid decay of the rate occurs. Decay type kinetic curves for ethylene polymerization using Cp_2ZrCl_2/MAO have been reported earlier in the literature.[7,10-12] Addition of TMA to MAO slightly reduces the peak rate. However, with addition of TMA, the kinetic profile changes from a decay type to a buildup type curve. At a [Al]$_{\text{total}}$/[Zr] ratio of 167 000 (curve VI), the rate shows negligible decay, exhibiting essentially a steady-state kinetic behavior for over 2 h. To the best of our knowledge, such a beneficial effect of added TMA in a MAO/metallocene catalyst system from the point of view of practical catalysis is not explicitly evident in the prior literature. Interestingly and contrary to data published in prior literature, molecular weight is only marginally depressed by addition of free TMA to MAO, under the conditions of this study.

We also examined the behavior of a sterically hindered aryloxy derivative of TMA, namely $AlMe(BHT)_2$, as cocatalyst for ethylene polymerization. $AlMe(BHT)_2$ can be isolated as a crystalline solid, free of complexed TMA. In conjunction with zirconocene, a toluene solution of $AlMe(BHT)_2$ failed to initiate polymerization of ethylene. However, upon addition of TMA (entries 10 and 11) the catalyst showed pronounced activity. There was a small but definite enhancement of initial rate over the TMA/zirconocene catalyst. A decay type kinetic profile, reminiscent of MAO, was observed (Figure 3).

These results have significant implications on the metallocene–methylaluminoxane-catalyzed polymerization of olefins. They establish that the [Me]/[Al] ratio in MAO needs to be suitably adjusted to produce a catalyst of high activity and long kinetic lifetime. This result also has a bearing on the choice of synthesis conditions for obtained MAO with a defined [Me]/[Al] ratio.[3,13] Apart from contributing to catalyst activity, TMA plays the more important role of stabilizing the active centers and extending catalyst lifetime. A sterically hindered aryl oxide of TMA, which is monomeric in nature and bears a close similarity to the structure of oligomeric aluminoxane, also exhibits a kinetic behavior similar to that of MAO. However, catalyst productivity is far inferior.

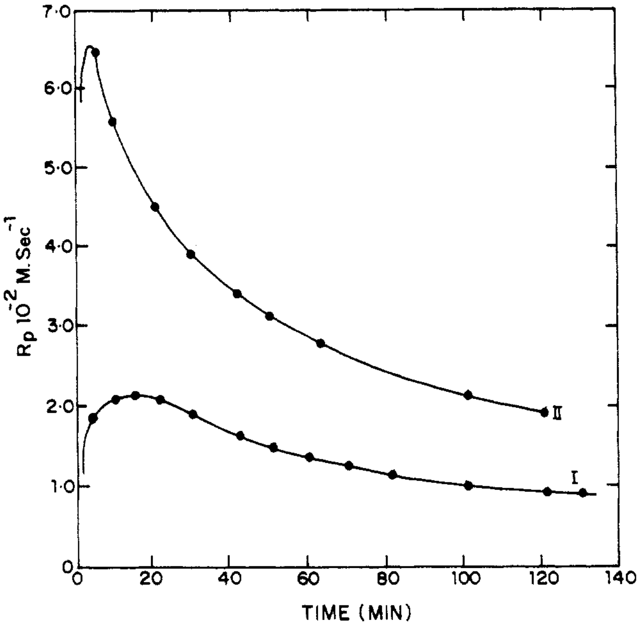

Figure 3. Polymerization of ethylene using zirconocene–AlMe(BHT)$_2$ + TMA catalyst: (I) $[\mathrm{Al}]_{\mathrm{total}}/[\mathrm{Zr}] = 1676$; (II) $[\mathrm{Al}]_{\mathrm{total}}/[\mathrm{Zr}] = 16\,760$.

Nevertheless, this raises the hope that a simple organoaluminum compound can be found that mimics the essential features of the more complex MAO-based catalyst system. Systematic research, in pursuit of this goal, is currently underway in our laboratory.

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(13) These results indicate that data from published literature, especially originating from different laboratories, must be compared with caution. Only in a very few instances is complete characterization of MAO including the TMA content explicitly indicated in published papers or patents.