Methylaluminoxane: synthesis, characterization and catalysis of ethylene polymerization

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Summary

Three types of methylaluminoxanes (MAO-1, 2 and 3) were synthesized with different average molecular weights. In each MAO synthesis, two types of MAOs were isolated (Fractions A and B). Fractions A and B differ by the presence of different methyl/aluminum molar ratio and mol% trimethylaluminum. Kinetics of ethylene polymerization were studied using both fractions A and B of MAOs 1,2 and 3 as cocatalysts and Cp_2ZrCl_2 as catalyst at atmospheric pressure of ethylene. The poly(ethylene)s were analyzed for their molecular weight.

Introduction

The discovery of homogeneous bis(cyclopentadienyl)titanium(IV)dichloride alkylaluminum catalyst system by Breslow and Newburg (1) for ethylene polymerization kindled considerable interest in the area of soluble catalysts for olefin polymerization (2). However, for over twenty years homogeneous catalysts did not attract wide spread interest because of the poor catalyst activity, short kinetic life time and lack of stereospecificity.

The accidental observation of an increase in catalytic activity in presence of moisture for the polymerization of ethylene using alkylaluminum cocatalysts lead to the discovery of methylaluminoxane (MAO), as cocatalyst (3). This fact stimulated renewed commercial and scientific interest in homogeneous Ziegler-Natta catalysis. MAO is prepared by controlled and partial hydrolysis of trimethylaluminum (TMA). The typical structural element of MAO is an oxygen atom joining two aluminum atoms that still bear a methyl group. MAO is found to be oligomeric in nature with repeating unit -[-O-Al(CH3)-]-. The precise structure of MAO is, however, still shrouded in mystery (4).

Among the several methods available for the synthesis of MAO, it is generally prepared by controlled and partial hydrolysis of TMA with hydrated salts dispersed in toluene. Depending on the nature of the salt used and the reaction conditions, MAO with widely differing activities as cocatalysts in polymerization of ethylene is formed (5). The controlled and partial hydrolysis of TMA was first performed by the reaction of TMA with crystal water of copper sulfate. Later, aluminum sulfate hydrates were chosen as the water source for the hydrolysis, in order to prevent the contamination of MAO from soluble Cu(I) alkyl compounds complexed with TMA (5). The resulting hydrolysis product is

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filtered and the filtrate (hereafter designated as Fraction-A) can be used as such as cocatalyst. Solid MAO is obtained by distilling out and pumping off volatiles from Fraction-A. A toluene solution of this solid MAO (hereafter designated as Fraction-B) is also used as cocatalyst. Both fractions A and B differ by the presence of different amounts of free TMA in MAO which will eventually affect the cocatalytic effect of MAO on the polymerization.

Although, MAO has been extensively used in olefin polymerization and is even commercially available, very little has been reported (6) regarding reaction variables associated with its synthesis, their effect on MAO properties [methyl/aluminum (Me/Al) molar ratio, mol % TMA, average molecular weight or degree of oligomerization] and their effect on kinetics of ethylene polymerization, and the molecular weight of poly(ethylene) formed. This paper reports the effect of some synthetic parameters on the properties of MAO (above mentioned) and their effect on polymerization of ethylene using Cp_2ZrCl_2 as catalyst at 70 °C.

Experimental

All manipulations involving air sensitive compounds were performed inside a Laboconco Model 50004 inert atmosphere glove box continuously purged with high purity nitrogen (<5 ppm moisture and <5 ppm oxygen), or under a positive pressure of high purity nitrogen, or using standard bench top inert atmosphere techniques.

Materials: TMA (Schering-A.G., Germany) and Cp_2ZrCl_2 (Aldrich chemicals, USA) were used as received. Sulphur free toluene and benzene (Loba-AR grade, Bombay) were purified by refluxing over sodium and subsequent distillation under nitrogen prior to use. $Al_2(SO_4)_3 16H_2O$ (Loba-AR grade) was used as such for the synthesis of MAO. Polymerization grade ethylene was obtained from the C_2-C_3 cracker unit of Indian Petrochemical Corporation Limited at Nagothane, India (oxygen <3 ppm, moisture <4 ppm).

Synthesis of MAO: All the apparatus used was oven dried overnight and cooled under a nitrogen atmosphere before use. A typical synthesis of MAO is carried out according to the procedure described below.

TMA (8.35g, 0.1185 mol) was placed in a 100 mL conical flask and was diluted with 35 mL dry toluene. In a four necked 250 mL round bottomed flask equipped with a teflon magnetic needle 11.35 g of $Al_2(SO_4)_3 16H_2O$ was dispersed in 60 mL of dry toluene. The two necks of the flask were connected to nitrogen inlet and outlet respectively. The third neck was fitted with a rubber septum and the fourth neck with a thermowell. Both the TMA containing flask and $Al_2(SO_4)_3 16H_2O$ containing flasks were cooled to -10 °C using ice + salt mixture. The toluene solution of TMA was added dropwise into the $Al_2(SO_4)_3 16H_2O$ containing flask under a positive pressure of nitrogen using a cannula and under vigorous stirring. After the complete addition of toluene solution of TMA the reaction mixture was slowly heated to 30 °C (no external heating is required). The temperature was maintained more or less constant throughout the reaction. After 4h of reaction at 30 °C, the temperature was increased to 50 °C for six more hours using a controlled temperature bath. The Me/Al molar ratio was determined periodically during the reaction.

After 10 h the reaction mixture was filtered into a two necked round bottomed flask under a positive pressure of nitrogen. Half of this filtrate was stored for use as cocatalyst in ethylene polymerization. From the rest of the filtrate the volatiles were distilled off under reduced pressure (0.1 mm Hg) at room temperature (30 °C) until a white solid appeared. This solid was further dried for about 30 minutes under the same conditions. The free flowing white solid, dissolved in dry benzene was also used as cocatalyst for ethylene polymerization.

Characterization of MAO: Me content was determined by estimating the amount of methane evolved upon hydrolysis using a gas buret. Al content was estimated by EDTA back titration. Mol of methane evolved divided by mol of Al gives the Me/Al molar ratio of the MAO. Mol% TMA in MAO was calculated by two different techniques.
(1) using Me/Al molar ratio: [It was calculated by neglecting the chain ends of MAO (i.e., -O-Al(CH$_3$)$_2$) if the compound is linear]. It is determined by using equation (a+3b)/(a+b) = Me/Al. where "a" corresponds to MAO and "b" corresponds to TMA. From the repeating unit of MAO it is noted that MAO contains "a" mol of Me and "a" mol of Al. TMA contains "3b" mol of Me and "b" mol of aluminum. Therefore the total Me content of MAO (MAO + TMA) is "a+3b" and total Al content is "a+b". By substituting the value of Me/Al molar ratio the value of "b" i.e., mol %TMA present in MAO was calculated. (2) using ^{1}H NMR: ^{1}H NMR was taken in toluene-d$_8$ on a Brucker AC-200 spectrometer. Mol % TMA in MAO was calculated from the integrations of the MAO broad peak (-0.35 ppm) and TMA sharp peak (-0.20 ppm) as reported by Resconi *et al.* (7). The mol % TMA in MAO values calculated using Me/Al molar ratio were in good agreement with the values obtained using the ^{1}H NMR. The average molecular weight of MAO was determined by cryoscopy using benzene as solvent.

Polymerization: Ethylene polymerization was conducted at 70 °C in a jacketed glass reaction cell connected to a one L glass gas buret. The desired amounts of MAO were placed into 30 mL of dry toluene saturated with ethylene in the cell. The reaction was initiated by addition of toluene solution of Cp$_2$ZrCl$_2$. 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, the product filtered, and dried under vacuum to a constant weight. Intrinsic viscosities of the polymers were determined at 135 °C using decalin as solvent.

Results and Discussion

Three reactions were performed for the synthesis of MAO by employing different reaction conditions given below.
MAO-1: Reaction temperature 30 °C and reaction time 6h. MAO-2: Reaction temperature 30°C for 4h and then temperature raised to 50°C for further 4h. MAO-3: Reaction temperature 30°C for 4h and then temperature raised to 50°C for further 6h.

TMA:H$_2$O mol ratio for all three reactions were taken as 1:2 (TMA:H$_2$O = 0.143:0.282 mol). The concentration of toluene solution of TMA (3.2 gAl/100 mL) was also the same in the three reactions. The properties of these synthesized MAOs are shown in Table 1.

In each MAO synthesis, two types of MAOs were isolated. One of the filtrate from the reaction mixture (Fraction A), and the other is obtained by drying the filtrate MAO under vacuum and dissolving the resulting solid in benzene (Fraction B). Fractions A and B will differ by the presence of different Me/Al molar ratio and mol% TMA. It is to be noted that MAO always contains some TMA which even after distillation in the presence of cumene or complexation with tetrahydrofuran retains one molecule of strongly associated TMA (8). The presence of residual TMA in MAO has also been detected by ^{1}H NMR (7) as well as GPC (9).

Table 1. Properties of Synthesized Methylaluminoxanes

Properties	MAO-1		MAO-2		MAO-3	
	A	B	A	B	A	B
Me/Al mol ratio	2.07	1.63	1.75	1.55	1.65	1.50
Mol% TMA	53.0	29.0	37.5	27.5	32.5	25.5
Average mol. wt.		420		590		805

Upon increase in reaction time as well as temperature the Me/Al molar ratio and mol% TMA decreased and average molecular weight of MAO increased (Figure 1). This can be attributed to the increase in the degree of oligomerization as a result of increase of extent of condensation reaction between water and TMA. As expected Fraction-A shows higher Me/Al and higher TMA content compared to Fraction-B in all the three reactions (Table 1). This is because of the removal of some TMA while distilling out from Fraction A to obtain Fraction-B.
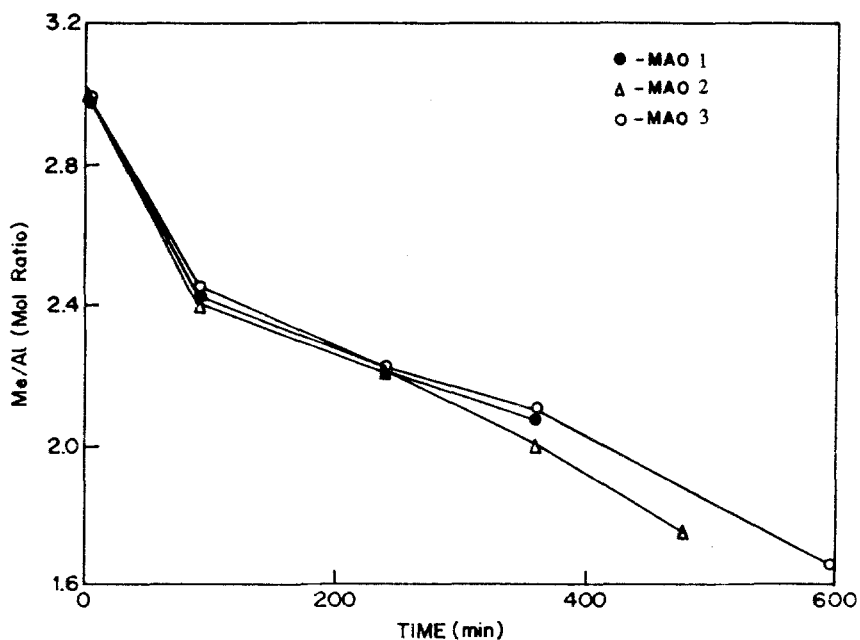

Figure 1. Plot of Me/Al molar ratio vs time during the preparation of MAOs 1,2 and 3

Ethylene polymerizations were conducted in toluene using Cp_2ZrCl_2 catalyst in combination with MAOs (both fractions A and B from reactions 1,2 and 3) as cocatalysts at 70 °C. All the polymerizations were conducted at [Al] = 8.8 x 10^{-2} mol/L, [Zr] = 8.8 x 10^{-7} mol/L and [Al]/[Zr] = 100000. The results are shown in Table 2 and in Figure 2.

Table 2. Ethylene Polymerization using Cp_2ZrCl_2-Synthesized MAOs[a]

	MAO parameters			Polymerization		
Type of MAO	Me/Al (mol ratio)	TMA (mol%)	Average Mol. Wt.	Activity (Kg-PE/gZr.h.atm)	Initial Rp.10^{-4} (M. Sec^{-1})	Intrinsic viscosity[b]
MAO-1A	2.07	53.0		280	0.6	1.04
MAO-1B	1.63	29.0	420	330	0.9	1.50
MAO-2A	1.75	37.5		785	2.6	2.90
MAO-2B	1.55	27.5	590	719	2.3	3.00
MAO-3A	1.65	32.5		1040	5.4	3.20
MAO-3B	1.50	25.5	805	860	3.4	3.10
MAO - (Schering)	1.60	30.0	850	1000	4.0	1.70

[a]Polymerization conditions: [Al] = 8.8 x 10^{-2} mol/L, [Al]/[Zr] = 100000, Temperature = 70°C, Toluene = 30 mL, [b]Intrinsic viscosity determined at 135°C in decalin (dL/g)

For Fraction-A (in case of MAOs 2 and 3) catalyst activity as well as initial Rp for ethylene polymerization was found to be higher when compared to Fraction-B from the corresponding reaction (Table 2). This is due to the presence of high TMA content in Fraction-A (MAOs 2 and 3). Recently we have reported that the addition of TMA to MAO causes a dramatic increase in catalyst activity as well as initial Rp (10). It has been speculated that TMA might be the actual cocatalyst in MAO-based catalyst systems (7). But in case of MAO-1 Fraction-A shows less catalyst activity and less initial Rp when compared to Fraction-B. This is because of the presence of very high TMA content (53%) which influences Fraction-A of MAO-1 to behave more like a TMA-based rather than a MAO-based system (11). MAO-3 with low Me/Al (1.65) and low TMA content (32.5%) shows the highest catalytic activity and high rate of polymerization when compared to MAOs 1 and 2. This is because of higher average molecular weight (805) of MAO-3. It is generally recognized that in order to obtain good catalyst activity, the MAO must have a minimum average molecular weight (5).

The Rp versus time curve for ethylene polymerization showed a decay type curve for MAO-3 (Fractions A and B) cocatalyzed polymerizations (Figure 2). For MAO-1 cocatalyzed polymerizations the Rp versus time curve is an initial build up type which subsequently attains steady state. For MAO-2 it is observed that the Rp versus time curve
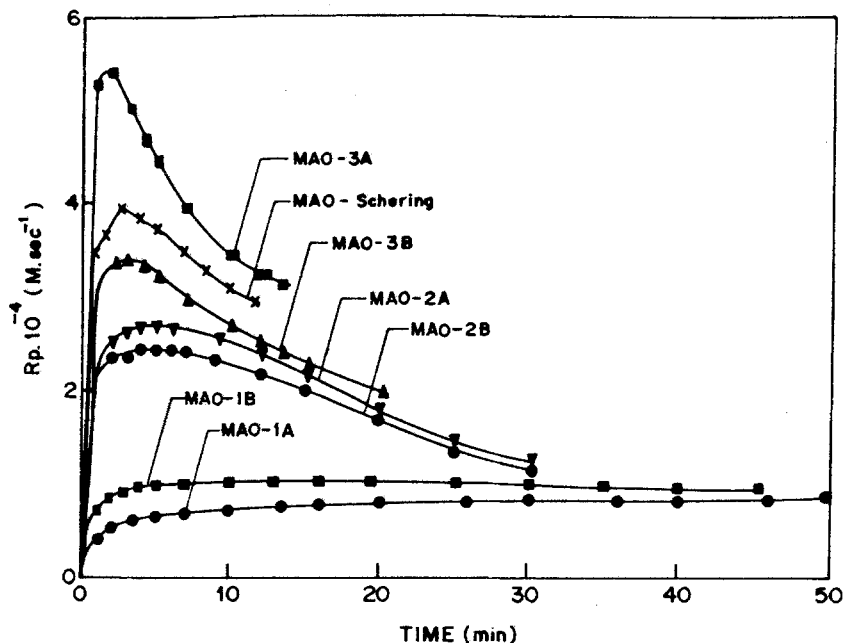
Figure 2. Rate curves for ethylene polymerization

is a moderate decay type curve. It may be recalled that TMA cocatalyzed ethylene polymerization shows a kinetic profile of build up type and MAO cocatalyzed ethylene polymerization shows a decay type kinetic profile (10,12-14). MAO-1 having an average molecular weight of 420 behaves more like TMA which is due to its lower molecular weight and higher TMA content. MAO-3 having an average molecular weight of 805 shows a decay type kinetic profile similar to that observed for commercial MAO (Schering-A.G., Germany) cocatalyzed ethylene polymerization (Figure 2). MAO-2 with an average molecular weight of 590 shows an intermediate behavior between the two extreme cases. Therefore it can be understood that higher molecular weight MAOs are required to achieve high rates of polymerization. These observations are in agreement with earlier reports concerning the catalyst activity of $Cp_2Ti(CH_3)_2$ which increased with an increase in the degree of oligomerization of MAO, for ethylene polymerization (5).

The intrinsic viscosity of the poly(ethylene)s obtained using Fraction-A and Fraction-B cocatalyzed polymerizations (in case of MAOs 2 and 3) (Table 2) is essentially similar. Intrinsic viscosity of poly(ethylene) obtained using MAO-3 is found to be higher. This is due to the presence of lower mol% TMA. TMA has been reported to act as a chain transfer agent when $Cp_2Zr(CH_2C_6H_5)_2$-MAO catalyst system was used for the polymerization of ethylene (5). The properties of two MAOs (MAO-3 and Schering-MAO) and the kinetic profiles for ethylene polymerization obtained using these MAOs are quite comparable (Table 2 and Figure 2).

These results show that both TMA content in MAO as well as its average molecular weight play an important role in achieving high catalytic activities and high molecular weight poly(ethylene)s. And also these results suggest that in order to get high catalytic activity with high initial Rp and high molecular weight poly(ethylene), MAO average molecular weight should be higher than a critical minimum which is around 800, have a Me/Al of around 1.6 and TMA content of approximately 30 mol% (within the limits of this study). These results will have implications on the choice of method for the synthesis of MAO and its use in the polymerization of olefins.

Acknowledgements

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