

# Effect of aluminoxane on semi-batch polymerization of ethylene using zirconocene dichloride

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(Received 8 August 1997; revised 14 January 1998; accepted 15 January 1998)

Several types of commercial and developmental aluminoxanes were studied in the semi-batch polymerization of ethylene using bis(cyclopentadienyl) zirconium dichloride (Cp<sub>2</sub>ZrCl<sub>2</sub>). High temperature gel permeation chromatography (GPC) measurements of polyethylene (PE) formed using various types of aluminoxanes approximated Flory's most probable distribution from a single site-type with PE  $M_w/M_n$ s approaching 2.0 for polymerization temperatures ranging from 50 to 90°C. The structure and type of aluminoxane co-catalyst were found not to influence the molecular weight distribution (MWD) of PE although to influence the activity of the Cp<sub>2</sub>ZrCl<sub>2</sub> catalyst. In general, modified methylaluminoxanes (MMAOs) and methylaluminoxanes (MAOs) were found to have similar activities, whereas isobutylaluminoxane (IBAO) gave a very low activity in the polymerization of ethylene. Increasing isobutyl content in the aluminoxane co-catalyst led to a continual decrease in catalyst activity. Increasing aluminium/zirconium (Al/Zr) molar ratio, by increasing the MAO concentration, led to increasing catalyst activity up to a maximum activity at an Al/Zr molar ratio of 2400. Like the structure and type of the aluminoxane co-catalyst, the Al/Zr molar ratio was found not to influence the PE MWD. Mixing in additional trimethylaluminium (TMA) with MAO was found not to alter the MWD but gave lower activity at similar Al/Zr molar ratios than that from MAO itself. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: metallocene catalyst; methylaluminoxane; polyethylene)

## INTRODUCTION

Metallocene polymerization is a revolution in the polymer industry for producing both specialty and commodity polyolefins. The advantage of metallocene catalysts is that they are extremely active<sup>1–3</sup> and depending on catalyst structure, they may contain one or more catalytically active site-types. Each site-type gives a narrow molecular weight distribution (MWD)<sup>3,4</sup> with a polydispersity index (PDI) approaching 2 as defined by Flory's most probable MWD<sup>5</sup>. It also gives an extremely narrow chemical composition distribution (CCD) as defined by Stockmayer's bivariate distribution<sup>6</sup>.

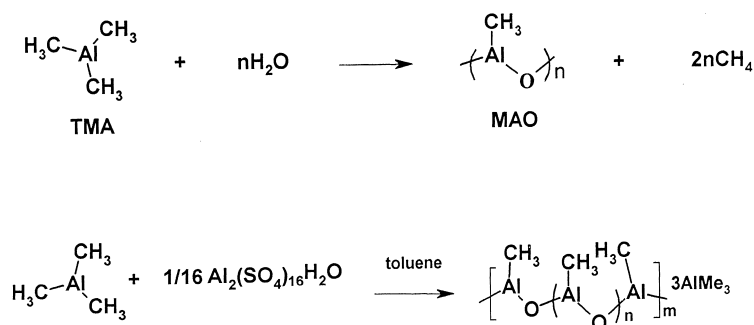
Until 1973, it was assumed that homogeneous Group IV-B metallocene catalysts were inactive in olefin polymerization. However, it was surprisingly found that when water was added to bis(cyclopentadienyl)titaniumdimethyl/trimethylaluminium (TMA), (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Ti(CH<sub>3</sub>)<sub>2</sub>/Al(CH<sub>3</sub>)<sub>3</sub>, system, the activity increased to such a degree that ethylene could be polymerized<sup>7,8</sup>. The reaction of water with TMA has been found to eliminate methane and to form an aluminium–oxygen–aluminium structure (Figure 1) which has been called methylaluminoxane or MAO<sup>9–11</sup>.

MAO can be prepared in several different methods by the careful controlled partial hydrolysis of an alkylaluminium. The reaction of water with alkylaluminium is extremely rapid and highly exothermic and careful synthetic routes are

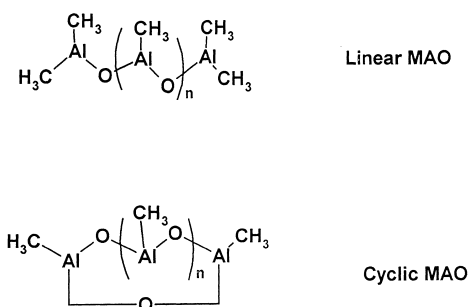
necessary for its controlled and safe formation. In the laboratory, often the hydrated salt method is utilized for formation of aluminoxane, which consists of reacting a hydrated salt such as hydrated aluminium, copper, or iron sulfate with TMA or other trialkylaluminiums<sup>12,13</sup> (Figure 1). Several other methods for synthesizing aluminoxanes have been reported which generally involve either a wet solvent<sup>14</sup> and/or gas to control the aluminoxane formation<sup>15,16</sup>. However, there are several disadvantages with these methods including long reaction times with hydrated salts, low yields (50% or lower), potential of explosion and formation of solid by-products, small amounts of the transition metal when using hydrated iron or copper sulfate<sup>16,17</sup>, use of low temperatures (–10°C and below) in order to obtain optimum yields, poor reproducibility, use of expensive raw materials or unusual reactors and conditions etc.<sup>18,19</sup>. Due to these disadvantages, these methods are not favoured industrially and various other methods are employed<sup>20</sup>, such as directly contacting trialkylaluminium with water vapour or atomized water vapour under carefully controlled conditions<sup>21</sup>.

All of the above synthetic techniques to produce aluminoxanes inevitably produce aluminoxanes with different structures, different degrees of oligomerization, and different amounts of unreacted TMA. Both cyclic and linear oligomers have been proposed to be produced in the formation of aluminoxanes with a degree of oligomerization between 10 and 20<sup>22</sup> (Figure 2). More recently, 3-D cage structures with four-coordinate aluminium centres have

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**Figure 1** Formation of methylaluminoxane (MAO): (a) basic formation of MAO by reaction of trimethylaluminium (TMA) with water; (b) hydrated salt method of formation of MAO by reaction of TMA with hydrated aluminium sulfate



**Figure 2** Forms of MAO: (a) linear; (b) cyclic

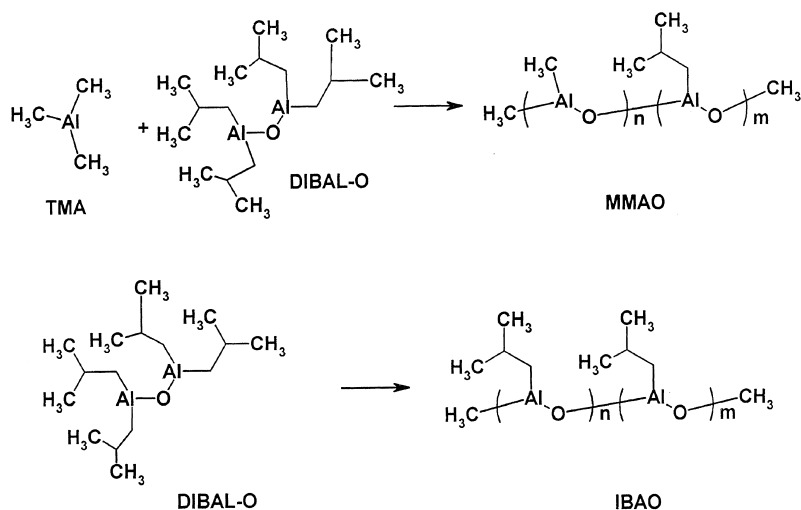
been demonstrated for aluminoxanes produced from  $\text{Al}(\text{tBu})_3$ <sup>23</sup> with similar structures demonstrated for methylaluminoxanes<sup>24</sup>. These cage structures are theorized to be involved in the interaction between aluminoxane and transition metal in an active catalyst site, with the aluminoxane involved in more than just catalyst activation<sup>23</sup>.

It has also been demonstrated that in the partial hydrolysis of TMA to MAO some unreacted TMA always remains in the MAO solution<sup>25,26</sup>, even when the solution is dried under vacuum<sup>27</sup>. By <sup>13</sup>C NMR spectroscopy, Tritto *et al.*<sup>28-30</sup> found that TMA is most likely bound to MAO, bridging two or more MAO chains together and that the amount of TMA influences the active cationic metallocene concentration. A cage structure has been reported which contains unreacted

TMA inside a 3-D MAO cage<sup>24</sup>. However, presently the exact structure of the MAO oligomer is unknown as studies to analyse this system suffer from the dynamic behaviour of MAO, which by multiple equilibria such as disproportionation, changes its size and structure with both temperature and solvent<sup>31,32</sup>. The term 'black box' is used to describe the inherent difficulties in trying to elucidate the structure of MAO<sup>23</sup>.

Hydrolysis of aluminoxane to give a gas/Al ratio gives an indication of the structure of aluminoxane. Conventional MAO, when hydrolysed, gives methane as the sole gaseous product from methyl aluminium species. A form of MAO known as modified methylaluminoxane (MMAO) can be formed by the reaction of TMA with a tetraalkyldialuminoxane containing ethyl or higher alkyl groups with the optional presence of water<sup>20</sup> (Figure 3). Unlike conventional MAO, MMAO contains alkyl substituents derived from tetraalkyldialuminoxane and/or polyalkylaluminoxane and gives C2+ products such as isobutane, *n*-butane etc. upon hydrolysis. The mole% methane and mole% higher alkane depend on the relative quantity of TMA to polyalkyldialuminoxane introduced. IBAO is a type of MAO that consists entirely of isobutyl groups with no methyl groups present and can be formed from di-isobutylaluminoxane.

Advantages of MMAO over conventional MAO are due to the isobutyl groups of MMAO which lead to high solubility in both aliphatic and aromatic solvents, whereas conventional MAOs exhibit only limited solubility in



**Figure 3** Formation of (a) MMAO by reacting TMA with tetraisobutyldialuminoxane (DIBAL-O); (b) IBAO by reacting DIBAL-O

aliphatic solvents. Aliphatic or saturated hydrocarbon solvents are preferred for industrial solution and slurry ethylene polymerization and are also believed superior for the formation of long chain branches<sup>33</sup>. MAO has the additional advantage of having a longer shelf-life than conventional MAO which tends to gel over time and hence lose its co-catalytic ability<sup>32</sup>.

The interactions of oligomeric MAO with unreacted TMA and metallocene catalyst are complicated and unknown. The MAO co-catalyst is believed to alkylate the metallocene catalyst and functions as a Lewis acid, promoting the formation of an active cationic form of metallocene catalyst<sup>34</sup>. It has been found by <sup>1</sup>H and <sup>13</sup>C NMR studies with Cp<sub>2</sub>Ti(CH<sub>3</sub>)(X) complexes where X is CH<sub>3</sub> or Cl, that (1) MAO was a better alkylating agent than TMA; and (2) MAO had a greater capacity for producing and stabilizing cation-like complexes than TMA<sup>27</sup>. This study, and several others for similar systems, found that the following equilibrium takes place: Cp<sub>2</sub>TiMe<sup>+</sup>[-Al(Me)O]<sup>-</sup><sub>n</sub> ⇌ Cp<sub>2</sub>TiMe<sup>+</sup>S[-Al(Me)O]<sup>-</sup><sub>n</sub>, where S is a solvent molecule and that the active catalytic species (Cp<sub>2</sub>TiMe<sup>+</sup>S[-Al(Me)O]<sup>-</sup><sub>n</sub>) is a cation-like species. The equilibrium is believed to be shifted to the right for higher Al/Group IV metal molar ratios, thus increasing the concentration of the active cationic catalyst and hence increasing the activity of the catalyst. Of course, a maximum activity will be produced at a certain co-catalyst/catalyst ratio depending on various conditions such as catalyst type and concentration, co-catalyst type and concentration, solvent type (especially polarity), impurity/active site concentration, temperature, and monomer concentration in the diluent.

The structure of aluminoxane has been reported to have a marked influence on the activity of a metallocene/aluminoxane catalytic system, with methylaluminoxane (MAO) being reported to give higher activity than other aluminoxanes such as ethylaluminoxane (EAO) or isobutylaluminoxane (IBAO)<sup>35</sup>. Increasing the degree of oligomerization of aluminoxane is also reported to increase the catalytic activity<sup>1</sup>. The effect of the structure and degree of oligomerization of aluminoxane co-catalyst on the MWD of produced PE has not been well established. It has been suggested for the polymerization of ethylene using Cp<sub>2</sub>ZrCl<sub>2</sub>/MAO that the PE MW decreases when the concentration of aluminoxane increases<sup>36</sup>. For the same system, when using an additional alkylaluminium, the PE MWs were found to increase with increasing concentration of TMA or TEA through a maximum at a TMA/MAO or TEA/MAO ratio of about 0.5 with decreasing PE MWs at higher ratios. Increasing the TIBA/MAO ratio gave a decrease in PE MW<sup>36,37</sup>. TIBA was suggested to give PE MWs that were higher than those obtained with TMA or TEA due to the bulkier isobutyl group in aluminium alkyl which reduced the occurrence of chain transfer to aluminium<sup>36</sup>.

The role of aluminoxane co-catalyst in the active catalytic site-type is still very much in question and a thorough polymerization and polymer characterization study was undertaken to elucidate its role with the metallocene catalyst Cp<sub>2</sub>ZrCl<sub>2</sub>. This paper deals with the investigation of the effects of various commercial and developmental aluminoxanes on the catalyst activity and resulting polymer MWD in the ethylene polymerization. The addition of extra TMA to MAO was also studied to determine its role in the catalyst activation and site-type formation.

## EXPERIMENTAL

### Materials

Fisher Optima (Whitby, ON) toluene was used as diluent for all reactions and purified by distillation over sodium benzyl ketyl. Research grade ethylene was purchased from Matheson Gas (Mississauga, ON) and purified by passing over beds of CuO catalyst and then molecular sieves. The MAOs studied were supplied by either Akzo-Nobel (Dear Park, TX) or the Albemarle Corporation (Baton Rouge). All MAOs were used as received without further purification. TMA 2.0 M in toluene and zirconocene dichloride were purchased from Aldrich Chemical (Mississauga, ON) and used as received. All manipulations of catalyst and co-catalyst were performed in a Vacuum Atmospheres glovebox which reduces the impurities O<sub>2</sub> and H<sub>2</sub>O to less than 1 ppm.

### Reactor set-up and method of polymerization

The polymerization reactor utilized for all experiments was an Autoclave Engineers 1 litre autoclave with 2" dispersimax impeller. All wetted parts were either 316 stainless-steel or teflon. All experiments were performed at 1200 rpm, in toluene. A weighed amount of diluent was transferred to the nitrogen purged reactor with additional purging of the reactor with nitrogen, then ethylene. Co-catalyst was injected by syringe into the reactor next, then the reactor was pressurized with ethylene. The polymerization was initiated by injection of catalyst into the reactor within 5 min of injection of co-catalyst. The reactor temperature was monitored continuously by a J type thermocouple placed in a thermocouple well of the reactor. Temperature was maintained ± 0.2°C. Ethylene flow to the reactor was measured by a Sierra Instruments Model 830 thermal mass flowmeter. The reaction was terminated by depressurizing and injection of methanol into the reactor. The formed PE was washed with acidic methanol to remove the MAO residue, then methanol, filtered and dried under vacuum.

### High temperature GPC

All GPC measurements were performed with a Waters-Millipore SEC instrument model 150-C high temperature GPC with a differential refractive index detector at 140°C using 1,2,4-trichlorobenzene (TCB) as solvent. The following operation conditions were adopted: (1) column and sample compartment temperature, 140°C; (2) flow rate of mobile phase, 1.0 ml/min; (3) sample injection volume, 200 µl; (4) no sample spinning; (5) no sample filtering; (6) sample concentration, 0.1 wt% in TCB.

Calibration of the high temperature GPC was performed at 140°C directly with a calibration curve obtained using narrow MWD PE standards purchased from the National Bureau of Standards. Additionally, both narrow MWD polystyrene (PS) standards from the Tosoh Corporation (Minato-ku, Tokyo) and broad MWD PE standards from American Polymer Standards (Mentor, OH) and Polymer Laboratories Ltd (Church Stretton, UK) were used to check the calibration curve. The Mark-Houwink constants for the calibration curve were for  $K_{PS} = 1.21 \times 10^{-4}$  and  $a_{PS} = 0.707$  and for  $K_{PE} = 3.92 \times 10^{-4}$  and  $a_{PE} = 0.725$ .

## RESULTS

### Effect of aluminoxane structure on catalyst activity

Ten different commercially supplied MAOs were studied at a polymerization temperature of 70°C and an Al/Zr molar ratio of 1600. Table 1 lists the MAOs studied with their

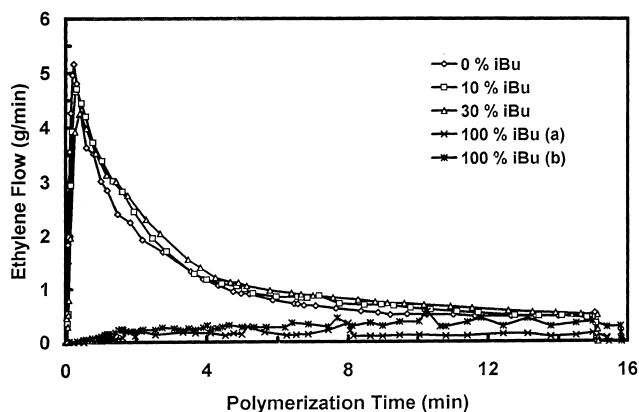
**Table 1** Types and composition of aluminoxanes studied

MAO Type	Structure	Composition	Stabilizers
MAO-1	-(Al(CH <sub>3</sub> )O)-	> 99% Methane	Yes
MAO-2	-(Al(CH <sub>3</sub> )O)-	> 99% Methane	Yes
MAO-3	-(Al(CH <sub>3</sub> )O)-	> 99% Methane	No
MMAO-1	(Al(CH <sub>3</sub> )O) <sub>m</sub> -(Al(i-Bu)O) <sub>n</sub>	29 mol% Isobutane	—
MMAO-2	(Al(CH <sub>3</sub> )O) <sub>m</sub> -(Al(i-Bu)O) <sub>n</sub>	12 mol% Isobutane	—
IBAO-1	(Al(i-Bu)O)	H <sub>2</sub> O/Al = 0.65	—
IBAO-2	(Al(i-Bu)O)	H <sub>2</sub> O/Al = 0.80	—
DIBAL-O	(i-Bu) <sub>2</sub> AlOAl(i-Bu) <sub>2</sub>	—	—
MAO-4	-(Al(CH <sub>3</sub> )O)-	N/A	—
MAO-5	-(Al(CH <sub>3</sub> )O)-	N/A	—
MAO-6	-(Al(CH <sub>3</sub> )O)-	N/A	—
MAO-7	-(Al(CH <sub>3</sub> )O)-	N/A	—

**Table 2** Polymerization results of 10 aluminoxanes

MAO Type	Maximum activity ( $\times 10^{-3}$ )	Average activity ( $\times 10^{-3}$ )	$M_n$ ( $\times 10^{-3}$ )	$M_w$ ( $\times 10^{-3}$ )	$M_z$ ( $\times 10^{-3}$ )	$M_w/M_n$	$M_z/M_w$
MAO-1	58.7	11.9	143	347	650	2.42	1.88
MAO-2	42.3	10.4	147	345	639	2.34	1.88
MMAO-1	48.6	13.6	147	337	637	2.29	1.89
MMAO-2	53.5	13	155	351	649	2.26	1.85
IBAO-1	4	3.6	137	335	643	2.45	1.92
IBAO-2	2.3	1.6	144	341	650	2.37	1.90
DIBAL-O	0	0	—	—	—	—	—
MAO-4	25	8.4	141	327	604	2.31	1.85
MAO-5	29	9.9	156	340	621	2.17	1.83
MAO-6	27.8	7.2	140	332	630	2.36	1.90
MAO-7	29	9	147	354	666	2.41	1.88

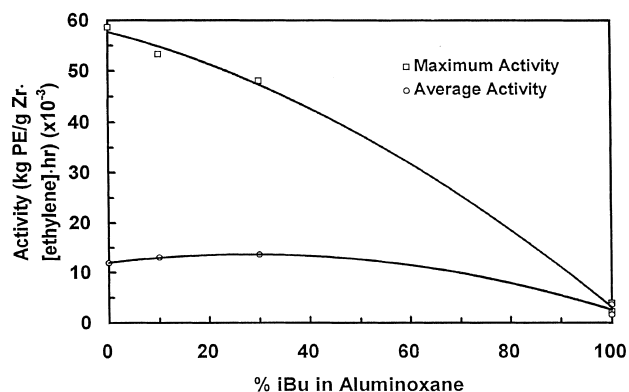
Polymerization conditions: temperature = 70°C; [Zr]<sub>0</sub> = 0.65 μM; Al/Zr = 1600; [ethylene] = 0.18 mol/l (ethylene pressure = 35 psia); solvent = toluene; activity = kg PE/(g Zr·[ethylene]·h)



**Figure 4** Rate-time curves for the polymerization of ethylene with Cp<sub>2</sub>ZrCl<sub>2</sub> utilizing different aluminoxanes. The polymerization conditions were: T = 70°C, [ethylene] = 0.18 mol/l (ethylene pressure = 35 psia), [Zr] = 0.65 μM, Al/Zr = 1600, diluent = toluene

composition, while Table 2 summarizes the polymerization activity and gives the resultant PE MWs and PDIs.

Figure 4 gives the rate-time traces for different aluminoxanes containing different amounts of isobutyl content. From this figure we see that the highly active MAOs (0–30% iBu content) gave an almost immediate maximum (less than 1 min) in the rate of polymerization after initiation by injection of catalyst into the pressurized reactor. The almost instantaneous maximum in

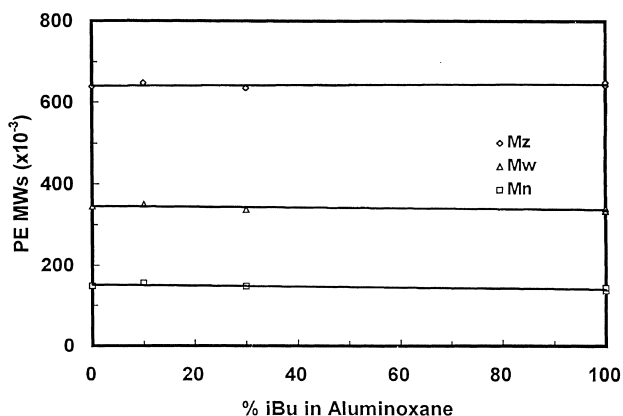


**Figure 5** Plot of catalyst activity versus % isobutyl content in aluminoxane for the polymerization of ethylene with Cp<sub>2</sub>ZrCl<sub>2</sub>. The points are experimental data. The polymerization conditions were the same as in Figure 4

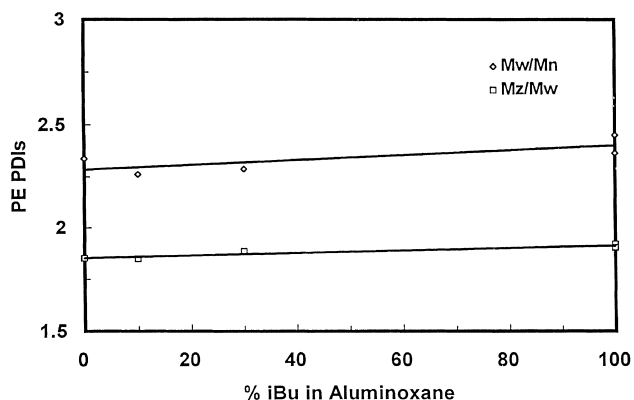
polymerization is followed by a rapid decay in the rate. We have discussed this behaviour more thoroughly in another publication<sup>38</sup>. The two IBAOs studied gave much lower and more constant rate-time curves with slower initiation and an apparent steady state.

Figure 5 plots the catalyst activity versus % iBu content in the aluminoxane co-catalyst, with the upper curve (maximum activity) being determined from the maximum in the rate-time curves and the lower curve (average

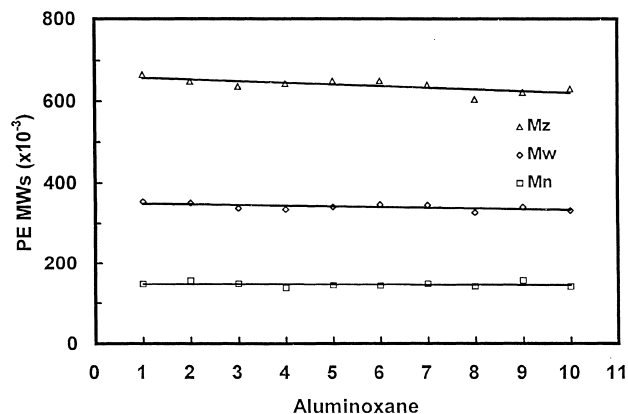
activity) being determined from the overall rate-time curves. We have defined activity here as  $A = \text{kg PE}/(\text{g Zr} \cdot [\text{ethylene}] \cdot \text{h})$  using the concentration of ethylene in the diluent. The  $[\text{ethylene}]$  values are calculated from the ethylene pressures in the reactor headspace using the ethylene solubility in toluene data<sup>39,40</sup>. However, due to the mass transfer limitations caused by the high catalyst activities, the ethylene concentrations in toluene are lower than the saturated concentrations<sup>38</sup>. The top trace in Figure 5 illustrates the relationship of decreasing maximum activity with increasing iBu content in aluminoxane. Plain MAO (0% iBu) gives the highest maximum activity, while MMAO with 12 mol% i-butyl content gives a slightly higher maximum activity than MMAO with 29 mol% i-butyl content. The two 100% i-butyl aluminoxanes (IBAOs) give significantly lower maximum activities than MMAOs or plain MAO IBAO with the  $\text{H}_2\text{O}/\text{Al}$  ratio of 0.65 gives slightly higher activity than IBAO with  $\text{H}_2\text{O}/\text{Al}$  ratio of 0.80. The bottom trace shows the relationship of the average activity over 15 min of polymerization time versus % iBu content in aluminoxane. Here we see that the activity increases very slightly with increasing % iBu content from 0–30% iBu. The two IBAOs again give much lower activities. Thus, the activities in the polymerization of ethylene utilizing  $\text{Cp}_2\text{ZrCl}_2/\text{aluminoxane}$  are very similar using either MAOs or MMAOs as co-catalysts but much lower for IBAO co-catalysts.



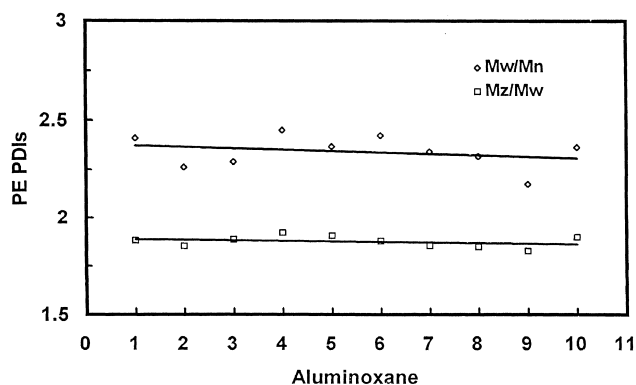
**Figure 6** Effect of % iBu in aluminoxane on the PE MWs. The points are experimental data and the lines are linear least-square regression fit to the points. The polymerization conditions were the same as in Figure 4



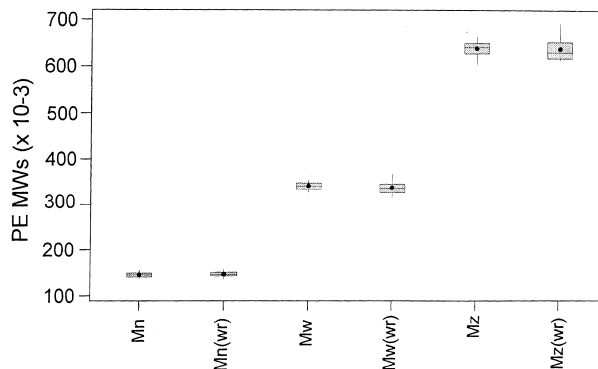
**Figure 7** Effect of % iBu in aluminoxane on the PE PDIs. The points are experimental data and the lines are linear least-square regression fit to the points. The polymerization conditions were the same as in Figure 4



**Figure 8** Effect of aluminoxane type on the PE MWs. The points are experimental data and the lines are linear least-square regression fit to the points. The polymerization conditions were the same as in Figure 4



**Figure 9** Effect of aluminoxane type on the PE PDIs. The points are experimental data and the lines are linear least-square regression fit to the points. The polymerization conditions were the same as in Figure 4



**Figure 10** Boxplot of PE  $M_n$ ,  $M_w$ , and  $M_z$  values for 10 different aluminoxanes used as co-catalyst versus variation of  $M_n$ ,  $M_w$ , and  $M_z$  values for PE produced from a single run in the polymerization of ethylene with  $\text{Cp}_2\text{ZrCl}_2$  as catalyst. The polymerization conditions were the same as in Figure 4

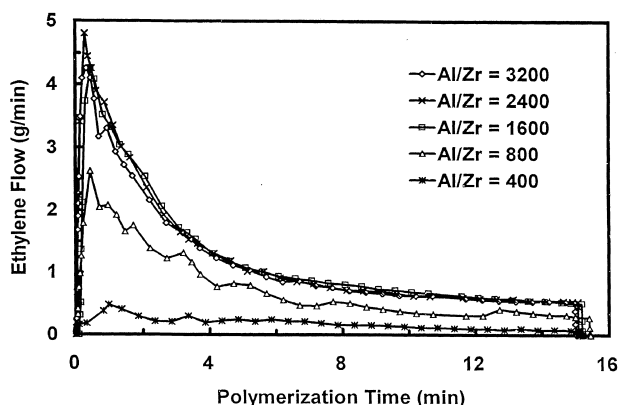
#### Effect of aluminoxane on PE MWD

Figure 6 and Figure 7 provide the plots of PE MWs and PDIs versus the % iBu content in the aluminoxane co-catalyst. It is clear from these plots that the % iBu content in aluminoxane co-catalyst has no discernible effect on the PE MWs and PDIs. Additionally, Figure 8 and Figure 9 provide the plots of PE MWs and PDIs for each of the 10 different aluminoxanes studied at this particular set of polymerization conditions which were found to minimize

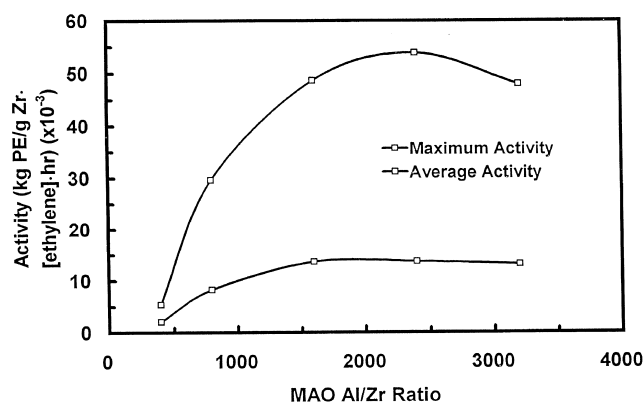
diffusion limitations<sup>38</sup>; i.e. temperature = 70°C, [ethylene] = 0.18 mol/l, Al/Zr molar ratio = 1600 and [Cp<sub>2</sub>ZrCl<sub>2</sub>] = 0.7 μM. The lines are least-square regression lines through the data points which show that each of the aluminoxane co-catalysts produce identical PE samples, independent of the type of aluminoxane.

In order to determine the variation of PE MWs and PDIs produced (a) from within a polymerization run; and (b) by the high temperature GPC, one of the polymerization runs was chosen at random and six samples of PE were run through the high temperature GPC. Figure 10 shows a boxplot (box-and-whisker plot) of the statistical comparison of the two means of (a) the MWs of the 10 PE samples produced with different aluminoxane co-catalysts ( $M_n$ ,  $M_w$ , and  $M_z$ ); and (b) the MWs from the six PE samples produced with the same aluminoxane within the same run ( $M_n(wr)$ ,  $M_w(wr)$  and  $M_z(wr)$ ). In the boxplot diagram the circles give the mean of the data, the middle line of the box is the median, the bottom of the box is the first quartile (Q1) and the top is the third quartile (Q3), while the whiskers extend from the top and bottom of the box to the lowest and highest observations. It is clear from this plot that all the different aluminoxane co-catalysts produce PE with statistically identical MWs for this particular polymerization condition.

This is an important result as each of these aluminoxanes are produced by different processes with different starting



**Figure 11** Rate-time curves for the polymerization of ethylene with Cp<sub>2</sub>ZrCl<sub>2</sub> utilizing different concentrations of MAO. The polymerization conditions were:  $T = 70^\circ\text{C}$ , [ethylene] = 0.18 mol/l (ethylene pressure = 35 psia), [Zr] = 0.65 μM, diluent = toluene.



**Figure 12** Plot of the catalyst activity versus MAO Al/Zr molar ratio for the polymerization of ethylene with Cp<sub>2</sub>ZrCl<sub>2</sub>. The points are experimental data. The polymerization conditions were the same as in Figure 11

materials and different formation conditions. The aluminoxanes have different compositions, some with different types of stabilizers present, and inevitably they have different degrees of oligomerization and different structures. Yet, each of these co-catalysts produces identical PE.

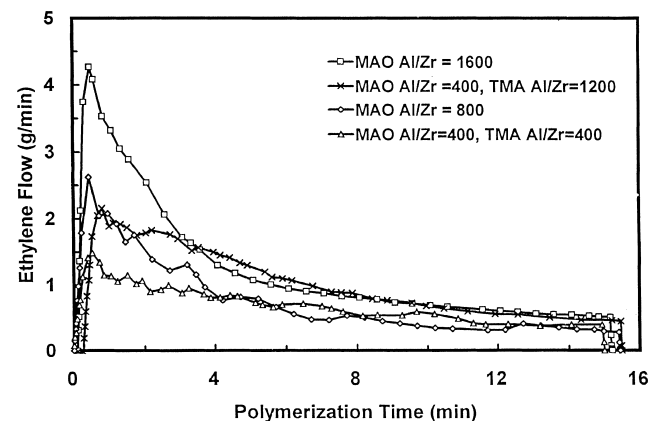
#### Effect of MAO Al/Zr ratio and added TMA on catalyst activity

In order to investigate the effects of aluminoxane Al/Zr molar ratio on the catalyst activity and PE MWs and PDIs, polymerizations of ethylene were performed with Cp<sub>2</sub>ZrCl<sub>2</sub> at 70°C and varying Al/Zr ratios from 400 to 3200. Figure 11 gives the rate-time traces for polymerizations containing various concentrations of MAO. The rate-time traces are very similar for Al/Zr ratios from 1600 to 3200, with an almost immediate maximum in the rate of polymerization and then a rapid decay. With the Al/Zr ratio of 400 the induction period to reach the maximum is much longer and the rate-time curve is more constant with an apparent steady-state. Figure 12 provides plots of catalyst maximum and average activity versus Al/Zr molar ratio. We see that in the trace of maximum activity versus Al/Zr ratio a maximum in the curve is reached at an Al/Zr ratio of 2400, while further increasing the Al/Zr molar ratio decreases the activity. Notice that for the average activity the maximum is reached at an Al/Zr ratio of 1600 which remains constant up to the highest Al/Zr ratio studied of 3200.

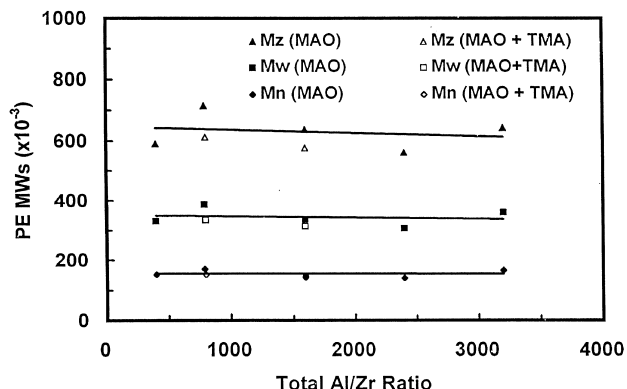
In order to determine the effect on polymerization activity by adding TMA along with MAO to the polymerization mixture, two additional experiments were performed. Figure 13 gives the rate-time traces for runs with and without TMA based on the same total Al/Zr molar ratio. The runs with TMA give much lower initial rates of polymerization, but also give more steady rate-time curves with less decay than those based on MAO at the same total Al/Zr molar ratio. With the same total Al/Zr molar ratio investigated here, MAO gives a higher initial rate of polymerization than the combination of TMA and MAO, but similar average values.

#### Effect of MAO Al/Zr ratio and added TMA on PE MWD

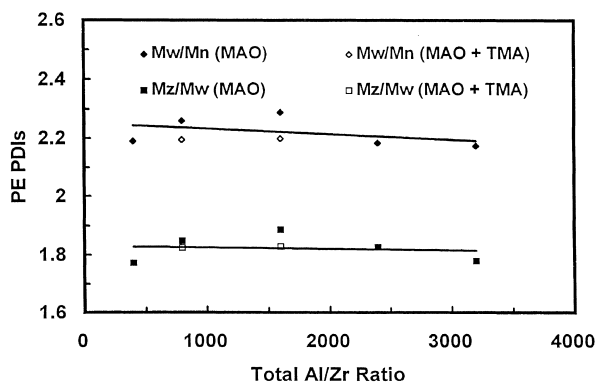
Figure 14 plots the PE MWs versus Al/Zr molar ratio for runs with varying concentrations of MAO. The two runs with added TMA are also plotted. Figure 15 plots the PE



**Figure 13** Rate-time curves for the polymerization of ethylene with Cp<sub>2</sub>ZrCl<sub>2</sub> utilizing different Al/Zr ratios of MAO and TMA. The polymerization conditions were:  $T = 70^\circ\text{C}$ , [ethylene] = 0.18 mol/l (ethylene pressure = 35 psia), [Zr] = 0.65 μM, diluent = toluene



**Figure 14** Effect of the molar Al/Zr ratio on the PE MWs. The points are experimental data and the lines are linear least-square regression fit to the points. The polymerization conditions were the same as in *Figure 13*



**Figure 15** Effect of the molar Al/Zr ratio on the PE PDIs. The points are experimental data and the lines are linear least-squares regression fit to the points. The polymerization conditions were the same as in *Figure 13*

PDIs versus Al/Zr molar ratio for varying concentration of MAO and the two runs with TMA added. It is clear from these plots that the Al/Zr molar ratio has no significant effect on the PE MWs or PDIs at 70°C for the ranges of the ratio studied. It is also clear that the additional TMA has no effect on the PE MWs or PDIs. *Table 3* gives the experimental conditions and results for these polymerization runs.

### 2<sup>3</sup> Designed experiment for comparison of MAO with temperature and Al/Zr ratio

In order to compare the performance of MAO and MMAO at different Al/Zr and polymerization temperature levels and to see if the previous conclusions on the aluminoxane co-catalyst can be generalized in the semi-batch polymerization of ethylene using Cp<sub>2</sub>ZrCl<sub>2</sub> in toluene,

**Table 4** Experimental runs in comparison of MAO and MMAO in 2<sup>3</sup> designed experiment

Run number	Polymerization temperature (°C)	Al/Zr Ratio	iBu Content
1	50	800	0
2	50	2400	29
3	50	800	29
4	90	2400	0
5	90	800	29
6	90	800	0
7	90	2400	29
8	50	2400	0

Polymerization conditions: [Zr]<sub>0</sub> = 0.65 μM; ethylene pressure = 35 psia; solvent = toluene

a 2<sup>3</sup> designed experiment (eight runs) was performed<sup>41,42</sup>. This experiment was designed to determine how polymerization activity and PE MWs and PDIs were effected by: (a) aluminoxane type (MAO = 0% iBu and MMAO = 30% iBu); (b) Al/Zr ratio (800 and 2400); and (c) polymerization temperature (50 and 90°C). *Table 4* summarizes the experimental conditions for the runs performed in this study, while *Table 5* summarizes the polymerization results. All analysis and plot generations were performed using Minitab for Windows v.11.

*Figure 16* and *Figure 17* give the effects plots generated from this analysis which illustrate how the maximum and average activities of polymerization are affected by the three variables of (a) temperature; (b) Al/Zr ratio; and (c) iBu content. For these effects plots, of the eight total runs in the designed experiment, four are averaged at each of the levels i.e. for the maximum activity versus temperature, of the four different runs performed at 50°C the average maximum activity value is plotted and of the four different runs performed at 90°C the average maximum activity value is plotted, with a line drawn between the two average values to help visualize the trend. From this analysis we see that both the maximum and average activities increase with increasing temperature, significantly with increasing Al/Zr molar ratio, and decrease slightly with increasing the iBu content in aluminoxane. Thus, for the designed experiments MAO and MMAO with iBu content up to 30% give very similar activities in the temperature range of 50–90°C with the activities sharply increased with increasing aluminoxane concentration or Al/Zr ratio. Note: a further increase in the iBu content above 30% will significantly reduce the activity (see *Figure 5*).

*Figures 18–20* give the various effects plots for the PE MWs. The PE MWs (*M<sub>n</sub>*, *M<sub>w</sub>*, and *M<sub>z</sub>*) were found to depend only on polymerization temperature and to be rather insensitive to the iBu content and Al/Zr molar ratio. *Figures 21 and 22* give the various effects plots for the

**Table 3** Polymerization results to examine Al/Zr ratio and effect of additional TMA

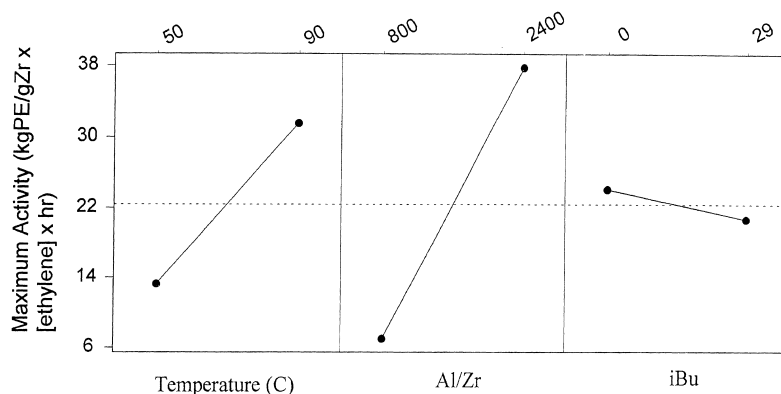
MAO Al/Zr	TMA Al/Zr Ratio	Total Al/Zr	Max. Act. (×10 <sup>-3</sup> )	Avg. Act. (×10 <sup>-3</sup> )	<i>M<sub>n</sub></i> (×10 <sup>-3</sup> )	<i>M<sub>w</sub></i> (×10 <sup>-3</sup> )	<i>M<sub>z</sub></i> (×10 <sup>-3</sup> )	<i>M<sub>w</sub>/M<sub>n</sub></i>	<i>M<sub>z</sub>/M<sub>w</sub></i>
1600	0	1600	48.6	13.6	147	337	637	2.29	1.88
2400	0	2400	53.8	13.7	141	307	561	2.18	1.83
3200	0	3200	48	13.2	166	361	643	2.17	1.78
400	0	400	5.4	2	152	333	590	2.19	1.77
800	0	800	29.6	8.2	171	387	714	2.26	1.85
400	400	800	17	7.6	153	335	612	2.19	1.82
400	1200	1600	24.4	11.4	143	315	576	2.20	1.83

Polymerization conditions: temperature = 70°C; [Zr]<sub>0</sub> = 0.65 μM; ethylene pressure = 35 psia; solvent = toluene; Activity = kg PE/(gZr·[ethylene]·h)

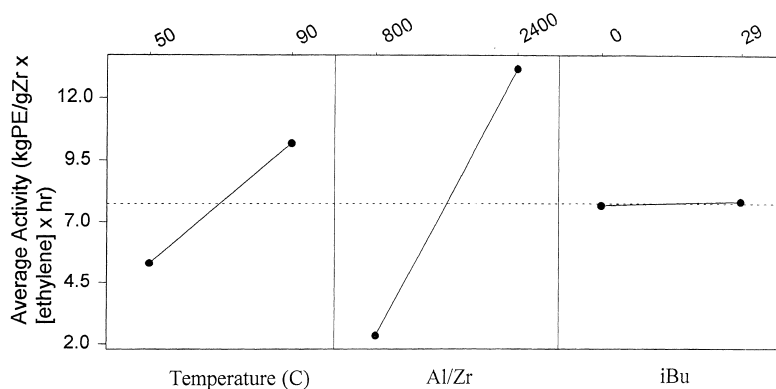
**Table 5** Polymerization results for designed experiment

Run No.	Maximum activity ( $\times 10^{-3}$ )	Average Activity ( $\times 10^{-3}$ )	$M_n$ ( $\times 10^{-3}$ )	$M_w$ ( $\times 10^{-3}$ )	$M_z$ ( $\times 10^{-3}$ )	$M_w/M_n$	$M_z/M_w$
1	11.6	4.3	125	262	470	2.10	1.79
2	13.3	6.7	162	376	696	2.32	1.85
3	8.5	4	176	431	871	2.45	2.02
4	60	19.4	73	158	269	2.17	1.70
5	2.6	0.1	53	116	191	2.17	1.65
6	5.1	0.8	65	138	232	2.12	1.68
7	58.5	20.4	77	167	285	2.17	1.70
8	19.6	6.1	152	334	620	2.20	1.86

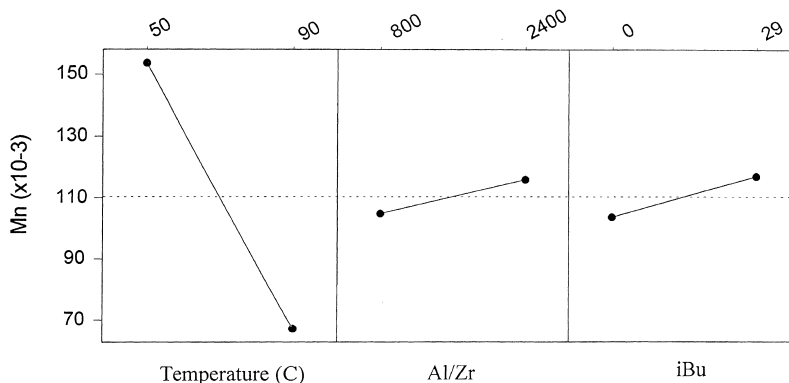
Activity = kg PE/(gZr·[ethylene]·h)



**Figure 16** Effects plots for the maximum catalyst activity in the polymerization of ethylene utilizing  $Cp_2ZrCl_2$ . The polymerization conditions were ethylene pressure = 35 psia,  $[Zr] = 0.65 \mu M$ , diluent = toluene



**Figure 17** Effects plots for the average catalyst activity over 15 min of polymerization time in the polymerization of ethylene utilizing  $Cp_2ZrCl_2$ . The polymerization conditions were the same as in Figure 16



**Figure 18** Effects plots of PE  $M_n$  in the polymerization of ethylene utilizing  $Cp_2ZrCl_2$ . The polymerization conditions were the same as in Figure 16



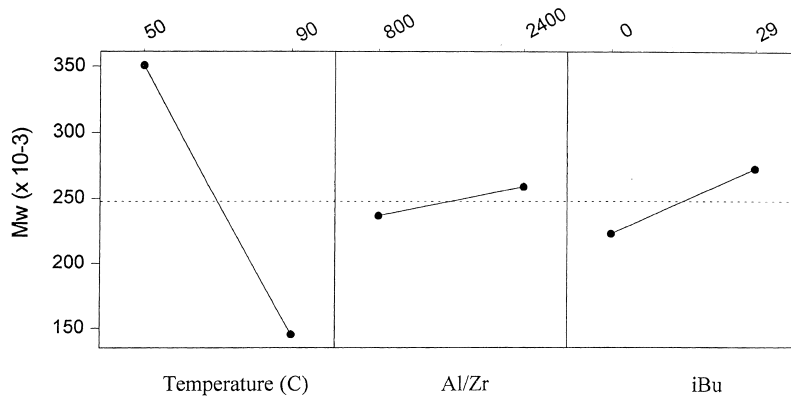


Figure 19 Effects plots of PE  $M_w$  in the polymerization of ethylene utilizing  $Cp_2ZrCl_2$ . The polymerization conditions were the same as in Figure 16

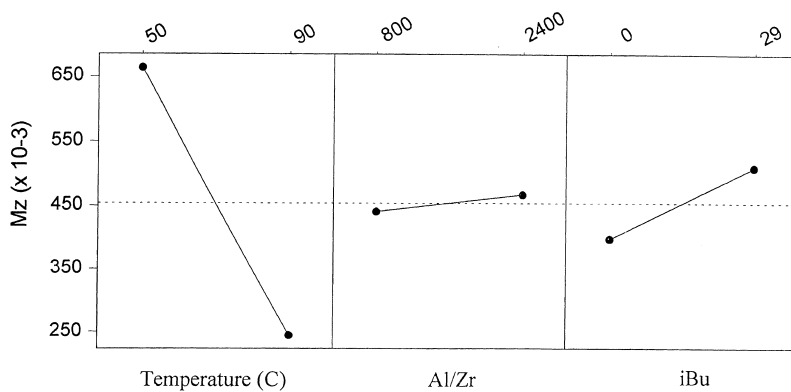


Figure 20 Effects plots of PE  $M_z$  in the polymerization of ethylene utilizing  $Cp_2ZrCl_2$ . The polymerization conditions were the same as in Figure 16

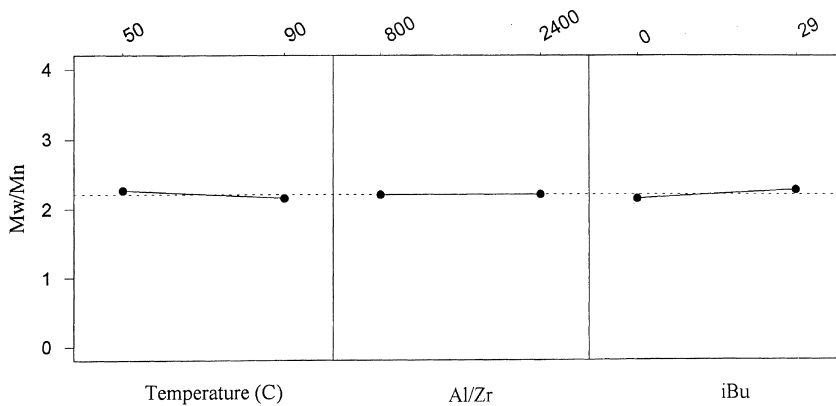


Figure 21 Effects plots of PE  $M_w/M_n$  in the polymerization of ethylene utilizing  $Cp_2ZrCl_2$ . The polymerization conditions were the same as in Figure 16

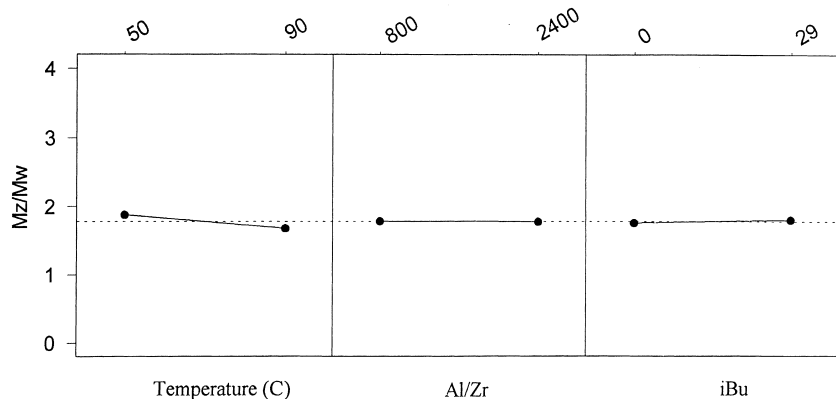


Figure 22 Effects plots of PE  $M_z/M_w$  in the polymerization of ethylene utilizing  $Cp_2ZrCl_2$ . The polymerization conditions were the same as in Figure 16

PE PDIs which were found to be independent of temperature, Al/Zr ratio, and *i*Bu content of the MAO (note that the PDIs vary within small ranges of less than 0.2, which as we saw earlier in the GPC reproducibility study are not significant). We can safely conclude that the PE produced under these conditions with  $\text{Cp}_2\text{ZrCl}_2$  in toluene approximates Flory's most probable distribution for the ranges studied.

## DISCUSSION

Although there have been data published in the literature about the effect of aluminoxane structure on polymerization activity, very little information is available as to the effect of aluminoxane type, concentration and structure on the PE MWD. As each site-type produces PE with a  $M_w/M_n$  PDI = 2.0 and  $M_z/M_w$  PDI = 1.5, as defined by Flory's most probable distribution<sup>5</sup>, a careful examination of the GPC traces of PE produced with different types and concentrations of aluminoxane provides definitive information on the active catalytic site-type(s) and if those active site-type(s) are being affected by the structure and concentration of the aluminoxane co-catalyst.

Increasing the *i*Bu content in aluminoxane was found to only minimally decrease the  $\text{Cp}_2\text{ZrCl}_2$  catalyst activity in the polymerization of ethylene over the range of 0–30%, whereas 100% *i*Bu content (or IBAO) was found to give very low activities. The *i*Bu groups of MMAO or IBAO which alkylate zirconocene catalyst to initiate polymerization, may give a less active cationic centre than the cationic centre formed when the  $\text{CH}_3$  group of plain MAO alkylates it. The *i*Bu alkylated form of zirconocene catalyst presumably has a significantly higher activation energy for the first few steps of ethylene insertion. This higher barrier to ethylene insertion may be due to both steric and electronic considerations. The steric factors would strongly inhibit transmetallation reactions of the Al–*i*Bu compounds. The alkylation of  $\text{Cp}_2\text{ZrCl}_2$  is thus expected to be much slower for IBAO than for MAO. Although the *i*Bu content in MAO affected the activity of polymerization, no significant effect was observed on the PE MWD. For all of the various MAO co-catalysts studied, with both known and unknown compositions, the PE MWD was unaffected in the semi-batch polymerization of ethylene with  $\text{Cp}_2\text{ZrCl}_2$  from 50 to 90°C.

Due to the high levels of MAO necessary for polymerization (Al/Zr ratios upwards of 1000:1 were most reproducible) MAO is believed to act as a scavenger, mopping up active-site impurities in the diluent like  $\text{O}_2$  and  $\text{H}_2\text{O}$ . Aluminoxanes are known for their ability to react with the impurities  $\text{O}_2$  and  $\text{H}_2\text{O}$ <sup>31,43</sup>. As metallocene polymerization is essentially cationic in nature, this form of polymerization is extremely sensitive to impurities which would react with the active site and kill polymerization. In order to have a significant active-site/impurity ratio, a sufficient amount of MAO must be present in order to mop up impurities in the diluent for a reproducible polymerization.

In the evolution of metallocene polymerization of olefins from academic interest to commercial success, it has been necessary to reduce the amount of MAO co-catalyst in order to reduce material costs and minimize separation problems. Chien has reported that approximately 90% of MAO can be replaced with traditional alkylaluminium co-catalysts with little effect on the catalyst performance towards the polymerization of ethylene<sup>3</sup>. We found that addition of extra TMA to MAO gave significantly lower activity than pure MAO at the same total Al/Zr molar ratio. We also found that addition of extra TMA to MAO had no effect on

the PE MWD when ethylene was polymerized with  $\text{Cp}_2\text{ZrCl}_2/\text{MAO}/\text{TMA}$ .

For all the different aluminoxanes studied here, and for all the different MAO and TMA concentrations, it is clear that the role of MAO or TMA/MAO mixture is that of a co-catalyst in the activation of the catalyst. MAO may also act as a scavenger in the removal of impurities from the polymerization mixture and may, as an oligomer or polymeric form, have a role in the prevention of the precipitation of polymer chains. There is no evidence that MAO is actively involved in the active site-type for  $\text{Cp}_2\text{ZrCl}_2$  as the catalyst termination to propagation ratio,  $\tau$ , is unaffected by both type and concentration of MAO, and the addition of any extra TMA. In all cases Flory's most probable distribution was approximated for polymerization with a single site-type catalyst with resultant PE  $M_w/M_n$  values approaching 2.0 and  $M_z/M_w$  approaching 1.5 as predicted. There was also no evidence from this study that chain transfer to Al is occurring to any significant extent for the termination of polymer chains and hence may be ignored in any kinetic analysis.

The fact that the structure and type of aluminoxane show no effect on the PE MWD lead us to believe that the active cationic form of the metallocene catalyst  $\text{Cp}_2\text{ZrCl}_2$  is not coordinated with the active anionic form of the co-catalyst MAO. The active MAO is most likely in the form of a non-coordinating anion, similar to that of the non-coordinating anion,  $\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3^-$ , which is formed upon reaction of tri(pentafluorophenyl)boron and a metallocene dimethyl compound. This anion is often used as the co-catalyst of choice in the polymerization of olefins with a purely cationic metallocene such as the Dow Chemical Company's Insite catalyst<sup>44</sup>. To be a non-coordinating anion, the coordination of the anionic co-catalyst to the metal centre must not be competitive with the coordination of the olefin to the metal centre. It has been found by electrochemical and optical spectroscopy means that MAO forms an exceptionally non-coordinating anion in toluene, even more non-coordinating than  $\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3^-$  anion<sup>45</sup>. Clearly, if the coordination of MAO co-catalyst was competitive with coordination of ethylene to the active form of the zirconocene complex, changes in the MAO structure and MAO concentration would affect the catalyst termination to propagation ratio,  $\tau$ , and one would observe changes in the PE MWD, which were not observed.

## CONCLUSIONS

Aluminoxane structure and any added stabilizers were found to have no effect on the catalytically active zirconocene site type. The type of aluminoxane influenced the activity of the catalyst with generally,  $\text{MAO} \geq \text{MMAO} \gg \text{IBAO}$  for polymerization activity. By increasing the MAO concentration (increasing Al/Zr molar ratio), the polymerization activity was found to increase up to a maximum at an Al/Zr ratio of 2400, after which further increase of Al/Zr molar ratio decreased the catalyst activity. The studied polyethylene MWs and PDIs were found not to vary with MAO type or concentration. Use of TMA, along with MAO, gives lower activity than MAO by itself for a given Al/Zr molar ratio, but has no effect on MWs or PDIs of the formed PE. Our results, by carefully studying the PE MWD and catalytic activity, agree with the hypothesis of a single active cationic metallocene site-type for the simple metallocene system  $\text{Cp}_2\text{ZrCl}_2/\text{MAO}/\text{TMA}$ . For the polymerization of ethylene with zirconocene dichloride, the

aluminoxane was found to function solely as a co-catalyst in activating the catalyst and was not found to be involved in the catalyst site-type having no effect on the termination to propagation ratio.

#### ACKNOWLEDGEMENTS

We greatly appreciate financial support from the Natural Sciences and Engineering Research Council of Canada (NSERC) for this work. We also thank Dr Kris Kostanski for analysis of PE samples by GPC.

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