Mass Spectrometric Characterization of Methylaluminoxane

Tyler K. Trefz, Matthew A. Henderson, Miles Y. Wang, Scott Collins,* and J. Scott McIndoe*

Department of Chemistry, University of Victoria, P.O. Box 3065, Victoria, BC V8W3 V6, Canada

S *Supporting Information*

ABSTRACT: Electrospray ionization mass spectrometric studies of poly(methylaluminoxane) (MAO) in the presence of Cp_2ZrMe_2, octamethyltrisiloxane (OMTS), or $[Bu_4N]Cl$ in fluorobenzene solution are reported. The results concur with the hypothesis that MAO is partially ionized in sufficiently polar media, where the contact ion pairs are of the general formula $[Me_2Al][(MeAlO)_x(AlMe_3)_yMe]$. A limited number of compositions of this type are detected; the most abundant has $x = 23$ and $y = 7$, where the cation $[Me_2Al(OMTS)]^+$ (with m/z 293) and the anion (with m/z 1853) were detected in the presence of OMTS, which stabilizes the Me_2Al cation. The results demonstrate that MAO ionizes Cp_2ZrMe_2 by acting as a source of this electrophilic cation, giving rise to an ion pair featuring a large and weakly coordinating aluminoxanate counterion.
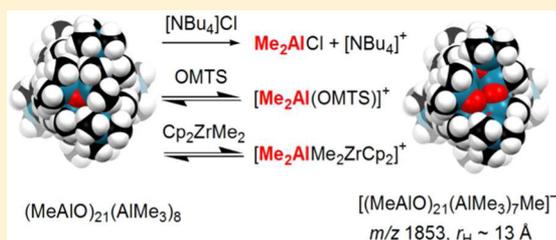
Ever since its discovery by Sinn and Kaminsky,[1] MAO has been used extensively as an activator of single-site, olefin polymerization catalysts.[2] MAO is believed to activate single-site catalysts such as metallocene complexes by alkylation and ionization, as depicted in eqs 1 and 2. Although much is known about the chemistry of the cationic moiety, an alkylmetallocenium ion,[3] much less is known about the structure and composition of the counteranion.

$$
\begin{array}{c}
Cp_2ZrCl_2 \\
+ \\
(MeAlO)_n{\cdot}AlMe_3
\end{array}
\longrightarrow
\begin{array}{c}
Cp_2ZrCl(Me) \\
+ \\
(MeAlO)_n{\cdot}AlMe_2Cl
\end{array}
\quad (1)
$$

$$
\begin{array}{c}
Cp_2ZrCl(Me) \\
+ \\
(MeAlO)_n{\cdot}AlMe_2X \\
X = Cl \text{ or } Me
\end{array}
\rightleftharpoons
\begin{array}{c}
[Cp_2ZrMe]^+ \\
[(MeAlO)_n{\cdot}AlMe_2X_2]^-
\end{array}
\quad (2)
$$
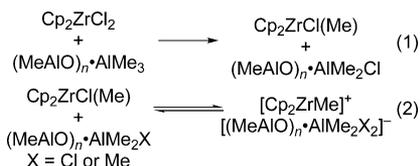
MAO is made by the controlled hydrolysis of trimethylaluminum[4] or by reaction of $AlMe_3$ with, for example, C=O compounds,[4b] resulting in an oligomeric mixture that has defied definitive structural characterization. There are few diagnostic spectroscopic handles, and the MAO oligomers can interconvert in the presence of free $AlMe_3$. Proton NMR studies have indicated that the empirical formula of the MAO repeat unit is $[AlO_{0.75-0.8}Me_{1.4-1.5}]_n$,[5] while multinuclear NMR studies confirm the presence of tetrahedral AlMe groups and pyramidal O.[6]

The X-ray structures of discrete *tert*-butylaluminoxanes (TBAO) reveal cages featuring tetrahedral Al and pyramidal O, and some of these were used to activate metallocene complexes for olefin polymerization.[7] Analogous cage structures for MAO are supported by theoretical studies,[2c,8] while much larger, symmetrical cages have been studied for the parent aluminoxane $(HAlO)_n$,[9] and it has been shown recently that extended structures, such as nanotubes, are favored over cages for MAO compared with TBAO.[10]

The TBAO cages are known to undergo cleavage, due to "latent Lewis acidity" or ring strain,[7] to afford contact ion pairs on reaction with metallocene complexes. In the case of MAO, similar behavior has been invoked,[2c,8] with formation of more dissociated ion pairs, at sufficiently high Al:M ratios. The latter findings are based on extensive solution NMR, UV−vis, and other spectroscopic studies of the metallocenium ions formed *in situ* from metallocene complexes and MAO.[3,11]

The hydrodynamic radius (r_h) and MW (molecular weight) of MAO, as well as the ion pairs formed from MAO and Cp_2ZrMe_2, have been estimated by a number of techniques.[12] Values of r_h between 7.5 and 9.7 Å and MW values between 0.5 and 3.0 kg mol^{-1} have been reported for MAO at ambient temperature. A larger value of $r_h = 12-12.5$ Å has been reported for ion pairs derived from MAO.[12a] The various, and disparate, estimates of MW vs size can be reconciled if the shape of MAO oligomers and the ion pairs derived from this material are not spherical.[10a] In particular, for rigid-rod molecules with one long axis, r_h will approximate the length of this axis as the molecule randomly tumbles in solution, while MW scales with r_h instead of r_h^3.[3,13] What is required is a measurement of *absolute* MW for MAO or these ion pairs in solution to shed further light on this issue.

Electrospray ionization mass spectrometry (ESI-MS) is an obvious choice for detection of ions in MAO solutions, at least in polar media, but few MS studies of MAO have been reported.[14] Repo and co-workers have reported detection of MAO using ESI-MS in THF and found that the positive ion spectra consisted of oxidized material.[15] Analysis of metallocenium ions by ESI-MS, initially by Chen[16] and later by Metzger,[17] has shed light on the reactivity of the metal complex, but these studies were not concerned with the identity of the anionic components of MAO. We report here the first systematic, negative and positive ion studies of MAO by ESI-MS in fluorobenzene (PhF).

When a solution of MAO in toluene (1.54 M, Aldrich Chemical Co.) is diluted with anhydrous PhF to ca. 0.05 M and the solution injected into an ESI mass spectrometer under anaerobic conditions,[18] the total ion current (TIC) is very low (<10 counts), consistent with a solution of nonpolar material containing few ions.[19] On the other hand, addition of small amounts of an electrolyte such as [Bu$_4$N]Cl, or neutral additives such as 18-crown-6, octamethyltrisiloxane (OMTS),[19] and Cp$_2$ZrMe$_2$, leads to a significant increase in negative ion intensity. At low levels of these additives the spectra are surprisingly simple, consisting of one major peak at m/z 1853 (Figure 1), with the other ions routinely detected summarized in Table 1.
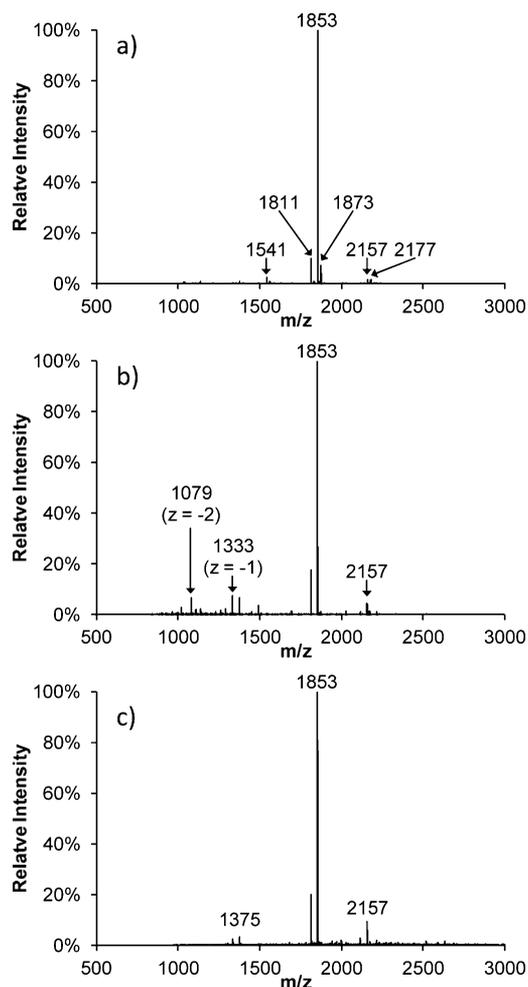
Figure 1. (a) ESI-MS spectra of MAO (0.037 M) and [Bu$_4$N]Cl (Al:Cl = 37:1), (b) MAO (0.055 M) and OMTS (Al:OMTS = 26:1), and (c) MAO (0.067 M) and Cp$_2$ZrMe$_2$ (0.23 mM, Al:Zr = 290:1) in PhF. Major singly charged ions detected are listed in Table 1.

It is important to point out that the *same* ions are detected, *regardless* of the nature of the additive. In particular, chlorine-containing ions do not predominate in mixtures of MAO + [Bu$_4$N]Cl, except at higher levels of added salt, and they appear to form via chlorination of the parent ions, as they are separated in mass by +20 Da (i.e., M − CH$_3$ + Cl; see, e.g., the ion at m/z 1873 in Figure 1a). It appears that some ions are more susceptible to chlorination than others. For example, the intensities of the ions at m/z 2157 and 2177 are nearly equal in Figure 1a vs the very different intensities for 1853 and 1873.

There is a unique, chlorinated ion detected at m/z 1541 in the presence of [Bu$_4$N]Cl (Figure 1a) that may have no precursor ion and that is also very susceptible to further chlorination with ions detected at m/z 1561, 1581, and 1601 with 2, 3, and 4 Cl atoms, respectively. MS/MS experiments reveal that all chlorinated ions easily lose chlorine, as AlMe$_2$Cl, and at low collision energies (see Supporting Information).

In the presence of OMTS or Cp$_2$ZrMe$_2$ the spectra are similar (Figure 1b,c). In the positive ion spectrum, a single, intense peak at m/z 293 is observed in the presence of OMTS, whose nominal mass and isotope pattern are consistent with [Me$_2$Al(OTMS)]$^+$,[19] while the dominant ion observed in the presence of Cp$_2$ZrMe$_2$ is [Cp$_2$Zr(μ-Me)$_2$AlMe$_2$]$^{+3,11}$ at m/z 307 with the isotope ratio expected for this species.[20] Dimethylsiloxane oligomers also provide strong spectra containing ions of the form [Me$_2$Al{Me$_3$SiO-(SiMe$_2$O)$_n$SiMe$_3$}]$^+$, a discovery made when MAO solution came in contact with stopcock grease. The ion [(18-crown-6)AlMe$_2$]$^{+21}$ was observed in the presence of 18-crown-6 at much lower levels of this additive (see Supporting Information).

At higher levels of these additives, and at higher total [Al], doubly charged ions appear in the negative ion mass spectrum at m/z 800−1300 with an increase in complexity (see, e.g., Figure 1b). These doubly charged ions form at the expense of the higher mass, singly charged ions.

Finally, at sufficiently high levels of added [Bu$_4$N]Cl, phase separation due to ion-pair aggregation is observed (cloudiness at these concentrations). The TIC of the PhF phase decreases significantly, and the spectra are dominated by low molecular weight ions derived from AlMe$_3$, AlMe$_2$Cl (formed *in situ*, *vide infra*), and ion clusters involving these ions (see Supporting Information).

Our interpretation of these events is as follows: At sufficiently low levels of additives, only the most reactive components of MAO form "free" or solvated ions, which are detected by ESI-MS, with the vast majority of species existing as neutrals or tightly bound ion pairs. As electrolyte or additive concentration increases, formation of solvated ions increases due to the increased dielectric constant of the medium[22] or by ion exchange (*vide infra*); evidently, some of the anions that form can support an additional negative charge under these conditions. Finally, a liquid clathrate[23] or aggregated ionic phase forms, and only the least Lewis acidic and neutral components, which remain in the PhF phase, are detectable.

These findings mean that the accepted view of MAO as a mixture of neutral Lewis acids that abstract halide or methide ions from neutral metallocene complexes should be refined. Instead, a more consistent interpretation is that MAO serves as a source of [AlMe$_2$]$^+$,[24] which is the most reactive Lewis acid present in these mixtures. As [Bu$_4$N]Cl is titrated in, the available [AlMe$_2$]$^+$ reacts with Cl$^-$ to form AlMe$_2$Cl, leading to formation of less strongly bound [Bu$_4$N][MAO] ion pairs, which are more sensitively detected by ESI-MS. At sufficiently high levels of AlMe$_2$Cl, MAO and the derived ions are modified via redistribution reactions.

To assign a composition, each ion detected was selected for MS/MS studies, and their fragmentation patterns were analyzed. For example, the ion at m/z 1811 fragments with 10 successive losses of 72 Da as the collision energy is increased to its maximum value of 200 V (Figure 2). At higher collision energies, a second set of ions, also separated by 72 Da, but 16 Da lower in mass compared to the previous series is evident.

Table 1. Summary of Singly Charged Anions Detected in MAO When Treated with Cp_2ZrMe_2, OMTS, or $[Bu_4N]Cl^a$

obsd m/z	intensity (%)^b	emp. formula	calcd m/z	formula for anion based on MS/MS results^c	formula for anion based on $[(MeAlO)_x(AlMe_3)_yMe]^-$	Me:Al:O
1333.4	7.4	$C_{29}H_{87}Al_{22}O_{19}$	1333.2	$[Al_7O_{11}(MeAlO)_8(AlMe_3)_7]^-$	$x = 19, y = 3$	1.32:1:0.86
1375.4	6.6	$C_{35}H_{105}Al_{22}O_{16}$	1375.3	$[Al_3O_5(MeAlO)_{11}(AlMe_3)_8]^-$	$x = 16, y = 6$	1.59:1:0.73
1491.4	3.6	$C_{37}H_{111}Al_{24}O_{18}$	1491.3	$[Al_3O_5(MeAlO)_{13}(AlMe_3)_8]^-$	$x = 18, y = 6$	1.54:1:0.75
1695.5	1.3	$C_{37}H_{111}Al_{28}O_{24}$	1695.2	$[Al_7O_{11}(MeAlO)_{13}(AlMe_3)_8]^-$	$x = 24, y = 4$	1.32:1:0.85
1811.4	17.4	$C_{39}H_{117}Al_{30}O_{26}$	1811.2	$[Al_{11}O_{17}(MeAlO)_9(AlMe_3)_{10}]^-$	$x = 26, y = 4$	1.30:1:0.87
1853.4	100	$C_{45}H_{135}Al_{30}O_{23}$	1853.4	$[Al_5O_8(MeAlO)_{15}(AlMe_3)_{10}]^-$	$x = 23, y = 7$	1.30:1:0.77
2027.4	1.5	$C_{48}H_{144}Al_{33}O_{26}$	2027.4	$[Al_7O_{11}(MeAlO)_{15}(AlMe_3)_{11}]^-$	$x = 26, y = 7$	1.45:1: 0.79
2115.5	1.2	$C_{46}H_{138}Al_{35}O_{30}$	2115.3	$[Al_{11}O_{17}(MeAlO)_{13}(AlMe_3)_{11}]^-$	$x = 30, y = 5$	1.31:1:0.86
2157.5	4.3	$C_{52}H_{156}Al_{35}O_{27}$	2157.4	$[Al_7O_{11}(MeAlO)_{13}(AlMe_3)_{12}]^-$	$x = 27, y = 8$	1.49:1:0.77
2173.5	1.3	$C_{47}H_{141}Al_{36}O_{31}$	2173.3	$[Al_{13}O_{20}(MeAlO)_{11}(AlMe_3)_{12}]^-$	$x = 31, y = 5$	1.31:1:0.86
2215.6	1.0	$C_{53}H_{159}Al_{36}O_{28}$	2215.4	$[Al_7O_{11}(MeAlO)_{17}(AlMe_3)_{12}]^-$	$x = 28, y = 8$	1.47:1:0.78

^{a}Additional ions at m/z 1541 $\{[Al_5O_8(MeAlO)_{13}(AlMe_3)_6(AlMe_2Cl)]^-$ according to MS/MS spectra$\}$, 1561, 1581, 1601 and at M+ 20 Da for the other ions listed are seen in the presence of $[Bu_4N]Cl$ with a relative intensity dependent on salt concentration. See Figure 1a and text for discussion. ^{b}Relative intensities are based on the spectrum depicted in Figure 1b and are given as percentages of the base peak. ^{c}MS/MS spectra indicate how many $AlMe_3$ or $AlMe_3$ equivalents are present; see text.
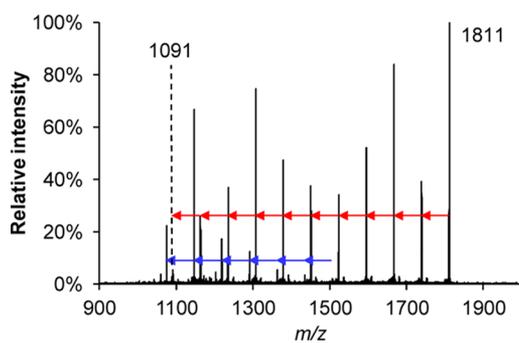
Figure 2. MS/MS spectrum of the anion with m/z 1811. Ten losses of 72 Da from the parent ion are indicated by red arrows with a second series of fragment ions occurring at −16 Da, between m/z 1075 and 1507, depicted by blue arrows.

Evidently, these ions fragment by loss of $AlMe_3$ and also by loss of CH_4 at higher energy. We suspect some of the $AlMe_3$ lost arises via direct dissociation, while at higher energy, more elaborate rearrangements may be involved, as suggested in eq 3 for an aluminoxane fragment.[8] We are unable to distinguish between genuine losses of $AlMe_3$ and those formed by rearrangement.
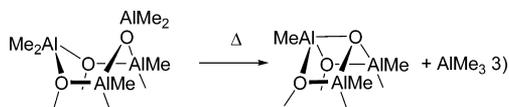
On the basis of these results, the anion at m/z 1811 can be formulated as $[(Al_{11}O_{17})(MeAlO)_9(AlMe_3)_{10}]^-$, consisting of an anionic aluminoxane core, decorated by 10 $AlMe_3$ groups. All of the ions characterized by MS/MS were analyzed in this fashion (see Supporting Information), and their resulting compositions are listed in Table 1.

As we accept that not all of the observed losses are genuine, and noting the mass relationship $(AlOMe)_3 \equiv Al_2O_3 + AlMe_3$, an equivalent formulation for m/z 1811 is $[(AlO_2)-(MeAlO)_{24}(AlMe_3)_5]^-$. A more logical anionic fragment than $[AlO_2]^-$ is $[Me_2AlOAl(Me)O]^-$, the addition of Me^- to the simplest, cyclic aluminoxane, or the addition of $AlMe_3$ to $[AlO_2]^-$. We can thus formulate this anion as $[(MeAlO)_{24}\{OAl(Me)OAlMe_2\}(AlMe_3)_4]^-$ or $[[(MeAl-$

$O)_{26}(AlMe_3)_4Me]^-$, recognizing that two MeAlO units make up the anionic fragment. The last formulation corresponds to the classical view of MAO, with anions being formed via *formal* methide abstraction.[25] These compositions are also listed in Table 1.

Although these compositions are somewhat arbitrary because we are not able to quantitate the amount of bound $AlMe_3$, it is satisfying to note that the composition of each ion is similar to the average composition of MAO determined by ^1H NMR spectroscopy (see Table 1). We note the compositions show considerable variation with respect to $AlMe_3$ vs MeAlO units (13−27 mol % $AlMe_3$) and the ions are not strictly ordered by their degree of polymerization given common mass differences of 42 vs 58 Da. We do note that those ions with the same number of MeAlO units, differing only in the amount of $AlMe_3$, at m/z 1811 and 2027, show the same fragment ions in their MS/MS spectra, confirming a structural homology.

Our results show that the anions (and ion pairs) present in PhF in the presence of $[Bu_4N]Cl$, OMTS, or Cp_2ZrMe_2 are much lower in MW than the estimate based on diffusion measurements in toluene.[12a] The negative ion spectra are largely invariant to additive levels below 1−2 mol %, and we have not detected ions higher in mass than ca. 3500 Da. Our results are in good agreement with earlier estimates of MW for MAO itself, while the predominant ions have compositions that appear related to the more stable, large cages or other structures for MAO predicted by theory. The results, in conjunction with the available data on the size of MAO or ion pairs formed from it, support the hypothesis that MAO and the ion pairs that are present have extended shapes such as nanotubes.

Future work, which will be guided by these initial results, will focus on anion and cation speciation in reactions of MAO with metallocene complexes under catalytically relevant conditions (i.e., nonpolar media[26]). In particular, ESI-MS should provide useful information relating to the *amount* of available $[AlMe_2]^+$ present per mole of MAO under various conditions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details; additional MS and MS/MS spectra of all ions detected. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: mcindoe@uvic.ca, scottcollins@shaw.ca.

Notes
The authors declare no competing financial interest.

■ REFERENCES

(1) Andresen, A.; Cordes, H. G.; Herwig, J.; Kaminsky, W.; Merck, A.; Mottweiler, R.; Pein, J.; Sinn, H.; Vollmer, H. J. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 630−632.

(2) (a) Kaminsky, W. *Macromolecules* **2012**, *45*, 3289−3297. (b) Severn, J. R. In *Tailor-Made Polymers*; Severn, J. R.; Chadwick, J. C., Eds.; Wiley-VCH, 2008; pp 95−138. (c) Zurek, E.; Ziegler, T. *Prog. Polym. Sci.* **2004**, *29*, 107−148.

(3) (a) Bochmann, M. *Organometallics* **2010**, *29*, 4711−4740. (b) Chen, E. Y.-X.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391−1434.

(4) (a) Pasynkiewicz, S. *Polyhedron* **1990**, *9*, 429−453. (b) Smith, G. M.; Palmaka, S. W.; Rogers, J. S.; Malpass, D. B. U.S. Patent 5,831,109 1998, and references therein.

(5) Imhoff, D. W.; Simeral, L. S.; Sangokoya, S. A.; Peel, J. H. *Organometallics* **1998**, *17*, 1941−1945.

(6) Bryant, P. L.; Harwell, C. R.; Mrse, A. A.; Emery, E. F.; Gan, Z.; Caldwell, T.; Reyes, A. P.; Kuhns, P.; Hoyt, D. W.; Simeral, L. S.; Hall, R. W.; Butler, L. G. *J. Am. Chem. Soc.* **2001**, *123*, 12009−12017 and references therein.

(7) (a) Barron, A. R. In *Metallocene-Based Polyolefins*; Scheirs, J.; Kaminsky, W., Eds.; Wiley, 2000; Vol. *1*, pp 33−67. (b) Mason, M. R.; Smith, J. M.; Bott, S. G.; Barron, A. R. *J. Am. Chem. Soc.* **1993**, *115*, 4971−4984. (c) Harlan, J.; Bott, S. G.; Barron, A. R. *J. Am. Chem. Soc.* **1995**, *117*, 6465−6474.

(8) Zurek, E.; Ziegler, T. *Inorg. Chem.* **2001**, *40*, 3279−3292.

(9) Linnolahti, M.; Luhtanen, T. N. P.; Pakkanen, T. A. *Chem.—Eur. J.* **2004**, *10*, 5977−5987.

(10) (a) Linnolahti, M.; Severn, J. R.; Pakkanen, T. A. *Angew. Chem., Int. Ed.* **2008**, *47*, 9279−83. (b) Linnolahti, M.; Severn, J. R.; Pakkanen, T. A. *Angew. Chem., Int. Ed.* **2006**, *45*, 3331−3334.

(11) (a) Babushkin, D. E.; Semikolenova, N. V.; Zakharov, V. A.; Talsi, E. P. *Macromol. Chem. Phys.* **2000**, *201*, 558−567. (b) Wieser, U.; Brintzinger, H.-H. *Organometallic Catalysts and Olefin Polymerization*; Blom, E., Follestad, A., Rytter, E., Tilset, M., Ystenes, M., Eds.; Springer-Verlag: Berlin, 2001; p 3. (c) Pedeutour, J. N.; Cramail, H.; Deffieux, A. *J. Mol. Catal.* **2001**, *176*, 87−94. (d) Tritto, I.; Donetti, R.; Sacchi, M. C.; Locatelli, P.; Zannoni, G. *Macromolecules* **1997**, *30*, 1247−1252.

(12) (a) Babushkin, D. E.; Brintzinger, H. H. *J. Am. Chem. Soc.* **2002**, *124*, 12869−12873. (b) Hanson, E. W.; Blom, R.; Kvernberg, P. O. *Macromol. Chem. Phys.* **2001**, *202*, 2880−2889. (c) Babushkin, D. E.; Semikolenova, N. V.; Panchenko, V. N.; Sobolev, A. P.; Zakharov, V. A.; Talsi, E. P. *Macromol. Chem. Phys.* **1997**, *198*, 3845−3854. (d) von Lacroix, K.; Heitmann, B.; Sinn, H. *Macromol. Symp.* **1995**, *97*, 137−142. (e) Cam, D.; Albizzati, E. *Makromol. Chem.* **1990**, *191*, 1641−1647.

(13) Chalmers, J. M.; Meier, R. J. *Molecular Characterization and Analysis of Polymers*; Elsevier, 2008.

(14) The EI-MS of volatile components of MAO has been reported: Sinn, H. W.; Kaminsky, W. O.; Vollmer, H. J. C.; Woldt, R. O. H. H. U.S. Patent 4,404,344, 1983.

(15) Castro, P. M.; Lahtinen, P.; Axenov, K.; Viidanoja, J.; Kotiaho, T.; Leskela, M.; Repo, T. *Organometallics* **2005**, *24*, 3664−3670.

(16) (a) Rouholahnejad, F.; Mathis, D.; Chen, P. *Organometallics* **2010**, *29*, 294−302. (b) di Lena, F.; Chen, P. *Helv. Chim. Acta* **2009**, *92*, 890−896. (c) Dietiker, R.; Di Lena, F.; Chen, P. *J. Am. Chem. Soc.* **2007**, *129*, 2796−2802. (d) Quintanilla, E.; di Lena, F.; Chen, P. *Chem. Commun.* **2006**, 4309−4311. (e) di Lena, F.; Quintanilla, E.; Chen, P. *Chem. Commun.* **2005**, 5757−5759.

(17) Santos, L. S.; Metzger, J. O. *Angew. Chem., Int. Ed.* **2006**, *45*, 977−981.

(18) (a) Henderson, M. A.; Trefz, T.; Wang, M.; Collins, S.; McIndoe, J. S. *Organometallics* **2013**, *32*, 2079−2083. (b) Lubben, A. T.; McIndoe, J. S.; Weller, A. S. *Organometallics* **2008**, *27*, 3303−3306.

(19) Solutions of MAO in CH_2Cl_2 are very weakly conducting: (a) Sangokoya, S. A.; Goodall, B. L.; Simeral, L. S. PCT Int. WO 03/082879 2003. (b) Sangokoya, S. A. U.S. Patent 5,731,253, 1999.

(20) At low Al:Zr ratios the dominant ion present is the dinuclear cation $[(Cp_2ZrMe)_2\mu\text{-Me}]^+$ with m/z 485 (see Supporting Information), in agreement with other studies.[3,11]

(21) Bott, S. G.; Alvanipour, A.; Morley, S. D.; Atwood, D. A.; Means, C. M.; Coleman, A. W.; Atwood, J. L. *Angew. Chem.* **1987**, *99*, 476−478.

(22) Henderson, M. A.; McIndoe, J. S. *Chem. Commun.* **2006**, 2872−2874.

(23) (a) Sangokoya, S. A. U.S. Patent 5,922,631, 1999. (b) Atwood, J. L. In *Coordination Chemistry of Aluminum*; VCH Publishers, 1993; pp 197−224.

(24) (a) Tanskanen, J.; Linnolahti, M.; Severn, J. R.; Bochmann, M. *Abstr. Papers, 243rd ACS National Meeting & Exposition*; San Diego, CA, March 25−29, 2012, PHYS-291. (b) Diefenbach, S. P. *Pacifichem 2010*; 2010, MACRO-231. (c) Luo, L.; Sangokoya, S. A.; Wu, X.; Diefenbach, S. P.; Kneale, B. U.S. Patent Appl. 2009/0062492, 2009. (d) Kim, K. C.; Reed, C. A.; Long, G. S.; Sen, A. *J. Am. Chem. Soc.* **2002**, *124*, 7662−7663. (e) Klosin, J.; Roof, G. R.; Chen, E. Y.-X.; Abboud, K. A. *Organometallics* **2000**, *19*, 4684−4686.

(25) There is no compelling evidence for facile halide abstraction from $[Bu_4N]Cl$ by a neutral species in these spectra. We thus believe that the ionization process does not involve direct methide abstraction from $AlMe_3$ by MAO.

(26) The use of lipophilic ionic additives allows ESI-MS experiments to be conducted in apolar media such as toluene and hexane; however, of those previously reported,[21] none are compatible with MAO.