Real-time analysis of methylalumoxane formation

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Graphical Abstract

Abstract

Methylalumoxane (MAO), a perennially useful activator for olefin polymerization precatalysts, is famously intractable to structural elucidation, consisting as it does of a complex mixture of oligomers generated from hydrolysis of pyrophoric trimethylaluminum (TMA). Electrospray ionization mass spectrometry (ESI-MS) is capable of studying those oligomers that become charged during the activation process. We’ve exploited that ability to probe the synthesis of MAO in real time, starting less than a minute after the mixing of H₂O and TMA and tracking the first half hour of reactivity. We find that the process does not involve an incremental build-up of oligomers; instead, oligomerization to species containing 12-15 aluminum atoms happens within a minute, with slower aggregation to higher molecular weight ions. The principal activated product of the benchtop synthesis is the same as that observed in industrial samples, namely [(MeAlO)₁₆(Me₃Al)₈Me]⁻, and we have computationally located a new sheet structure for this ion 94 kJ mol⁻¹ lower in Gibbs energy than any previously calculated.
Introduction

Methylalumoxane (MAO) is an oligomeric activator for single-site olefin polymerization precatalysts, prepared by the reaction of trimethylaluminum with water.\(^{[1–5]}\) MAO is an effective activator through playing multiple roles: it acts as a scavenger of oxygen and water; it can alkylate the precatalyst; and it can ionize the precatalyst via abstraction of a methyl group.\(^{[6,7]}\) Trimethylaluminum is a capable scavenger on its own,\(^{[8]}\) and will also methylate metal-halogen bonds,\(^{[9,10]}\) but it is not able to ionize the precatalyst.\(^{[11]}\) The catalytic activity of MAO depends on the type of MAO (10 wt% or 30 wt%) and its synthesis history.\(^{[12,13]}\)

Ionization comes about via neutral MAO generating the reactive Lewis acidic species \([\text{Me}_2\text{Al}]^+\), with the resulting bulky MAO anions being sufficiently weakly coordinating to allow high reactivity towards alkenes at the cationic metal center.\(^{[14–18]}\) We have previously shown through mass spectrometric means that the anionic products of the activation process are dominated by a single ion, \([\text{(MeAlO)}_{16}\text{(Me}_3\text{Al)}_6\text{Me}]^-\) henceforth [16,6]-.\(^{[19]}\) The three dimensional structure of this anion has not been elucidated, but its unusually high abundance in the spectra of post-activation commercial MAO does raise all sorts of questions about why it is so prominent, since the synthesis of MAO does not on the face of it appear to be particularly selective, being the controlled mixing of water and pyrophoric trimethylaluminum.\(^{[20]}\) Laboratory scale syntheses of MAO use indirect methods of hydrolysis to slow the reaction, such as at low temperature by the use of ice,\(^{[21]}\) or hydrated salts.\(^{[22][23]}\) Alternative methods for preparation of MAO from reaction of benzoic acid or \(\text{CO}_2\) with TMA or from the reaction of TMA with \(\text{Me}_3\text{SnOH}\) have been reported.\(^{[24–26]}\)

The appearance of a “magic” ion that dominates a mixture with a broad distribution of possible products has always attracted attention from curious chemists. For example, time-of-flight mass spectra of laser-vaporized graphite reveals a range of \((\text{C}_2)_n\) ions, of which \(\text{C}_{60}\) was the most abundant component thanks to the special stability of the truncated icosahedral structure of that molecule.\(^{[27]}\) Protonated water droplets, \([\text{H(H}_2\text{O)}_n]^+\), feature \([\text{H(H}_2\text{O)}_{21}]^+\) as an especially prominent ion, thanks to the stability of a water molecule surrounded by 20 others in an icosahedral array.\(^{[28]}\) Understanding the special stability of \([\text{(MeAlO)}_{16}\text{(Me}_3\text{Al)}_6\text{Me}]^-\) is challenging due to the pyrophoric nature of the matrix itself, so separation of this component is exceptionally challenging. As such, we resolved to discover what we could about the generation of this ion by real-time monitoring of the synthesis process itself, and to delve deeper computationally into its structure.

ESI-MS reveals \([\text{(MeAlO)}_{x}\text{(Me}_3\text{Al)}_y\text{Me}]^-\) ions in MAO solutions in the presence of any additive that reacts readily with \([\text{Me}_2\text{Al}]^+\). \(\text{Cp}_2\text{ZrMe}_2\) generates \([\text{Cp}_2\text{ZrMe}]([\text{MeAlO)}_{16}\text{(Me}_3\text{Al)}_6\text{Me}]\), \([\text{NBu}_4]\text{Cl}\) generates \([\text{NBu}_4][([\text{MeAlO)}_{16}\text{(Me}_3\text{Al)}_6\text{Me}]\), but the most convenient way to make the ion is via addition of octamethyltrisiloxane \((\text{Me}_3\text{SiOSiMe}_2\text{OSiMe}_3,\text{OMTS})\). OMTS chelates available \([\text{Me}_2\text{Al}]^+\) to make the ion \([\text{Me}_2\text{Al}(\text{OMTS})]^+\). (Figure 1).\(^{[19,29]}\)
The resulting anions can be characterized in negative mode ESI-MS. We have used this technique to study alkyl exchange, aging, and oxidation of MAO, where the anion distribution changes in response to these processes. Here we report the dynamic behavior of MAO anions formed via the reaction of TMA and water.

**Results**

When water and TMA are combined, a fast exothermic reaction generates MAO with methane as a byproduct. We faced severe methodological challenges in studying this system mass spectrometrically, because of the evolution of methane, the low polarity of the toluene solvent generally used in synthesis, the propensity of the reacting solution to cause capillary blockages during analysis, and the inapplicability of normalization in the context of a system whose total ion count is changing. These factors conspired together to give extremely noisy time course data (see supporting information), though with consistent trends in speciation.

Toluene, fluorobenzene and difluorobenzene all provided essentially the same collection of ions but with increasingly better ion intensity as the solvent polarity increased. Speciation was largely unaffected by whether OMTS was added at the start of the reaction or at the time of analysis (see supporting information). The rate of reaction was significantly affected by the amount of water present, and the reaction could be slowed considerably by reducing the concentration of water used or by releasing it slowly using hydrated salts as the water source.

None of the reaction components (TMA, H₂O, OMTS, difluorobenzene) on their own provide significant quantities of ions, but their combination generates aluminoxane species capable of ionizing via capture of [Me₂Al]⁺ by OMTS. More than 99% of the ion current during the hydrolysis
experiments could be assigned to ions of the form \([(\text{MeAlO})_x(\text{Me}_3\text{Al})_y\text{Me}]^-\) (Figure 2), hence the general formula \((\text{MeAlO})_x(\text{Me}_3\text{Al})_y+1\) for the neutral precursors applies for those aluminoxanes competent to act as activators.

![Figure 2](image)

**Figure 2.** Summation of all negative ion ESI mass spectra collected for 30 minutes after mixing of \(\text{Me}_3\text{Al}\), wet difluorobenzene, and OMTS.

The empirical formula of bulk MAO has been established by NMR\(^{[35]}\) to fall in the range \(\text{Me}_{1.3-1.5}\text{AlO}_{0.75-0.85}\). Nearly all the activator species we observe are comparatively rich in \(\text{Me}_3\text{Al}\) (all of them having higher Me and lower O content, in the range \(\text{Me}_{1.5-1.8}\text{AlO}_{0.58-0.73}\)). Activator precursors have the empirical formula \((\text{MeAlO})_n(\text{Me}_3\text{Al})_{(0.36-0.71)n}\) and are only observed when \(n > 6\).

![Figure 3](image)

**Figure 3.** Plot of mass spectrometric intensities (proportional to circle area) from Figure 1 against \(x\) and \(y\). The pink area shows Me:Al ratios between 1.3 to 1.5, the proportions reported for bulk MAO.
The mass spectrometric results must be interpreted carefully because they encapsulate two separate processes: increase in molecular weight through oligomerization, and the propensity for species to ionize via \([\text{Me}_2\text{Al}]^+\) loss. As a result, the mass spectrometric abundance of a particular aluminoxane is proportional to both its concentration and its extent of ionization (complicated further somewhat by the fact that not all ions have the same response even at the same concentration due to variations in surface activity\[^{[38]}\], but given these ions are closely related these differences are likely to be comparatively minor). While the selectivity for ionized species complicates the analysis, it is nonetheless invaluable because it allows for molecular identification of only those species responsible for catalyst activation.

We can extract three collective data sets out of a monitoring run: the total ion count, the average Me:Al ratio and the average mass-to-charge ratio. The ion intensity is high when the reacting solution first reaches the mass spectrometer, but rapidly drops away, and subsequently climbs again slowly. The average \(m/z\) value starts at ~800, climbs rapidly to ~1300, and very slowly climbs to approximately \(m/z\) 1350. The average Me:Al ratio starts at ~1.75 and drops to ~1.6, slowly decreasing after that to ~1.58.

![Figure 4. Plot of total ion current (TIC, red), Me:Al ratio (green) and average \(m/z\) (blue) as a function of time, for the reaction of Me\(_3\)Al with water followed by ionization using OMTS.](image)

MAO oligomers are produced extremely rapidly (in the few 10s of seconds before the reaction solution even reaches the mass spectrometer), commensurate with the high reactivity of Me\(_3\)Al with water. The initial stages of reaction probably involve a cascade of hydrolysis, oligomerization,
Species of \( m/z +2 \) (ions with -OH in place of -Me) were observed only in trace amounts, suggesting that these components of the mixture are short-lived in solution. Computationally it is possible to predict the lowest energy structures for a given \( x,y \) combination,[41,42] but the solution is evolving extremely quickly and we expect it to be a complex soup of kinetic products, with linear, ring and ladder-type structures all present and prone to reaction with each other, any proximal -OH groups on other MAO oligomers, and with Me\(_3\)Al.[43–46]

Examination of the ions contributing to the total ion current provides a more complete picture of what is going on. Early on in the reaction, the initial high intensity is produced almost entirely by three ions: \([7,4]^-\), \([8,4]^-\) and \([9,4]^-\), suggesting that these ions are generated by the lowest mass precursors capable of acting as activators. Previous computations indicate that sheet structures dominate in this size domain, and beginning from (MeAlO)\(_8\)(Me\(_3\)Al)\(_5\), i.e. the neutral precursor for \([8,4]^-\) via [Me\(_2\)Al]\(^+\) loss, the sheets undergo transition from Al five-coordinate to Al four-coordinate structures.[14] Slower reactions were also performed using lower concentrations of H\(_2\)O and/or hydrated salts, and these three ions were still the lowest mass ions observed (see SI). The three ions have relatively high Me:Al ratios and are short lived, declining to baseline levels within a couple of minutes. Despite their effectiveness at ionization, they are unlikely to contribute to the performance of MAO, because their time in solution is so short-lived.

**Figure 5.** Ion intensity by \( x \) value, classified into different groups: blue (\( x = 7-9 \)), green (\( x = 10-15 \)), pink (\( x = 16 \)) and red (\( x >16 \)). \( x \) refers to the number of (MeAlO) units as the general formula for the anion is [(MeAlO)\(_x\)(Me\(_3\)Al)\(_y\),Me]\(^-\). Following the brief appearance of \([x,4]^-\) (\( x = 7, 8, 9 \)) the total ion current dips, and the three intense ions are not correspondingly replaced by incrementally larger oligomers. Instead, we see ions
mostly of much higher molecular weight, prominent amongst which is the “magic” \([16,6]^-\) ion, whose abundance steadily climbs over the 30 minutes or so of the reaction. Of the many potential ions of intermediate composition, we see only a limited subset: small amounts of \([11,4]^-\), \([12,5]^-\), \([14,5]^-\) and \([15,5]^-\). At long reaction times, we observe \([18,6]^-\) and \([19,7]^-\), ions previously observed in aged MAO solutions.\(^{[31]}\)

The very fast production of the \([x,4]^-\) \((x = 7, 8, 9)\) species and the gradual emergence of higher mass species suggests that the oligomerization process involves multiple processes with very different rates. Given the high reactivity of water and TMA, free water will not survive for an appreciable duration. The early stages of oligomerization are probably dominated by reactions involving methane loss (i.e. reactions between Al-OH and Al-Me) and incorporation of trimethylaluminum. The slower production of higher molecular weight species is likely the result of aggregation of smaller methylalumoxane fragments (Scheme 1).\(^{[47]}\)
Scheme 1. Plausible processes contributing to oligomerization: top, fast processes; bottom, slower aggregation. Structures shown are systematic examples; many isomers exist for each \( x,y \) combination.

The progressive reduction in Me:Al ratio as the reaction proceeds points towards aggregation processes accompanied by loss of \( \text{Me}_3\text{Al} \). A possible explanation for the drop in ion current after the initial surge is due to aggregation processes forming open, high molecular weight, Me-rich structures that are ineffective activators until \( \text{Me}_3\text{Al} \) attrition and subsequent rearrangement.
renders them capable of activation (ionization) through efficiently delocalizing the resulting negative charge.

Combining the experimental results to our ongoing computational studies on MAO using M06-2X[48] DFT functional of the Minnesota series (as recommended for systems with dispersive interactions due to bridging Al-Me bonds)[49] in combination with the def-TZVP basis set,[50] allows us to propose a new structural model for the dominant [16,6]− anion. The procedure for its location is long and involved and will be reported in full elsewhere.[51] This new model, shown in Figure 6, has a hexagonal Al 4-coordinate sheet structure, and it could form via aggregation of smaller sheet structures (see above). Comparison to its previously reported cage isomer formed by Me− abstraction[52] from the most stable neutral (16,6) cage located by DFT calculations[42] is eye-opening: The sheet anion is as much as 66 kJ mol−1 lower in total energy and 94 kJ mol−1 lower in Gibbs energy (gas phase, T = 298 K, p = 1 atm). The remarkable stability of the anion can be associated to chelation of Me− between two adjacent -Me2Al end groups at the edge of the sheet, thus forming a six-membered ring in resemblance of bulk of the sheet.

Figure 6. Calculated structure of [16,6]−. The chelated Me− is indicated by the blue circle. Hydrogens are omitted for clarity.

As such, rearrangement would be required subsequent to an aggregation event, explaining the slow appearance of [16,6]− following the rapid disappearance of the lower molecular weight species. Given the relatively low ion intensities observed even at the half hour mark compared to analyses of mature commercial samples, it is likely that only a fraction of the mixture has undergone all of the reactions (hydrolysis, aggregation, rearrangement) required for the formation of competent activators.
Conclusions

While exceptional precautions are required to successfully study the growth of MAO oligomers mass spectrometrically (conditioning the instrument with a solution of TMA as a drying agent is a far from routine procedure), a considerable pay-off is obtained in the form of the only meaningful data thus far collected on this process. The ability to examine the dynamics of individual oligomers having undergone activation is a considerable advance in characterization capability, and the production of a solution dominated by the same ion ([16.6]+) observed in commercial samples is a remarkable observation considering the differences in reaction conditions between a small syringe and an industrial-scale reactor. The time course information suggests that the formation of higher oligomers does not involve incremental additions of Al species, and instead arises via aggregation of oligomers of intermediate size followed by rearrangement processes that decrease the overall Me:Al ratio. The approach and results described here are a revealing first step towards understanding and optimizing the formation of those components of MAO most capable of behaving as activators.

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