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Modifying Methylalumoxane via Alkyl Exchange

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Abstract

Methylalumoxane (MAO) ionizes highly selectively in the presence of octamethyltrisiloxane (OMTS) to generate $[\text{Me}_2\text{Al}\cdot\text{OMTS}]^+ [(\text{MeAlO})_{16}(\text{Me}_3\text{Al})_6\text{Me}]^-$. We can take advantage of this transformation to examine the reactivity of a key component of MAO using electrospray ionization mass spectrometry (ESI-MS), and here we describe the reactivity of this pair of ions with other trialkyl aluminum (R_3Al) components. Using continuous injection methods, we found Et_3Al to exchange much faster and extensively at room temperature in fluorobenzene ($t_{1/2} \sim 2$ sec, up to 25 exchanges of Me for Et) than $i\text{Bu}_3\text{Al}$ ($t_{1/2} \sim 40$ sec, up to 11 exchanges) or Oct_3Al ($t_{1/2} \sim 200$ sec, up to 7 exchanges). The exchanges are reversible and the methyl groups on the cation are also observed to exchange with the added R_3Al species. These results point to the reactive components of MAO having a structure that deviates significantly from the cage-like motifs studied to date.

Introduction

Methylalumoxane (MAO) is an important activator for single-site, olefin polymerization catalysts.¹ Its utility as a cocatalyst arises from its multiple functions: it transforms the precatalyst by alkylation and ionization, forming a weakly coordinating anion that stabilizes the active catalyst, and is an effective scavenger of trace impurities such as water and oxygen.² Despite extensive use and decades of study MAO remains incompletely understood and its exact functioning and structure remain subject to ongoing investigations.³ The exact characteristics of this mixture vary with time and temperature making it hard to obtain concrete structural information. Its average composition, $(\text{Me}_{1.4-1.5}\text{AlO}_{0.75-0.80})_n$,⁴ molecular weight (MW, $\sim 1200-2000$)⁵ have been established

and, in combination with computational studies⁶ and structurally characterized aluminoxanes⁷ it is generally thought that MAO is made up of cage-like structures that have the general formula $(\text{MeAlO})_n(\text{Me}_3\text{Al})_m$.

MAO is supplied as a solution in toluene containing a variable amount of free trimethylaluminum (Me_3Al) arising from incomplete hydrolysis. The amount of excess Me_3Al is known to influence polymerization catalysis and often dramatically so.^{8,9} Me_3Al will reversibly bind to metallocenium ions leading to both stabilization of the active species but inhibiting direct insertion into the M-C bond,¹⁰ while efficiently participating in chain transfer reactions.¹¹ This latter feature is undesirable for many applications, requiring physical or chemical removal of excess Me_3Al .^{8,9} Moreover, the use of MAO for catalyst activation requires the use of toluene due to its low solubility and stability in pure hydrocarbons.¹²

In attempts to develop more economical activator/scavenger combinations, higher trialkylaluminums (R_3Al) have been used, with reduced amounts of MAO, in propene polymerization.¹³ In a very detailed kinetic study involving 1-hexene polymerization in hexane media, MAO, which had been previously depleted of free Me_3Al , was used in combination with either Me_3Al , $i\text{Bu}_3\text{Al}$ or $n\text{Oct}_3\text{Al}$ for catalyst activation and polymerization.¹⁴ In this case, there was no effect on polymerization rates (at constant total Al:Zr) but rather reduced rates of chain transfer to Al in the order $i\text{Bu}_3\text{Al} \sim n\text{Oct}_3\text{Al} < \text{Me}_3\text{Al}$.

MMAO prepared via non-hydrolytic routes from Me_3Al and R_3Al is widely used for activation and scavenging in pure hydrocarbon media.¹² In comparison to MAO, the activation of metallocene or other catalysts using MMAO is not as well studied.¹ MMAO or MAO that has been modified by $i\text{Bu}_3\text{Al}$ is a more effective reducing agent than MAO, and leads to the production of Zr-hydrides or Zr(III) complexes which are less active resting states or inactive, respectively.^{1a} In the kinetic study just discussed it was noted that extended activation times using MAO, modified by $n\text{Oct}_3\text{Al}$, resulted in a polymer featuring a bimodal MWD, resulting from more than one type of active species.¹⁴

Modification of MAO by R_3Al involves alkyl exchange, forming MMAO- and $\text{R}_n\text{AlMe}_{3-n}$ - type structures. Alkyl exchange between aluminum alkyls such as Me_3Al and $i\text{Bu}_3\text{Al}$ is known to be rapid.¹⁵ Studies of alkyl exchange in aluminoxanes are rare but it has been shown that strained $t\text{Bu}$ aluminoxanes undergo facile ring opening, and alkyl exchange with Me_3Al .¹⁶

We are not aware of attempts to establish the rate of Me exchange between Me_3Al and MAO, though separate signals for Me_3Al are seen at low temperature in toluene solution by NMR spectroscopy.¹⁷ Labeled compounds such as $\text{Cp}_2\text{Zr}(^{13}\text{CH}_3)_2$ undergo low energy scrambling reactions with both Me_3Al and MAO.¹⁸ NMR PFG-SE diffusion experiments on MAO and Me_3Al

suggest that the exchange of free and bound Me_3Al is more rapid than the time scale (< 50 msec) of those experiments.¹⁹

We have recently shown that electrospray ionization mass spectrometry (ESI-MS) can be used to study activation of metallocene catalysts by MAO in both positive and negative ionization mode and that the data obtained can be related to polymerization experiments.^{20,21,22} This technique gives information about individual MAO oligomers and their reactions.^{23,24} When MAO is exposed to a chelating Lewis base such as octamethyltrisiloxane (OMTS) a surprisingly clean spectrum is obtained.²³ Negative ion spectra of MAO and this additive show almost exclusively a species with m/z 1375 which is readily assignable as $[(\text{MeAlO})_{16}(\text{Me}_3\text{Al})_6\text{Me}]^-$ (henceforth **16,6** and containing 35 Me groups) partnered with a $[\text{Me}_2\text{Al}\cdot\text{OMTS}]^+$ cation as seen in the positive ion spectrum. These findings support the idea that MAO may act as a source of $[\text{Me}_2\text{Al}]^+$ during catalyst activation.²⁵

We wondered what happens when MAO is combined with simple R_3Al and also whether commercial MMAO could be characterized by this technique. Herein we use our previously developed, anaerobic real-time ESI-MS technique²⁶ to probe the effect of higher R_3Al species on MAO anions and gain new insights into the alkyl exchange process.

Results and Discussion

MMAO is sold under different trade names depending on the alkyl group (3A = *i*Bu, 7 and 12, = *n*Oct) and composition (3A ca. 85:15 Me:*i*Bu, 7 ca. 85:15 Me:*n*Oct, 12 ca. 95:5 Me:*n*Oct).¹² We investigated MMAO-12 using 5 mol% OMTS and obtained a reasonable total ion current with $[\text{Al}] = 0.01$ M in fluorobenzene (PhF). However, the negative ion mass spectrum consisted of a broad continuum of ions from ~ 1000 to >3000 Da. Expansion of the negative ion mass spectrum (see Supporting Information Figure S1) shows a multitude of signals separated in mass by 58 Da which can be tentatively assigned based on their nominal mass. The major peaks are “normal” MAO anions, while others are present which contain one octyl group (and one less Me group). There is also evidence of anion oxidation, containing one less MAO unit than their parent anion with the composition $[(\text{MeAlO})_{n-1}(\text{Me}_3\text{Al})_{m-1}(\text{Me}_2\text{AlOMe})\text{Me}]^-$.²⁴

The complex mixture of anions vs. that present in hydrolytic MAO likely reflects differences in their method of synthesis, along with random permutations of Me for *n*Oct, possibly coupled with physical aging and/or oxidation upon prolonged storage or repackaging. On the other hand, the corresponding positive ion mass spectrum consisted of only two species $[\text{Me}_2\text{Al}\cdot\text{OMTS}]^+$ (m/z 293) and $[\text{Me}(n\text{Oct})\text{Al}\cdot\text{OMTS}]^+$ (m/z 391) in about a 98:2 ratio (see Supporting Information Figure

S2). It thus seems that the mode of action of MMAO-12 is identical to that of MAO, though the anion distributions are different.

As the quality of the negative ion spectrum is marginal, we thus focused further work on modification of MAO by the direct addition of R_3Al . Addition of iBu_3Al to MAO, either before or after ionization with OMTS, cleanly led to multiple substitution of Me for iBu on the MAO anions. Depending on the amount added the extent of iBu/Me substitution on **16,6** could be controlled (Figure 1).

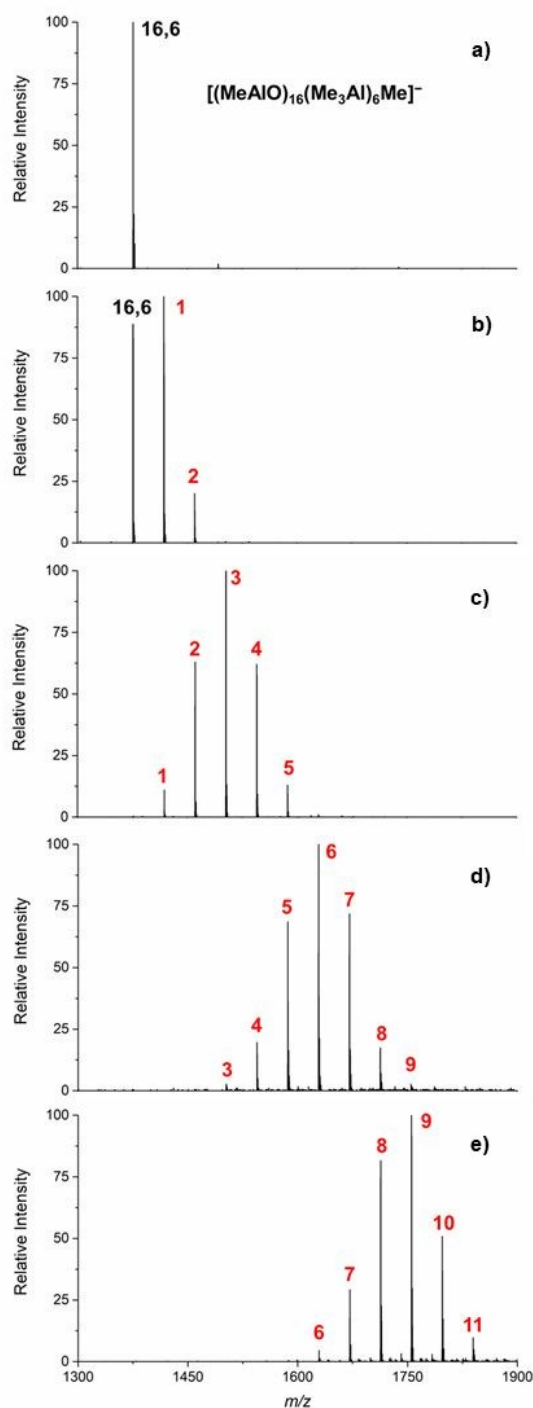
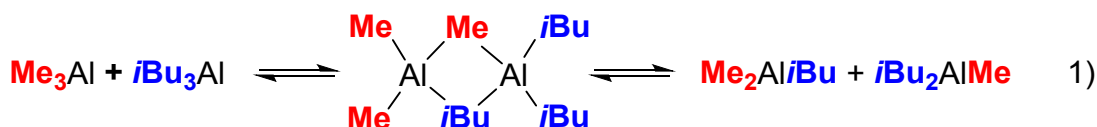


Figure 1. Room temperature negative ion ESI-MS spectra in PhF of 30 wt% MAO at equilibrium (5 minutes after mixing), (a) modified with 1 mol% $i\text{Bu}_3\text{Al}$ (b), 5 mol% $i\text{Bu}_3\text{Al}$ (c), 10 mol% $i\text{Bu}_3\text{Al}$ (d), 20 mol% $i\text{Bu}_3\text{Al}$ (e). All at an OMTS:Al ratio of 1:100. Number of Me/Bu substitutions in $[(\text{MeAlO})_{16}(\text{Me}_3\text{Al})_6\text{Me}]^-$ is shown in red.

Before addition of *i*Bu₃Al the expected spectrum, dominated by **16,6**, is obtained (Figure 1a). Addition of 1 mol % *i*Bu₃Al resulted in Me/*i*Bu exchange as indicated by the appearance of peaks 42 Da (the mass difference between *i*Bu and Me) higher than the parent ion (Figure 1b). An equilibrium was quickly reached and the distribution remained unchanged for the remainder of the measurement. The distribution is essentially statistical, it reaches a maximum at one *i*Bu substituent and has a weighted average of 0.63 *i*Bu groups. Since the 30 wt% MAO used in this study features 1.64 moles of Me groups per mole of Al, the use of 1.0 mol% of *i*Bu₃Al with respect to Al corresponds to a ratio of *i*Bu/Me groups of 0.03/1.64 = 0.0183 or 1.83 mol%. As previously mentioned **16,6** has 35 Me groups so upon addition of 1.0 mol% *i*Bu₃Al 0.21 Me substitutions would be expected on a statistical basis if only one *i*Bu group is exchanged per mole of *i*Bu₃Al to a maximum of 0.64 if all three *i*Bu groups are equilibrated.

Addition of 5 mol % *i*Bu₃Al leads to more extensive substitution, with a weighted average of 2.90 substituted Me groups (1.07-3.20 expected, Figure 1c). Addition of more *i*Bu₃Al leads to a maximal replacement of 11 Me groups (Figure 1d and 1e). The substitution process is reversible and upon addition of excess Me₃Al to the mixture the equilibrium is pushed backwards to give a spectrum that consists principally of **16,6** with a low level of residual mono-substituted product (see Supporting Information Figure S3).

The mechanism of alkyl exchange in simple R₃Al involves dissociation into monomeric R₃Al, followed by formation of mixed dimers.¹⁵ In the case of *i*Bu₃Al, which is largely dissociated, especially under these dilute conditions, exchange with MAO or the anions derived from MAO might involve dissociation of Me₃Al from the latter, followed by association of *i*Bu₃Al. On the other hand, anions with three *i*Bu groups are not prominent at low extents of substitution suggesting that a mixed alkyl such as Me₂Al*i*Bu is involved in the exchange process, having been formed by rapid scrambling between *i*Bu₃Al and excess Me₃Al (eqn. 1).



This expectation is borne out in the MS/MS fragmentation pattern which shows an over-represented amount of Me₂Al*i*Bu loss as compared to Me₃Al when the ion with *m/z* 1501 (three *i*Bu groups) undergoes collision-induced dissociation with argon (Figure 2 and Supporting Information Figures S9-S13). The MS/MS spectrum shows that the first R₃Al loss has a ~45% chance of *i*BuAlMe₂, but with only 3 of 35 R groups being *i*Bu we would expect the ratio to be ~

26% (chance of an *i*Bu loss in the first R_3Al loss is $3/35 + 3/34 + 3/33 = \sim 26\%$). This indicates that bound $iBuAlMe_2$ is especially labile compared with bound Me_3Al . There are no direct losses of either iBu_3Al or iBu_2AlMe from the parent ion, suggesting that if those compounds are involved in the exchange, they do so with incorporation of *i*Bu groups into less labile sites of the MAO oligomer.

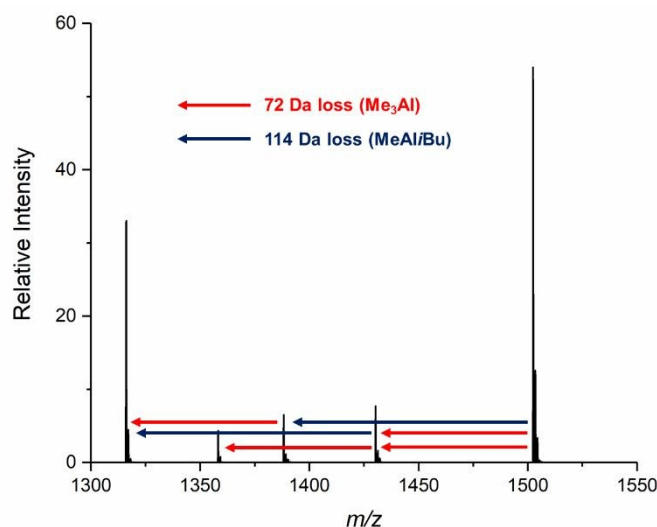


Figure 2. Partial MS/MS spectrum of the $[Me_{32}iBu_3Al_{22}O_{16}]^-$ species (i.e. **16,6** after three Me for Bu exchanges) at m/z 1501. Initial two losses shown only to illustrate preference for *i*Bu loss of Me for full spectrum see Supplemental Information Figure S11.

The positive ion mode spectra show a mixture of $[Me_n(iBu_{(2-n)})Al \cdot OMTS]^+$ cations upon addition of the iBu_3Al . However, unlike the corresponding negative ion spectra the order of addition of OMTS vs. iBu_3Al has a pronounced effect on the appearance of the positive ion spectra (Figure 3).

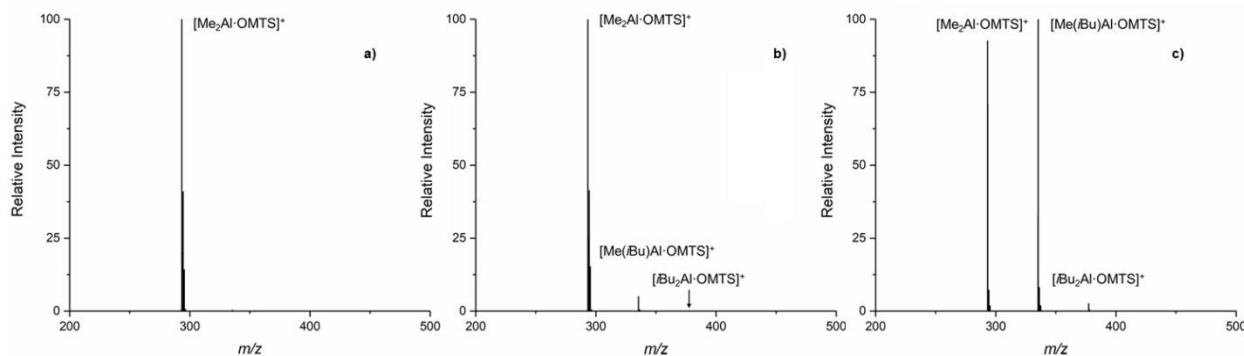


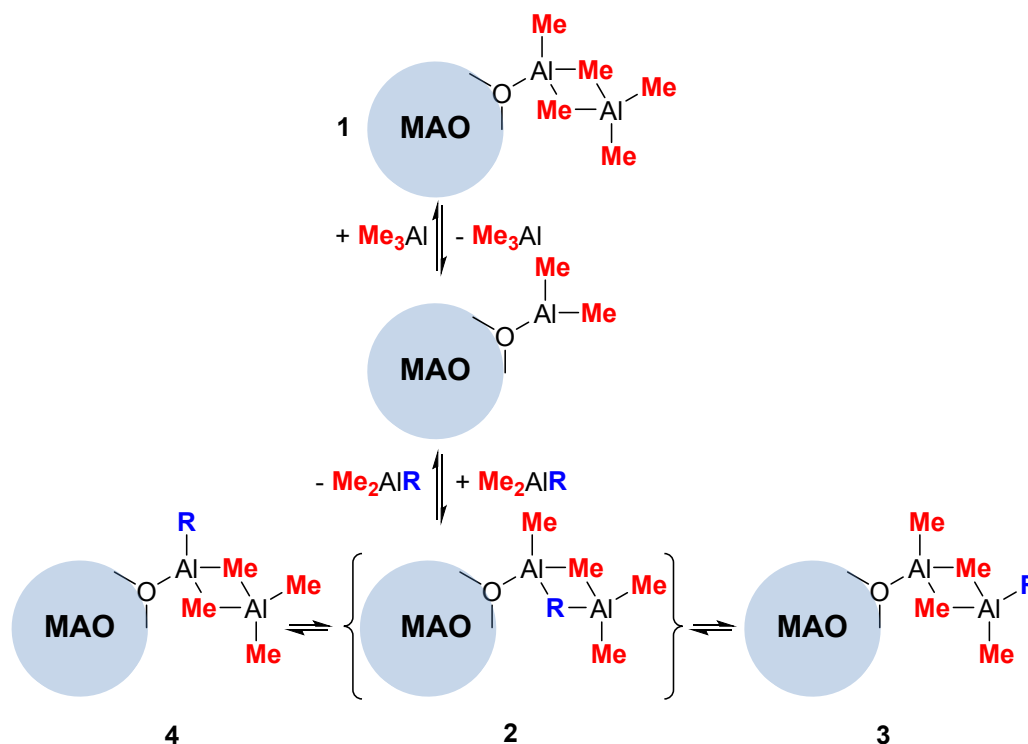
Figure 3. Positive ion spectra in PhF of 30 wt% MAO (a), 30 wt% MAO with 15% *i*Bu₃Al added after ionization (b) and 30 wt% MAO with 15% *i*Bu₃Al added before ionization (c). All at an OMTS:MAO ratio of 1:100.

When 15 mol% *i*Bu₃Al is added before ionization with OMTS, the main cation present is [Me(*i*Bu)Al·OMTS]⁺ (Figure 3c) whereas when the *i*Bu₃Al is added after ionization, the spectrum is dominated by [Me₂Al·OMTS]⁺ (Figure 3b). In the latter case, it is somewhat unanticipated to see *any* mixed alkyl cations given the chelating nature of the OMTS ligand. However, it is known that the alkyl exchange process involving R₃Al does proceed in the presence of strong donors like pyridine, where rate limiting dissociation of the donor adduct is involved.^{15b} Perhaps, a similar process is operative in the corresponding [R₂Al]⁺ cations. It is also possible that ionization of MAO is reversible, though one never observes a spectrum resembling Figure 3c. The order of OMTS addition does not change the equilibrium distribution of the anions, suggesting that alkyl exchange is equally facile between both neutral MAO and their ionized analogues.

When *i*Bu₃Al is added first to MAO, all labile AlMe_n (n = 1-3) sites are involved in the scrambling process, including those that are reactive to ion-pair formation via [R₂Al]⁺ abstraction when OMTS is added. In fact, at 15 mol% *i*Bu₃Al a *i*Bu:Me ratio of 0.45/1.64 = 0.274 in the corresponding cations is expected if there is no difference in reactivity between sites substituted by Me vs. *i*Bu. Figure 3c suggests a slightly higher ratio of ca. 0.35 indicating that there is preferential exchange at the active sites and/or that those active sites bearing an *i*Bu group are more reactive towards [R₂Al]⁺ abstraction.

In an earlier paper,²³ we identified two types of sites which are reactive towards [Me₂Al]⁺ abstraction in structures identified as stable aluminoxane products arising from the hydrolysis of Me₃Al.^{6b} One of those sites is shown generically in Scheme 1, and it is obvious from its structure that it should also be prone to exchange with R₃Al through loss of Me₃Al.¹⁵

Three isomeric structures (**2-4**) will result upon binding of $\text{Me}_2\text{Al}/i\text{Bu}$, though the one with $i\text{Bu}$ in the bridging position is expected to be unstable with respect to the other two. All three will interconvert through the process of alkyl exchange between bridging and terminal positions. In looking at structures **1-4**, only one of these will react with OMTS to produce $[\text{Me}(i\text{Bu})\text{Al}\cdot\text{OMTS}]^+$. Thus, on a statistical basis (which seems probable given that exchange is essentially complete at 20 mol% $i\text{Bu}_3\text{Al}$, and at 15 mol% $i\text{Bu}_3\text{Al}$, one expects an average labeling of 9.6 Me groups - cf. Figure 1e) one would expect a ratio of $[\text{Me}_2\text{Al}\cdot\text{OMTS}]:[\text{Me}(i\text{Bu})\text{Al}\cdot\text{OMTS}]^+$ of ca. 1:1 assuming all reactive sites are substituted by at least one $i\text{Bu}$ group. The ratio of these two cations in Figure 3c is close to that predicted.



Scheme 1. Alkyl exchange between MAO and Me_2AIR .

Analogous structures are possible for reaction with $\text{MeAl}/i\text{Bu}_2$ but in this case, only two feature bridging Me groups, while of these only one can react to form $[\text{Me}(i\text{Bu})\text{Al}\cdot\text{OMTS}]^+$, with the other forming $[i\text{Bu}_2\text{Al}\cdot\text{OMTS}]^+$. The latter cation is drastically under-represented on a statistical basis in Figure 3c. This suggests, as already mentioned, that $i\text{Bu}_2\text{AlMe}$ may not be involved in the exchange process or that an $\text{O}-(\text{Me})\text{AlMe}_2/i\text{Bu}_2$ site is much less reactive towards ionization.

The results with $i\text{Bu}_3\text{Al}$ suggest that only limited substitution can take place (up to 11 exchanges), but the isobutyl group is significantly bulkier than the methyl group. Substitution by

Et₃Al is expected to be much more like the self-exchange process involving Me₃Al. Indeed, Et/Me exchange is extremely fast and depending on the amount of Et₃Al that was added, 16,6 derivatives with over 24 Et groups could be observed (Figure 4a and S5). At the 30 mol% level used, the Et/Me ratio is 0.90/1.64 = 0.55 and thus the average level of substitution should be 19.2 vs. ~ 20 observed suggesting basically a statistical labeling of the MAO and the resulting anions.

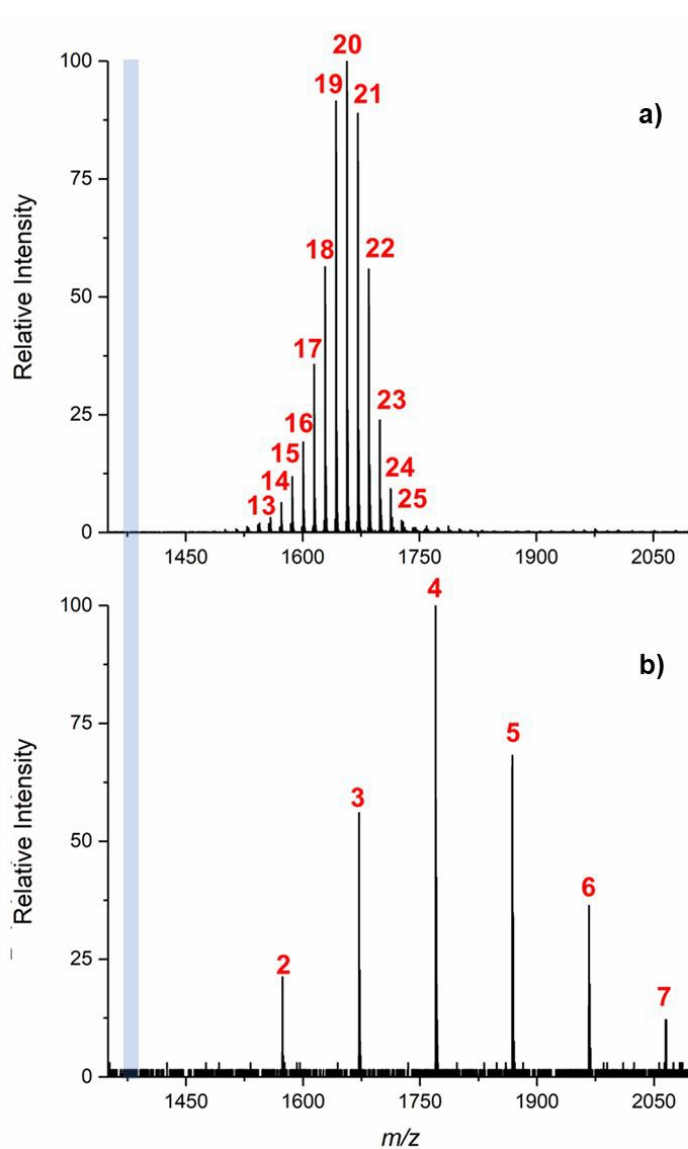


Figure 4. Negative ion ESI-MS spectra in PhF of 30 wt% MAO modified with 30 mol% Et₃Al (a) and 30 mol% Oct₃Al (b). Number of Me/R substitutions in [(MeAlO)₁₆(Me₃Al)₆Me]⁻ shown in red, blue box indicates original *m/z* value of 16,6.

However, at lower amounts of Et_3Al the distribution is far from statistical – for example at 1 mol% Et_3Al the average degree of substitution is between 2-3 Me groups vs. 0.64 Me groups for a statistical process (see Supporting Information Figure S5). It is possible that the ion-pairs are more reactive towards exchange than the neutrals in the case of Et_3Al at low levels of substitution. Some evidence for this is seen in the exchange of MAO vs. the ion-pairs with Me_2AlCl , admittedly where there is a strong driving force for substitution.²² On the other hand, MS/MS spectra reveal that loss of Me_3Al is significantly more favorable than loss of EtAlMe_2 from the parent ions (see Supporting Information Figures S18-21), while direct loss of e.g. Et_3Al is still not observed, suggesting that binding of EtAlMe_2 to labile sites on MAO is favored over that of Me_3Al , or more likely, that the Et group is rapidly scrambled into less labile sites on the MAO anions, as in structure **4**, Scheme 1.

These results point to R groups scrambling over the entire oligomer, meaning that the oligomer is highly dynamic with respect to exchange. The fact that the *i*Bu exchanges are more limited is probably a function of steric effects, because fitting the larger R groups into the oligomer becomes increasingly difficult (see Supporting Information for DFT results that support this hypothesis).

The most surprising results are obtained using $n\text{Oct}_3\text{Al}$. Despite being intermediate in steric hindrance (i.e. $\text{Et} < n\text{Oct} < i\text{Bu}$)²⁷ no more than 7 positions are substituted at the same 30 mol% loading (Figure 4b). Moreover, the rate of substitution is $\text{Et} > i\text{Bu} > n\text{Oct}$ (*vide infra*).

In comparing Figure 4b with e.g. Figure 1c where the anion substitution level is similar, it is obvious that the signal:noise ratio for $n\text{Oct}$ anions are very much reduced compared with *i*Bu. In fact, total ion counts decrease when the MAO anions are substituted by R groups in the order $\text{Et} < i\text{Bu} < n\text{Oct}$ at similar extents of substitution. Additionally, when monitoring substitution by pressurized sample infusion (*vide infra*) the more highly substituted ions are significantly less sensitively detected than those featuring lower degrees of substitution when $\text{R} = n\text{Oct}$ vs. Et (see Figure S7 vs. S8). Ions containing flexible alkyl chains are known to exhibit lower ESI-MS response than rigid ions due to aggregation.²⁸ This effect may be in play here, causing the distribution observed with $n\text{Oct}$ (Figure 4b) to not be representative of the actual degree of substitution.

To better understand the $\text{R}_3\text{Al}/\text{MAO-Me}$ exchange process we set out to study the reaction in real-time using pressurized sample infusion (continuous injection of solution into the mass spectrometer using a variant of cannula transfer).²⁶ Upon addition of 1% *i*Bu₃Al to MAO rapid exchange is observed resulting in the formation of the one, two, and three *i*Bu/Me substituted 16,6 derivatives (see Supporting Information Figure S6). These species equilibrate within a minute and

their ion counts thenceforth remain stable. Further insight into the alkyl exchange can be obtained upon addition of excess (10 mol% with respect to total Al) of *i*Bu₃Al to the MAO/OMTS mixture (Figure 5). Now a series of consecutive *i*Bu/Me exchanges can be observed over the course of 8 minutes.

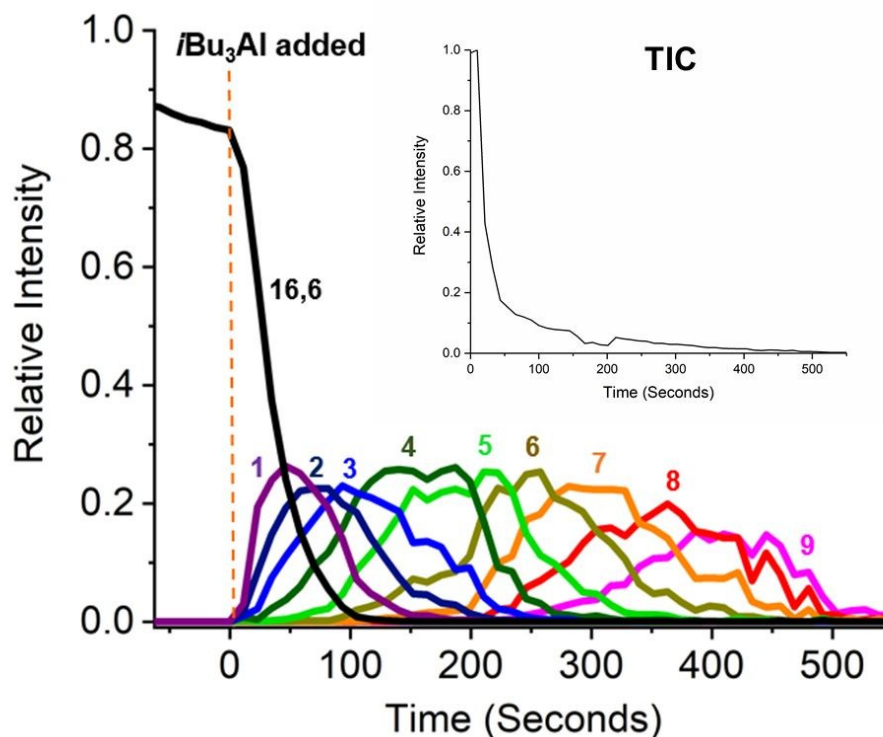


Figure 5. PSI of 10 mol% *i*Bu₃Al modified MAO/OMTS with Al:OMTS 100:1 in PhF. Inset: total ion counts over time (TIC).

During this period the total ion chromatogram (i.e. the sum of the intensities of all ions in the spectrum) shows a large decrease in intensity similar to that seen before (see Figure 5 inset). Real-time data of the addition of Et₃Al and *n*Oct₃Al to MAO/OMTS mixtures show similar trends as the *i*Bu₃Al data shown in Figure 5 (see Supplemental Information Figure S7 and S8). The speed at which the exchange takes place varies with the individual exchanges being on the second-time scale for Et ($t_{1/2} \sim 2$ sec for the disappearance of **16,6**), on the minute time scale for *i*Bu ($t_{1/2} \sim 40$ sec), and on the multi-minute time scale for *n*Oct ($t_{1/2} \sim 200$ sec).

The differential rates are likely a function of at least two different factors: the extent to which the R₆Al₂ dimer is dissociated ($K_d = 6.0, 1.7 \times 10^{-3},$ and 2.2×10^{-5} M for *i*Bu, *n*Oct, and Et at 25 °C in benzene),^{11,29} where low dissociation will lead to lower rates of exchange; and the relative rates at which monomeric R₃Al can compete with monomeric Me₃Al ($K_d = 9.0 \times 10^{-8}$ M) for occupation of

a vacant site on the “unsaturated” MAO (*i.e.* **16,5**; this rate will be slower for sterically encumbered R_3Al). Unfortunately, we are unable to quantitatively account for the observed differences in rate using these simple arguments. This suggests that the mechanism for exchange may well differ depending on R_3Al or at least the rate determining step in the substitution process is different for Et and *n*Oct vs. *i*Bu in order to account for the anomalous order in the observed rates.

In earlier theoretical work, we adopted a model for the precursor to this ion-pair that was especially stable relative to other aluminoxane structures located during a systematic but targeted grid search of the reactions between Me_3Al and H_2O .^{6b} This model and the corresponding anion formed by methide abstraction, share structural features which are associated to the reactivity of MAO but are common to many other cage structures that were located during this process. As shown in Figure 6, the model for $(MeAlO)_{16}(Me_3Al)_6$ has a total of 18 methyl groups that could be considered labile, in the sense that only Al-C bonds would be broken during exchange (they are highlighted in blue). While this might account for the results seen with *i*Bu₃Al (6 of these positions are bridging rather than terminal and thus disfavored – see Supporting information for DFT calculations), it falls short of the 24 low energy substitution reactions observed for Et₃Al.

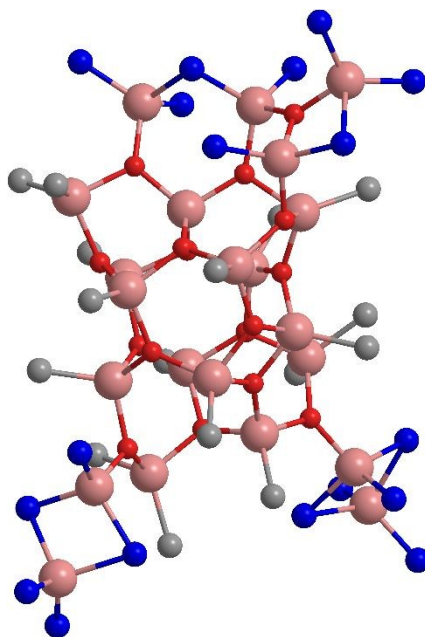


Figure 6. Optimized structure for neutral $(MeAlO)_{16}(Me_3Al)_6$ (Al pink, O red, and C grey).

In order to accommodate this number of substitutions, one would have to break Al-O bonds during the dynamic processes that interconvert R groups on the oligomer, and there is only one Al_2O_2 ring in this structure, with the rest being six membered, Al_3O_3 rings and thus relatively

strain free. A similar interconverting process involving strained Al_2O_2 rings has been used by Barron *et al.* to explain the different isomers observed during the reaction of $(t\text{BuAlO})_6$ with one equivalent of Me_3Al .¹⁶

Generally speaking, the most stable aluminoxane cages consist of six-membered rings, and either lack sites reactive towards Me_3Al or have few sites per cage (typically less than 4) competent for methide or $[\text{Me}_2\text{Al}]^+$ abstraction.^{6b,c} We have shown here that the latter are also sites for exchange with R_3Al given the present results.

Given the number of alkyl substitutions as well as their selectivity for a minor component of the mixture in the case of Et_3Al , the MAO activator(s) are likely to have unusual structures that depart significantly from the cage like motifs or even nanotubes that have been considered so far. We are currently investigating alternate structural motifs, which have a much higher proportion of active sites per molecule than do cages (*i.e.* a higher proportion of edge sites saturated with Me_3Al).

Conclusions

The selective ionization of MAO provided a unique opportunity to investigate a hitherto intractable problem: the modification of MAO with R_3Al species. Rapid reactivity followed by statistical equilibration was observed in case of $i\text{Bu}_3\text{Al}$, and the sequential reactivity suggested that scrambling of the R_3Al species with Me_3Al was faster than exchange with the MAO oligomer. The extent of substitution was very high with Et_3Al , pointing towards exchange being facile not just for the most exposed methyl groups on the oligomer but possibly also for Me groups which are less labile by virtue of incorporation into the aluminoxane structure. These observations will spur further examination of MAO's structure by computational approaches and provide encouragement that real-time kinetic analysis of MAO reactivity is possible.

Experimental

MAO (10 and 30 wt % in toluene) was obtained from Albemarle and stored in the glovebox freezer upon receipt. The samples were warmed to room temperature and thoroughly swirled to dissolve any precipitated content prior to use. OMTS (98%), Me_3Al (2M in toluene), Et_3Al (1.9 M in toluene), $i\text{Bu}_3\text{Al}$ (1M in toluene), and octyl_3Al (0.48M in toluene) were purchased from Sigma-Aldrich and used as received. Fluorobenzene (Oakwood) was refluxed over CaH_2 , distilled under N_2 , and dried over molecular sieves inside a glovebox for at least 3 days prior to use.

ESI-MS Details

In a typical procedure a stock solution (3 mL) was prepared by dilution of MAO (0.5 mL of 1.5 M (10%) or 0.15 mL of 4.6 M (30%)) and 0.5 mL of a premade PhF solution of OMTS (0.015 M) to give a mixture with an Al:OMTS ratio of 100:1. 0.2 mL of this solution was further diluted to 3 mL to give mixture with final [Al] of 0.0167M. To this mixture varying amounts of R₃Al (R = Et, *i*Bu, or octyl; for exact details see Supplemental Information) were added to give the desired MAO-Al:R₃Al ratios. The resulting solution was injected from the glove box to a Micromass QTOF micro spectrometer via PTFE tubing (1/16" o.d., 0.005" i.d.). Capillary voltage was set at 3000 V with source and desolvation gas temperature at 85 °C and 185 °C, respectively with the desolvation gas flow at 400 L/h. MS/MS data were obtained in product ion spectra using argon as the collision gas and a voltage range of 2-100 V.

For PSI experiments 0.4 mL of a MAO-OMTS solution was diluted with 6 mL of PhF and placed in a glass vial (0.0167M). The vial was attached to a rubber septum and a 178 µm ID PTFE tubing was immersed in the MAO-OMTS solution, and the other end of the tubing was connected to the MS source. PSI experiments were carried out by addition of the R₃Al to give the desired MAO-Al:R₃Al ratio (for exact details see Supplemental Information).

Conflicts of interest

The authors declare no conflict of interest.

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