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Modifying methylalumoxane *via* alkyl exchange†

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Methylalumoxane (MAO) ionizes highly selectively in the presence of octamethyltrisiloxane (OMTS) to generate $[Me_2Al{\cdot}OMTS]^+$ $[(MeAlO)_{16}(Me_3Al)_6Me]^-$. 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 ($t_{\frac{1}{2}}$ ~2 s, up to 25 exchanges of Me for Et) than iBu_3Al ($t_{\frac{1}{2}}$ ~40 s, up to 11 exchanges) or Oct_3Al ($t_{\frac{1}{2}}$ ~200 s, 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, $(Me_{1.4-1.5}AlO_{0.75-0.80})_n$,[4] molecular weight (MW, ~1200–2000)[5] have been established and, in combination with computational studies[6] and structurally characterized alumoxanes[7] it is generally thought that MAO is made up of cage-like structures that have the general formula $(MeAlO)_n(Me_3Al)_m$.

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, iBu_3Al or nOct$_3$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 $iBu_3Al \sim n$Oct$_3$Al < Me_3Al.

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 iBu_3Al 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 nOct$_3$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 R_nAlMe_{3-n}-type structures. Alkyl exchange between aluminum alkyls such as Me_3Al and iBu_3Al

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is known to be rapid.[15] Studies of alkyl exchange in alumoxanes are rare but it has been shown that strained *t*Bu alumoxanes 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 $Cp_2Zr(^{13}CH_3)_2$ 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 ms) 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.[20–22] 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 $[(MeAlO)_{16}(Me_3Al)_6Me]^-$ (henceforth **16,6** and containing 35 Me groups) partnered with a $[Me_2Al{\cdot}OMTS]^+$ cation as seen in the positive ion spectrum. These findings support the idea that MAO may act as a source of $[Me_2Al]^+$ 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 technique[26] 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 = iBu, 7 and 12, = *n*Oct) and composition (3A *ca.* 85 : 15 Me : iBu, 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 [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 ESI Fig. 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 $[(MeAlO)_{n-1}(Me_3Al)_{m-1}(Me_2AlOMe)Me]$.[24]

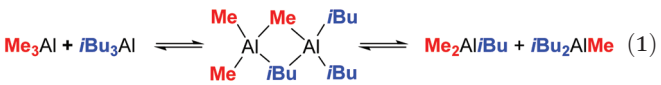
The complex mixture of anions *vs.* that present in hydrolytic MAO likely reflects differences in their method of synthesis, along with random permutations of Me for *n*Oct, possibly coupled with physical aging and/or oxidation upon prolonged storage or repackaging. On the other hand, the corresponding positive ion mass spectrum consisted of only two species $[Me_2Al{\cdot}OMTS]^+$ (*m*/*z* 293) and $[Me(nOct)Al{\cdot}OMTS]^+$ (*m*/*z* 391) in about a 98 : 2 ratio (see ESI Fig. 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 was marginal, we 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 (Fig. 1).

Before addition of iBu_3Al the expected spectrum, dominated by **16,6**, is obtained (Fig. 1a). Addition of 1 mol% iBu_3Al resulted in Me/iBu exchange as indicated by the appearance of peaks 42 Da (the mass difference between iBu and Me) higher than the parent ion (Fig. 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 iBu substituent and has a weighted average of 0.63 iBu groups. Since the 30 wt% MAO used in this study contains 1.64 moles of Me groups per mole of Al, the use of 1.0 mol% of iBu_3Al with respect to Al corresponds to a ratio of iBu/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% iBu_3Al 0.21 Me substitutions would be expected on a statistical basis if only one iBu group is exchanged per mole of iBu_3Al to a maximum of 0.64 if all three iBu groups are equilibrated.

Addition of 5 mol% iBu_3Al leads to more extensive substitution, with a weighted average of 2.90 substituted Me groups (1.07–3.20 expected, Fig. 1c). Addition of more iBu_3Al leads to a maximal replacement of 11 Me groups (Fig. 1d and e). The substitution process is reversible and upon addition of excess Me_3Al 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 ESI Fig. S3†).

The mechanism of alkyl exchange in simple R_3Al involves dissociation into monomeric R_3Al, followed by formation of mixed dimers.[15] In the case of iBu_3Al, which is largely dissociated, especially under these dilute conditions, exchange with MAO or the anions derived from MAO might involve dissociation of Me_3Al from the latter, followed by association of iBu_3Al. On the other hand, anions with three iBu groups are not prominent at low extents of substitution suggesting that a mixed alkyl such as Me_2AliBu is involved in the exchange process, having been formed by rapid scrambling between iBu_3Al and excess Me_3Al (eqn (1)).



This expectation is borne out in the MS/MS fragmentation pattern which shows an over-represented amount of Me_2AliBu

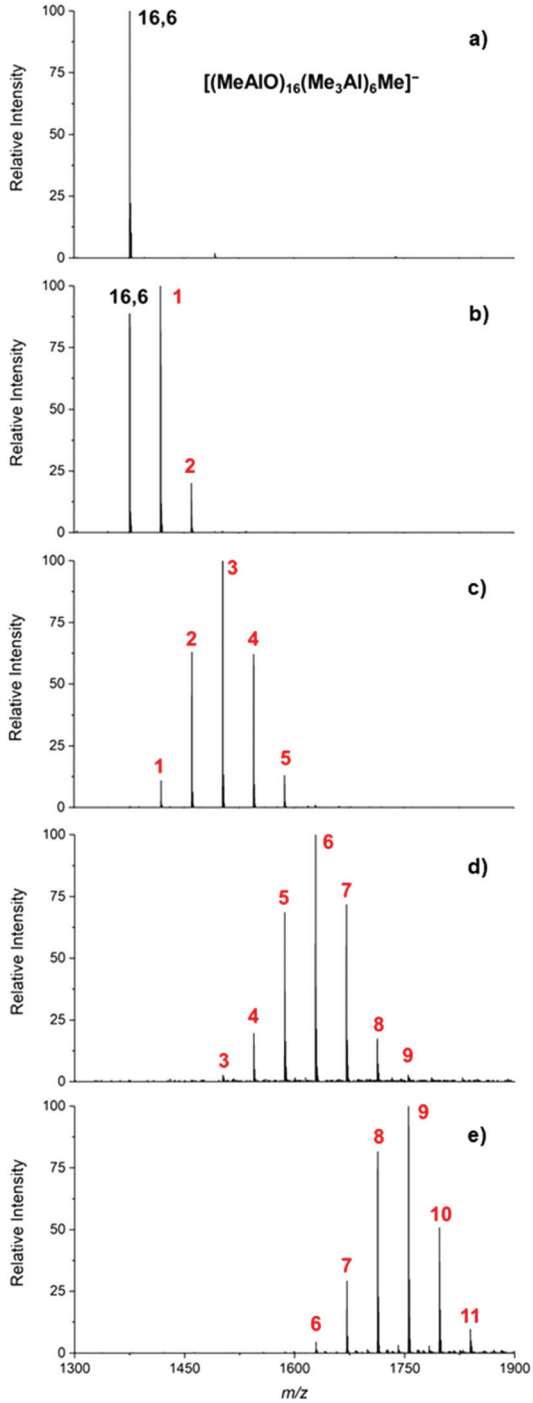


Fig. 1 Room temperature negative ion ESI-MS spectra in PhF of 30 wt% MAO at equilibrium (5 minutes after mixing), (a) modified with 1 mol% iBu_3Al (b), 5 mol% iBu_3Al (c), 10 mol% iBu_3Al (d), 20 mol% iBu_3Al (e). All at an OMTS : Al ratio of 1 : 100. Number of Me/iBu substitutions in $[(MeAlO)_{16}(Me_3Al)_6Me]^-$ is shown in red.

loss as compared to Me_3Al when the ion with m/z 1501 (three iBu groups) undergoes collision-induced dissociation with argon (Fig. 2 and ESI Fig. S9–S13†). The MS/MS spectrum shows that the first R_3Al loss has a ~45% chance of $iBuAlMe_2$, but with only 3 of 35 R groups being iBu we would expect the

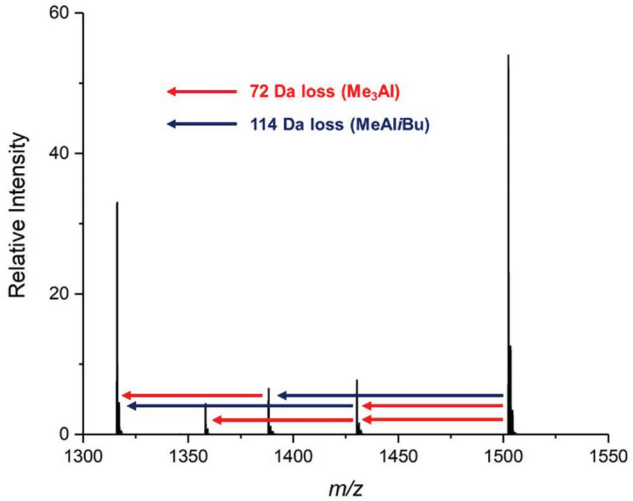


Fig. 2 Partial MS/MS spectrum of the $[Me_{32}iBu_3Al_{22}O_{16}]^-$ species (*i.e.* **16,6** after three Me for Bu exchanges) at m/z 1501. Initial two losses shown only to illustrate preference for iBu loss of Me for full spectrum see ESI Fig. S11.†

ratio to be ~26% (chance of an iBu loss in the first R_3Al loss is 3/35 + 3/34 + 3/33 = ~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 iBu groups into less labile sites of the MAO oligomer.

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 (Fig. 3).

When 15 mol% iBu_3Al is added before ionization with OMTS, the main cation present is $[Me(iBu)Al{\cdot}OMTS]^+$ (Fig. 3c) whereas when the iBu_3Al is added after ionization, the spectrum is dominated by $[Me_2Al{\cdot}OMTS]^+$ (Fig. 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 R_3Al 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 $[R_2Al]^+$ cations. It is also possible that ionization of MAO is reversible, though one never observes a spectrum resembling Fig. 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 iBu_3Al 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* $[R_2Al]^+$ abstraction when OMTS is added. In fact, at 15 mol% iBu_3Al a iBu : Me ratio of 0.45/1.64 = 0.274 in the corresponding cations is expected if there is no difference in reactivity between sites

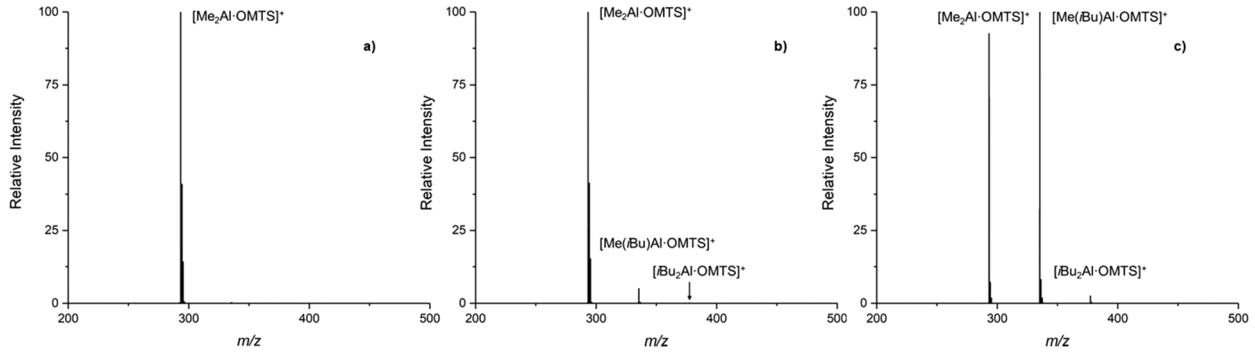


Fig. 3 Positive ion spectra in PhF of 30 wt% MAO (a), 30 wt% MAO with 15% iBu_3Al added after ionization (b) and 30 wt% MAO with 15% iBu_3Al added before ionization (c). All at an OMTS : MAO ratio of 1 : 100.

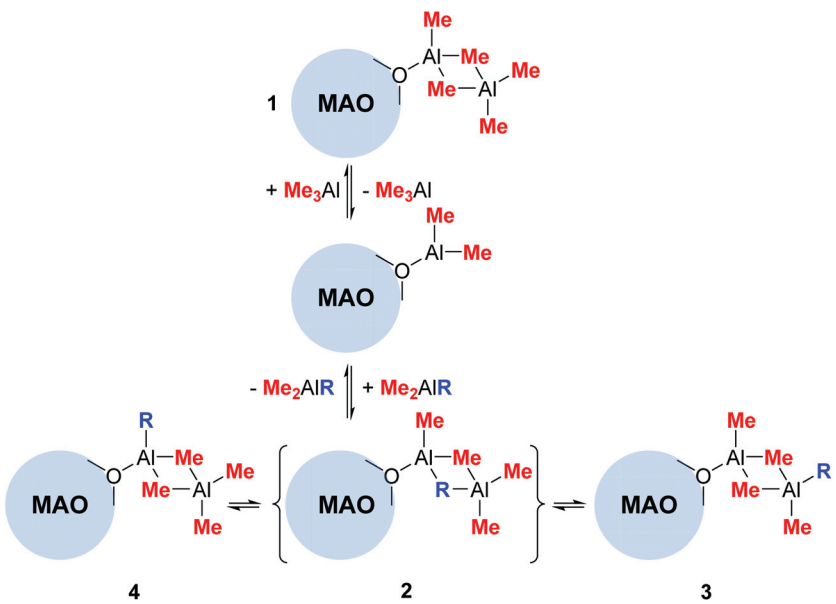
substituted by Me *vs.* iBu. Fig. 3c suggests a slightly higher ratio of *ca.* 0.35 indicating that there is preferential exchange at the active sites and/or that those active sites bearing an iBu group are more reactive towards $[R_2Al]^+$ abstraction.

In an earlier paper,[23] we identified two types of sites which are reactive towards $[Me_2Al]^+$ abstraction in structures identified as stable aluminoxane products arising from the hydrolysis of Me_3Al.[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 R_3Al through loss of Me_3Al.[15]

Three isomeric structures (**2–4**) will result upon binding of Me_2AliBu, though the one with iBu 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 $[Me(iBu)Al{\cdot}OMTS]^+$. Thus, on a statistical basis (which seems probable given that exchange is essentially complete at 20 mol% iBu_3Al, and at 15 mol% iBu_3Al, one expects an average labeling of 9.6 Me groups – *cf.* Fig. 1e) one would expect a ratio of $[Me_2Al{\cdot}OMTS] : [Me(iBu)Al{\cdot}OMTS]^+$ of *ca.* 1 : 1 assuming all reactive sites are substituted by at least one iBu group. The ratio of these two cations in Fig. 3c is close to that predicted.

Analogous structures are possible for reaction with $MeAliBu_2$ but in this case, only two feature bridging Me groups, while of these only one can react to form $[Me(iBu)Al{\cdot}OMTS]^+$, with the other forming $[iBu_2Al{\cdot}OMTS]^+$. The latter cation is drastically under-represented on a statistical basis in Fig. 3c. This suggests, as already mentioned, that iBu_2AlMe may not be involved in the exchange process or that an O-(Me)$AlMe_2AliBu_2$ site is much less reactive towards ionization.

The results with iBu_3Al 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 Et_3Al is expected to be much more like the self-



Scheme 1 Alkyl exchange between MAO and Me_2AlR.

exchange process involving Me_3Al. Indeed, Et/Me exchange is extremely fast and depending on the amount of Et_3Al that was added, **16,6** derivatives with over 24 Et groups could be observed (Fig. 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.

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 ESI Fig. 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 ESI Fig. 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.

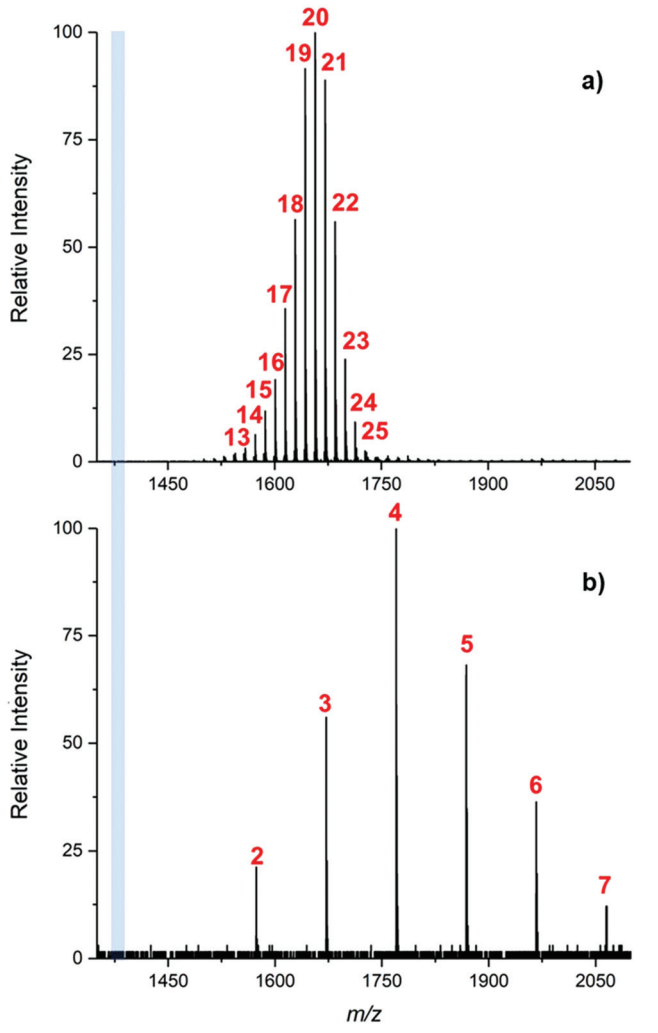


Fig. 4 Negative ion ESI-MS spectra in PhF of 30 wt% MAO modified with 30 mol% Et_3Al (a) and 30 mol% Oct_3Al (b). Number of Me/R substitutions in $[(MeAlO)_{16}(Me_3Al)_6Me]^-$ shown in red, blue box indicates original *m/z* value of **16,6**.

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 iBu exchanges are more limited is probably a function of steric effects, because fitting the larger R groups into the oligomer becomes increasingly difficult (see ESI† for DFT results that support this hypothesis).

The most surprising results are obtained using $n\text{Oct}_3Al$. Despite being intermediate in steric hindrance (*i.e.* Et < *n*Oct < iBu)[27] no more than 7 positions are substituted at the same 30 mol% loading (Fig. 4b). Moreover, the rate of substitution is Et > iBu > *n*Oct (*vide infra*).

In comparing Fig. 4b with *e.g.* Fig. 1c where the anion substitution level is similar, it is obvious that the signal : noise ratio for *n*Oct anions are very much reduced compared with iBu. In fact, total ion counts decrease when the MAO anions are substituted by R groups in the order Et < iBu < *n*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 that those featuring lower degrees of substitution when R = *n*Oct *vs.* Et (see Fig. 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*Oct (Fig. 4b) to not be representative of the actual degree of substitution.

To better understand the R_3Al/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% iBu_3Al to MAO rapid exchange is observed resulting in the formation of the one, two, and three iBu/Me substituted **16,6** derivatives (see ESI Fig. 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 iBu_3Al to the MAO/OMTS mixture (Fig. 5). Now a series of consecutive iBu/Me exchanges can be observed over the course of 8 minutes.

During this period the total ion chronogram (*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 Fig. 5 inset). Real-time data of the addition of Et_3Al and $n\text{Oct}_3Al$ to MAO/OMTS mixtures show similar trends as the iBu_3Al data shown in Fig. 5 (see ESI Fig. S7 and S8†). The speed at which the exchange takes place varies with the individual exchanges being on the second-time scale for Et ($t_{1/2}$ ~ 2 s for the disappearance of **16,6**), on the minute time scale for iBu ($t_{1/2}$ ~ 40 s), and on the multi-minute time scale for *n*Oct ($t_{1/2}$ ~ 200 s).

The differential rates are likely a function of at least two different factors: the extent to which the R_6Al_2 dimer is disso-

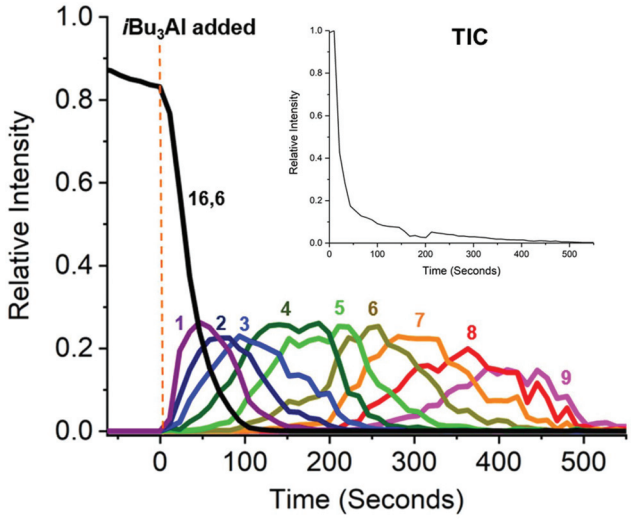


Fig. 5 PSI of 10 mol% iBu_3Al modified MAO/OMTS with Al : OMTS 100 : 1 in PhF. Inset: Total ion counts over time (TIC).

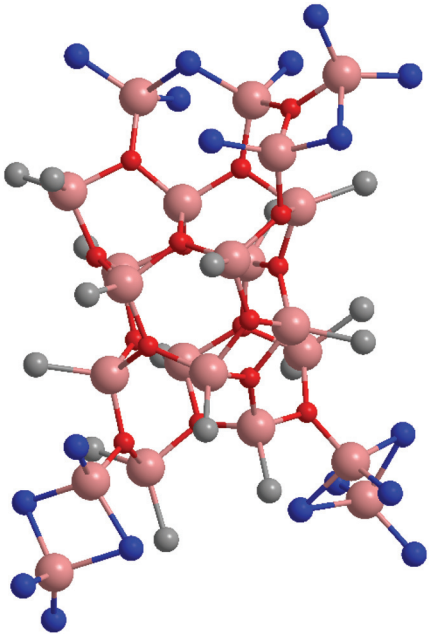


Fig. 6 Optimized structure for neutral $(MeAlO)_{16}(Me_3Al)_6$ (Al pink, O red, and C grey).

ciated (K_d = 6.0, 1.7 × 10^{-3}, and 2.2 × 10^{-5} M for iBu, *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 R_3Al can compete with monomeric Me_3Al (K_d = 9.0 × 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.* iBu 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 Fig. 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 iBu_3Al (6 of these positions are bridging rather than terminal and thus disfavored – see ESI† for DFT calculations), it falls short of the 24 low energy substitution reactions observed for Et_3Al.

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 alumoxane 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 $[Me_2Al]^+$ 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 iBu_3Al, 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 receival. The samples were warmed to room temperature and thoroughly swirled to dissolve any precipitated content prior to use. OMTS (98%), Me_3Al (2 M in toluene), Et_3Al (1.9 M in toluene), iBu_3Al (1 M in toluene), and $octyl_3Al$ (0.48 M 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 0.0167 M. To this mixture varying amounts of R_3Al (R = Et, iBu, or octyl; for exact details see ESI†) were added to give the desired MAO-Al : R_3Al 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^{-1}. 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 (0.0167 M). 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 R_3Al to give the desired MAO-Al : R_3Al ratio (for exact details see ESI†).

Conflicts of interest

The authors declare no conflict of interest.

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