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Characterization of Methylaluminoxanes and Determination of Trimethylaluminum Using Proton NMR

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New methods for characterization of methylaluminoxanes (MAO) and determination of trimethylaluminum (TMA) using proton NMR are reported. Addition of excess perdeuteriotetrahydrofuran to sharpen and shift the TMA peak followed by curve fitting to remove residual overlap between the TMA and MAO peaks allows accurate, precise, and rapid quantitation of TMA and MAO in solution. The analysis also provides determination of all the solution components of MAO preparations and the number of methyl groups per aluminum in MAO when combined with an independent determination of the aluminum content.

Introduction

Methylaluminoxane (MAO) is an important cocatalyst for the oligomerization and polymerization of a variety of monomers.[1−7] Despite the commercial importance of MAO and the considerable effort directed at its characterization, the structure of MAO remains unclear.[7−10] The presence of multiple equilibria and alkyl group exchange prevents easy direct structural characterization. Methylaluminoxane is usually written as the oligomer formula $[-Al(CH_3)O-]_n$, and the literature contains many postulated structures, including chains, cages, and rings of various sorts.[7−10] Further, residual trimethylaluminum (TMA) in MAO preparations clouds structural interpretations.[7,10,11]

Controlled hydrolysis of TMA in toluene or other hydrocarbon solvent to form MAO leaves residual TMA in the product solution.[7,10,11] The TMA in MAO is present as free and bound species according to the equilibrium

$$\mathrm{MAO} + \mathrm{Al(CH_3)_3} \rightleftarrows \mathrm{(MAO)\cdot Al(CH_3)_3} \qquad (1)$$

Commercial MAOs are known to contain significant quantities of TMA, which can have important effects on the catalytic activity of the MAO.[10,11] The amount of residual TMA is an important parameter for characterizing MAO and for controlling MAO product quality.

Several approaches to determine residual TMA have been explored in the literature: (a) determination of the volatile aluminum content from MAO solutions, (b) pyridine titration of total TMA,[12] (c) ^{31}P NMR spectroscopy,[11] (d) ^{13}C NMR spectroscopy,[13] and (e) proton NMR.[14] The determination of volatile aluminum content for TMA is inaccurate, since only the “free” TMA is volatilized. Pyridine titration assumes that pyridine complexes only with TMA and not with MAO. However, side reactions of pyridine with isolobal gallium sulfide and with other aluminoxanes have been reported.[15,16] Pyridine appears to complex with sites on the MAO, yielding a high TMA analysis.[11,13] Heteronuclear NMR methods (^{31}P and ^{13}C) use spectroscopic probe molecules to determine the residual TMA. These heteronuclear NMR methods indirectly determine the TMA using the chemical shift of the appropriate nucleus in the probe molecule. Since the probe molecules are typically Lewis bases, interaction of the probe or reporter molecule with MAO cannot be unequivocally ruled out in many cases. Further, heteronuclear chemical shifts are often very sensitive to solvent, concentration, and temperature

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effects. None of the above approaches address the characterization or analysis of MAO or any other species in solution.

Proton NMR has several advantages in the analysis of MAO products. The proton NMR spectrum shows NMR resonances for all proton-containing species present in the sample, including TMA, MAO, solvent, additives, and contaminants, even at very low concentrations (<0.1 wt %). A proton NMR analysis is a direct analysis of the components in solution. Further, the high sensitivity of proton NMR makes the analysis very rapid and, therefore, useful for quality control analysis. Previous reports ruled out the accurate and precise determination of TMA content using proton NMR because of the fluxional nature of MAO and severe overlap of the TMA and MAO Al−methyl group resonances.[10,11,14] We report here a new approach to the proton NMR analysis of TMA in MAO solutions which effectively eliminates the TMA/MAO spectral overlap and significantly narrows the methyl group resonance of TMA, allowing good quantitative determination of TMA and the other species in solution. The method we demonstrate is both rapid and precise.

Once the amount of TMA is accurately determined, some insight into the constitution of MAO can be determined directly from the proton NMR spectra. We show here that the proton NMR data combined with an independent determination of the aluminum content of the sample provides characterization of the MAO through determination of the number of methyl groups per aluminum atom in MAO. This allows further refinement of the molecular formula of MAO and helps set limits for possible structural elements. Determination of the number of methyl groups per aluminum begins to provide a basis for analytical comparisons of different MAOs. Further, the development of a rapid and accurate method for both MAO and TMA analysis eliminates the need for multiple labor- and time-intensive classical chemical methods widely used for MAO analysis.

Experimental Section

All sample preparations were performed under dry nitrogen in an inert-atmosphere glovebox. Perdeuteriobenzene, perdeuteriotetrahydrofuran (THF-d_8), perdeuterioacetonitrile, and perdeuteriodioxane were obtained from Cambridge Isotopes at 99.6% or higher deuterium content. The solvents were dried using sodium/potassium alloy and/or activated basic alumina. TMA was obtained from Albemarle Corp., and MAOs were obtained from Aldrich and Albemarle. Most of the spectra were obtained from samples of MAO in toluene to which the deuterated solvent was added for field/frequency lock. The toluene resonance was assigned to 2.09 ppm. Five millimeter NMR tubes were dried at 110 °C for at least 1 h before transfer to the glovebox for sample preparation.

Proton NMR spectra were obtained at 400 MHz on a Bruker DPX400 or a Bruker/GE Omega 400WB instrument and at 300 MHz on a Bruker/GE QE-300 instrument. Proton NMR spectra were obtained using 5 mm quad nucleus probes on the DPX400 and QE-300 instruments and a 5 mm inverse probe on the Omega 400WB instrument. Typical data collection parameters provided a digital resolution for the spectrum (real data points) of 0.1−0.3 Hz per data point for accurate quantitation of integrals. Relaxation times were measured using the inversion recovery method.

Considerable attention was paid to the details of the NMR instrument operation and parameters to ensure good quantitative results. We used 30° pulse widths and pulse intervals of 3−5 times the longest T_1 (recovery of $>99\%$ of signal intensity for a 30° pulse) of the components to be measured to ensure complete relaxation. The real data digital resolution used was typically 0.1−0.3 Hz per data point, which provided adequate digitization for all the resonances of interest. The spectral response of the instrument audio filtering was linear over the observed spectral region. This was assured by proper choice of sweep width and filter droop correction or by full use of linear digital filters (DPX400). The number of acquisitions was typically 4−8 at 400 MHz and 32−64 at 300 MHz, or enough to make the ^{13}C satellites of the toluene at least 10 times the height of the noise. Prior to integration careful peak phasing and correction for any baseline dc offsets or anomalies were performed. Integrals were taken over the peak regions broad enough to include the ^{13}C satellites. Curve fitting to remove the broad MAO resonance for integration of the TMA peak was performed using multifactor polynomial curve-fitting routines provided with the NMR instrument software.

Sample preparation differed for the two approaches discussed in this paper. For the internal standard approach about 0.3 g of the MAO sample solution in toluene along with 0.1 g of mesitylene (internal standard) was accurately weighed into a vial. After thorough mixing, 1 part by volume of this mixture was mixed with 4 parts of THF-d_8 directly in the NMR tube and again thoroughly mixed. For the normalization approach no weighings were required. One part of the MAO solution was added directly into a 5 mm NMR tube containing 4 parts of THF-d_8. The NMR measurements were made after thorough mixing of the sample. For both approaches substitution of perdeuteriodioxane or perdeuterioacetonitrile for the THF-d_8 yielded the same results.

Pyridine titration was performed by titrating a standardized stock solution of pyridine in toluene containing phenazine dye with the MAO solution.

Aluminum analyses were performed with equivalent results using two methods. Wet chemical total aluminum determination was performed by dissolving an aliquot of MAO solution in bis(2-methoxyethyl) ether, followed by alcoholysis. After acidification and addition of dithizone indicator, an EDTA/zinc acetate back-titration was performed. Inductively coupled plasma atomic emission (ICP-AE) spectroscopy was used to determine the aluminum in aqueous solutions obtained after hydrolysis followed by dissolution with hydrochloric acid. The organics were volatilized by boiling prior to introduction of the sample into the ICP.

Neutron activation analysis for total aluminum and oxygen in MAO was performed at the Texas A & M University Center for Characterization and Analysis, College Station, TX.

Results and Discussion

Aluminum alkyls complex reversibly with many Lewis bases to form adducts.[11,13,17] Lewis bases, such as pyridine and tetrahydrofuran (THF), are known to cleave alkyl-bridged dimers to form the adduct:

$$(\mathrm{AlR_3})_2 + 2\mathrm{B} \rightleftarrows 2(\mathrm{B}\cdot\mathrm{AlR_3}) \qquad (2)$$

Addition of excess THF to TMA solutions shifts the equilibrium to the right. In the proton NMR spectrum of TMA in aromatic hydrocarbon solvents, addition of excess THF narrows the TMA resonance significantly and shifts the TMA resonance upfield by about 0.5 ppm. Exchange of TMA between the free and complexed states is rapid, and a single sharp peak is observed. We use this information to aid the analysis of TMA in MAO solutions. Figure 1a shows the proton NMR spectrum

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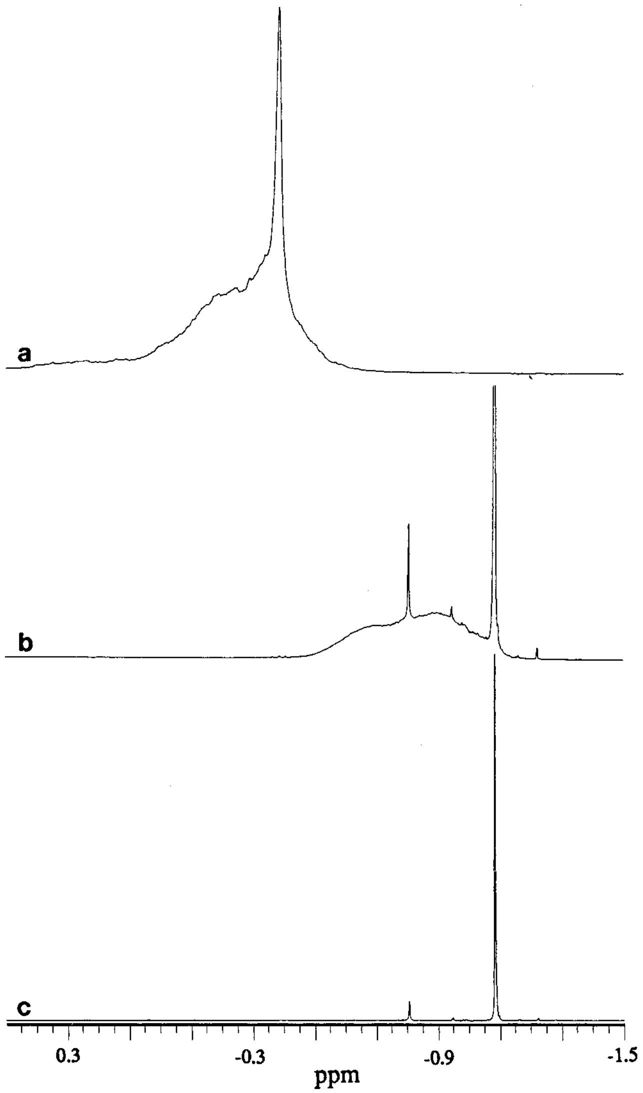

Figure 1. Proton NMR spectra of 30% MAO in toluene (400 MHz; 0.5 to −1.5 ppm). (a) Sample diluted in perdeuteriobenzene only. The TMA peak is at −0.37 ppm, while the broader feature, 0.5 to −0.7 ppm, is the MAO. (b) Sample diluted in 4 volumes of THF-d_8. The TMA peak is at −1.08 ppm. This spectrum is expanded vertically to show the broad MAO peak, −0.3 to −1.3 ppm. and (c) Spectrum b with the MAO removed via curve fitting. The small peak at −0.8 ppm is a low-molecular-weight species or end group from the MAO. The T_1 values of this peak closely matches the MAO and is much shorter than that of TMA.

of a 30% MAO in toluene solution diluted in perdeuteriobenzene to about 5% MAO. The MAO resonance is very broad and featureless. The broad and overlapping TMA peak (6−10 Hz line width at half-height) is superimposed on that of the MAO. Figure 1b shows the spectrum of the same sample to which excess THF-d_8 (4:1 v/v, or about 4:1 molar ratio of THF to total aluminum) has been added. The TMA resonance is now sharp (0.8−1 Hz line width at half-height) and is nearly resolved from the MAO. Further, the MAO resonance also shifts slightly upfield. The optimum shift and narrowing for TMA is observed at about a 4:1 v/v ratio of THF to MAO solution. Figure 1c shows the results of curve-fitting a "baseline correction" to the MAO resonance on both sides of the TMA peak, leaving the TMA peak completely resolved and easily integrated.

Table 1. Proton NMR Relaxation Times of MAO Solution Species

species	T_1 (s)	species	T_1 (s)
TMA	7.6	hydrocarbon	4.0
MAO	0.7	CH_3 (mesitylene)	5.7
CH_3 (toluene)	10.0	aromatic (mesitylene)	18.4
aromatic (toluene)	26		

Table 2. Weight Percent of TMA in MAO Solutions Using Proton NMR with an Internal Standard[a]

sample no.	TMA from NMR[b]	TMA from pyridine titration
1	5.2	7.3
2	2.1	3.3
3	1.7	2.3

[a] Dry mesitylene was used as the internal standard here. [b] The estimated precision is 4% relative at 1 standard deviation.

The addition of excess THF-d_8 followed by curve fitting to remove any residual overlap between the TMA and MAO peaks provides the basis for separation of the TMA and MAO resonances for quantitation. Use of acetonitrile or dioxane provides equivalent results. Excess THF-d_8 was used for the results reported here.

There are two approaches for proton NMR which can be used for the quantitation of TMA in MAO after the problem of peak overlap is solved using the THF-d_8 and curve-fitting procedures. One approach is to use a weighed internal standard and calculate the weight percent of TMA from the weight of sample and standard plus the integrals of standard and TMA. The second approach assumes all the solution species are known and the results are normalized to 100%. We report and discuss results of both methods.

Some care must be taken in choosing an internal standard for highly reactive chemicals, such as MAO and TMA. The internal standard must be inert toward TMA and MAO and have NMR peaks which do not overlap with any of the species in solution, including the solvent toluene. Mesitylene and 1,2-diphenylethane are two good choices. Chlorinated hydrocarbons must be avoided because of their reactivity with TMA and MAO.

Table 1 shows the T_1 values for 30% MAO in toluene with added mesitylene diluted 1:4 in THF-d_8. Clearly, the aromatic protons of toluene have the longest relaxation time. The relaxation times may seem unusually long for proton NMR. However, note that the MAO samples were prepared in the absence of oxygen and, therefore, a significant source of relaxation has been removed. Despite the length of the T_1 values, the sensitivity of the proton NMR experiment is such that data are obtained in less than 15 min for TMA analysis.

Table 2 compares the result of TMA determination using proton NMR and mesitylene as an internal standard with pyridine titration for the same samples. Note that the TMA concentration determined using proton NMR is substantially less than the pyridine titration results. High TMA values from pyridine titration are expected.[11,13] To determine whether all of the TMA is detected by this proton NMR procedure, we added additional known amounts of TMA to the samples in a "standard additions" approach. The added TMA plus TMA already present was completely recovered by the method. This work and others[11,13,15,16] point to high

Table 3. Data from the Normalized Weight Percent Analysis of MAO Solutions Using Proton NMR

	amt, wt %							
sample	TMA	TMA as Al	MAO	oil	toluene	CH_3 per Al on MAO	amt of gas, mmol/g of sample[a]	amt of gas, mmol/mol of Al[a]
ALB30	5.17	14.1	26.51	0.50	67.81	1.41	8.29	1.63
	(1.1)[b]	(1.1)	(0.21)	(2.2)	(0.03)	(0.31)	(0.27)	(0.25)
ALB20	3.50	14.5	17.48	0.34	78.69	1.41	5.51	1.64
ALB10	1.78	14.0	9.19	0.21	88.73	1.44	2.93	1.66
Aldrich 10%	4.01	30.4	7.79	0.85	87.35	1.48	3.55	1.94
ALB30D[c]	1.24	14.5	6.17	0.13	92.46	1.40	1.93	1.63
	[1.21][d]	[14.3]	[6.20]	[0.12]	[92.48]	[1.40]	[1.94]	[1.63]

[a] These values are also calculated from NMR data and the aluminum analysis. [b] The values shown in (parentheses) are the precision of the analysis in percent relative standard deviation. The precision was determined from 13 replicates obtained by 3 operators over 4 days. [c] The sample ALB30D is sample ALB30 diluted with dry toluene a factor of 4.277 times. [d] The values in [brackets] are the calculated numbers based on the dilution factors.

pyridine titration numbers from interaction of the pyridine with Lewis acid sites on the MAO. The pyridine appears to interact with sites on the MAO with reactivity similar to that of TMA.

It is important to recognize that more information can be obtained from the proton NMR analysis of MAO solutions. Just as we have measured the amount of TMA, the observed solvent (toluene) and residual amounts of process oil (a minor component left from the manufacturing process) can be quantitated. The only component remaining is the MAO, which can readily be calculated by difference. Direct measurement of the methyl groups of the MAO moiety is also possible. Subtraction of the TMA peak area from the entire integral for all methyl groups on aluminum, that is, the region between 0.0 and −1.3 ppm, yields the area of the MAO methyls. Quantitation of the MAO based on the methyl groups measured requires insight into the MAO unit formula. When we assumed an MAO repeating unit formula of $[-Al(CH_3)O-]_n$ with a ratio of 1:1:1 for CH_3, Al, and O, as is often proposed,[7] we found inconsistences between the MAO as measured using the NMR difference approach and the aluminum content as determined by wet chemical methods. The unit formula that fit all the data had a ratio of about 1.4:1:0.8 for methyls, aluminum, and oxygen, respectively.

From these results arose a simplified normalized NMR analytical method. This approach requires no internal standard and no weighings (for the NMR portion) and can be completed in less than 15 min. The amounts of TMA, MAO, toluene, and process oil are determined along with a measure of the number of methyl groups per aluminum atom in the MAO structure. Additionally, the number of millimoles of gas (methane) per gram of sample and moles of gas per mole of aluminum can be calculated. An independent method for the determination of the aluminum content is required. Accurate aluminum measurements are routinely made on MAO solutions by hydrolysis followed by wet chemical or ICP-AE spectroscopy methods. This aluminum content combined with the proton NMR measurements provide the complete analysis. This NMR procedure eliminates the need for the tedious and very time-consuming conventional gas evolution methods typically employed in the MAO industry.

Three assumptions are necessary in this NMR normalization approach.

(1) All the aluminum determined independently (ICP-AE or wet chemical) is present and is observed by the methyl groups of MAO or TMA. Species such as Al_2O_3, $AlCl_3$, $Al(OH)_3$, and free Al would not be seen by ^1H NMR; these are not expected, and most would be insoluble in toluene solution. Further, we find no evidence for such compounds in typical MAO preparations.

(2) All the components present are observed by ^1H NMR. Normalization methods require all components of significance to be measured. No nonproton materials, for example totally halogenated solvents and/or reactants, are used in the manufacturing process, and indeed none are expected. Very minor components which may not be detected would be insignificant in the normalization calculations.

(3) The valences of aluminum, oxygen and methyls in MAO are satisfied by the formula

$$[-(CH_3)_X AlO_{(3-X)/2}-]$$

Another plausible structural component of MAO is the hydroxyl group. Such groups have not been reported previously in commercial MAOs, and we find that treatment of MAO with various hydride reducing agents, such as lithium triethyl borohydride, yields insignificant amounts of hydrogen, indicating that very few, if any, hydroxyl groups were present. Additionally, neutron activation analyses for several MAO samples gave Al:O ratios of about 1:0.8 in MAO, consistent with the results obtained by this NMR procedure. Further, we find no evidence for methoxy groups in the proton NMR spectra of MAO samples unless they have been exposed to oxygen. Thus, we conclude that MAO is comprised of Al−methyl and Al−oxygen groups only.

Weight percentages are calculated according to the usual normalization methods. However, before these calculations are done, the number of methyl groups (X in the structure above) per aluminum of the MAO moiety must be determined. The aluminum content from independent analysis, plus the measured integrals for each component of concern, provide the necessary equations to solve for a discrete value for X. The molecular weight of the average MAO unit then is

$$MW_{MAO}\ (g/mol) = 51.0 + 7.0X \qquad (3)$$

Table 3 shows the results obtained for three typical MAO samples, labeled ALB30, ALB20, and ALB10, produced by Albemarle Corp. The Aldrich 10% sample was obtained from Aldrich Chemical, but the producer of this material is not known. Sample ALB30 was diluted with dry toluene to produce sample ALB30D. The calculated results based on the dilution factor are shown in brackets below the results obtained. The good agreement clearly shows that the method is indeed independent of the concentration of MAO and TMA. A precision study was performed using sample ALB30. This sample was prepared 13 times, and the NMR data were obtained at 400 MHz on the Bruker DPX400 by 3 operators on 4 different days. The percent relative standard deviation data are shown in parentheses below the sample values.

The precision and consistency of the data using the normalized proton NMR analysis are excellent. The relative standard deviation is about 1% at 5% TMA. The good agreement between calculated and found values for the diluted sample shows the method is indeed independent of MAO and TMA concentrations. The precision of the method is very good over a wide range of TMA concentrations and is good enough to allow detection of relatively subtle changes in MAO solution composition.

All the results on MAO samples, including that from Aldrich, show that the number of methyl groups on the aluminum of MAO (excluding TMA) is in the range of 1.4−1.5, while oxygen ranges from 0.75 to 0.80 atoms per aluminum. This method provides a characterization of the MAO moiety in toluene solution showing, on the average, 40−50% of the aluminum atoms have two methyl groups attached. This finding is contrary to many of the models found in the literature which predict or show a 1:1:1 ratio for CH_3, Al, and O. These “excess” methyl groups may contribute to MAO’s efficacy as a cocatalyst. It is suggested that they may provide a site or sites of activated methyl groups available for facile exchange with halogens or methyl groups on a metallocene catalyst. An MAO with a 1:1:1 ratio may be a very poor cocatalyst. These results suggest the formula for MAO is best represented as

$$[-(\mathrm{CH_3})_{1.4-1.5}\mathrm{AlO}_{0.80-0.75}-]_n$$

It is interesting to note that the Aldrich 10% MAO in Table 3 contains considerably more TMA than the comparable Albemarle MAO sample. The ALB samples contained 14−15% of the total aluminum as TMA, while the Aldrich contained about 30% as TMA. The role of TMA in MAO as a cocatalyst is not completely understood, but TMA activity as a cocatalyst is very much lower than MAO activity and ethylene polymerization productivity can be lower with increasing TMA concentrations.[18] Whatever TMA’s role, this method serves to accurately measure its presence and can be used to control its level in commercial MAO.

Conclusions

We have described here proton NMR methods to accurately measure the TMA content in MAO preparations. The normalized NMR method combines the aluminum content from an independent method to shed new insight into the MAO formula itself. The measurement of the number of methyl groups on aluminum in MAO is easily obtained. The NMR data allow the calculation of the amount of gas (methane) per gram of sample or per mole of aluminum that would be evolved if a lengthy and tedious gas evolution method were done (see Table 3).

This method provides a powerful means to monitor the MAO manufacturing process and the final MAO product. Although it by no means gives a complete description of the structure of MAO, it gives a new insight into its formula and structural elements. The method provides a time-efficient and cost-effective means to follow the level of TMA and help ensure a consistent MAO product.

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