

In Situ ^1H - and ^{27}Al -NMR Studies on Metallocene Catalyst Systems—Catalysts for Olefin Polymerization

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ABSTRACT: The process of partial hydrolysis reaction of TMA with water and the interaction of zirconocene dichloride (Cp_2ZrCl_2) with TMA, MAO, and the *in situ* partially hydrolyzed products of TMA were studied by *in situ* ^1H - and ^{27}Al -NMR spectroscopy. The ^1H -NMR spectra of MAO samples and the *in situ* hydrolyzed products of TMA with water under different conditions are different. A new peak at $\delta = -0.58$ ppm in ^1H -NMR spectra is observed, and is supposed to be due to the methyl resonance of MAO with low molecular weight. Alkylation reaction is observed between Cp_2ZrCl_2 and TMA, MAO, and the *in situ* hydrolyzed products of TMA, and TMA is supposed to be the actual alkylating agent. ^{27}Al -NMR studies show that MAO is tetra-coordinated. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 890–897, 2000

Key words: metallocene catalyst; *in situ* ^1H - and ^{27}Al -NMR; methylalumoxane (MAO); trimethylaluminum (TMA); *in situ* hydrolysis

INTRODUCTION

The discovery by Sinn and Kaminsky¹ that methylalumoxane (MAO) when combined with Group IV metallocenes gives extremely active catalysts for olefin polymerization, has made them potentially important industrial compounds. Depending on the substituent pattern and symmetry of metallocene compounds, they allow a strong control of regio- and stereoregularities and of molecular weight distributions of homopolymers, as well as the synthesis of copolymers with a uniform comonomer incorporation.

Despite the importance of alkylalumoxanes, in particular the methyl derivative (MAO), as highly active catalysts for the polymerization of a wide range of organic monomers, MAO, with widely

different activities as cocatalysts, can be found, depending on the synthetic method and reaction conditions. This was obviously closely related to the structure or composition of MAO. Various analysis methods have thus been developed to characterize MAO and its interaction with metallocene compounds. However, there is no generally accepted concept with regard to the effective structure of MAO and its reaction with metallocene compounds.

In the literature, MAO has been characterized by ^1H -NMR,² ^{13}C -NMR,³ ^{27}Al -NMR,^{4–6} IR,⁴ UV-Vis,³ and GPC,⁷ but all those characterizations were conducted with finished products, and therefore, can reflect neither the actual changes during the reaction nor the influence of hydrolysis conditions on structure or composition.

With the purpose of verifying the structure analysis on MAO with a different system, exploring the actual changes in components during the reactions and further interpreting the polymer-

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ization results, the partial hydrolysis reaction of trimethylaluminum (TMA) with water and the interaction of metallocene with MAO are monitored by ^1H - and ^{27}Al -NMR spectroscopy *in situ*.

EXPERIMENTAL

Materials

TMA and Cp_2ZrCl_2 were respectively purchased from the Ethyl Company and Aldrich Company, and MAO (D) from the ACROS Company (wt/v 10% toluene solution), and used as received. MAO (A, B, C) were prepared by using the conventional method under different conditions.

Benzene was dried over sodium and benzophenone, and distilled before use. Benzene-d was used as received.

All operations were carried out under dry nitrogen atmosphere.

The average molecular weights of MAO and the *in situ* hydrolyzed product of TMA with H_2O were determined by cryoscopy using benzene as the solvent.

Nuclear Magnetic Resonance (NMR)

^1H - and ^{27}Al -NMR spectra were obtained with a Bruker AM-500 MHz spectrometer (500 MHz ^1H , 130.3 MHz ^{27}Al).

The operating conditions of ^1H -NMR were as follows: pulse repetition = 2.0 s, number of scans = 64, spectral width = 10 KHz, internal standard $\text{C}_6\text{D}_6 = 7.15$ ppm, with benzene (0.5 mL) + C_6D_6 (0.1 mL) as solvents.

The operating conditions of ^{27}Al -NMR were as follows: pulse repetition = 0.1 s, number of scans = 1000, spectral width = 42 KHz, external standard $\text{Al}(\text{H}_2\text{O})_6^{3+} = 0.00$ ppm (in $\text{Al}_2(\text{SO}_4)_3$ aq.), with benzene (0.5 mL) + C_6D_6 (0.1 mL) as solvents.

A typical MAO sample was prepared in a glovebox by loading a 2-mm NMR tube with a certain amount of MAO benzene solution, and to which a certain amount of Cp_2ZrCl_2 benzene solution was introduced after the NMR analysis.

The *in situ* hydrolysis reaction of TMA was conducted by direct reaction with water in benzene. After a certain reaction time, 0.5 mL sample solution and 0.1 mL C_6D_6 were introduced into a 2-mm NMR, and to which a certain amount of Cp_2ZrCl_2 benzene solution was introduced after the NMR analysis.

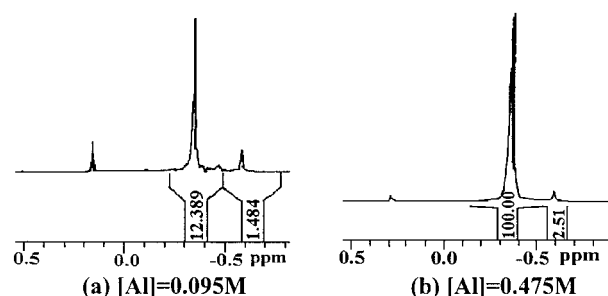


Figure 1 ^1H -NMR spectra of TMA at two different concentrations.

RESULTS AND DISCUSSION

On the basis of conventional ^1H - and ^{27}Al -NMR studies of TMA and MAO, the *in situ* hydrolysis reaction of TMA with water as well as its complex with Cp_2ZrCl_2 were further monitored by *in situ* ^1H - and ^{27}Al -NMR spectroscopy, to obtain useful data to interpret the formation of active site for polymerization.

^1H - AND ^{27}Al -NMR STUDY OF TMA AND MAO

TMA

The ^1H -NMR spectra of TMA at two concentrations are shown in Figure 1. Both have a sharp singlet at $\delta = -0.36$ ppm assigned to the methyl protons of TMA, as already reported by Resconi et al.,² and another small one at $\delta = -0.58$ ppm not reported in the published literature was also observed, which will be discussed later.

The ^{27}Al -NMR spectrum of TMA is shown in Figure 2.

The broad resonance at approximately 70 ppm is assigned to that of the NMR tube, because it is also observed for the NMR tube without any sample. This resonance was also observed by Nekhaeva et al.,⁴ while not observed by Sugano et al.⁵ and Mason et al.⁶ The chemical shift of TMA is approximately 154 ppm, which confirms the result reported by Sugano et al.⁵ and Mason et al.⁶

MAO

To demonstrate whether MAOs from different sources were identical, four MAO samples were investigated by ^1H -NMR spectroscopy, three of which were prepared in this laboratory (A, B, C)

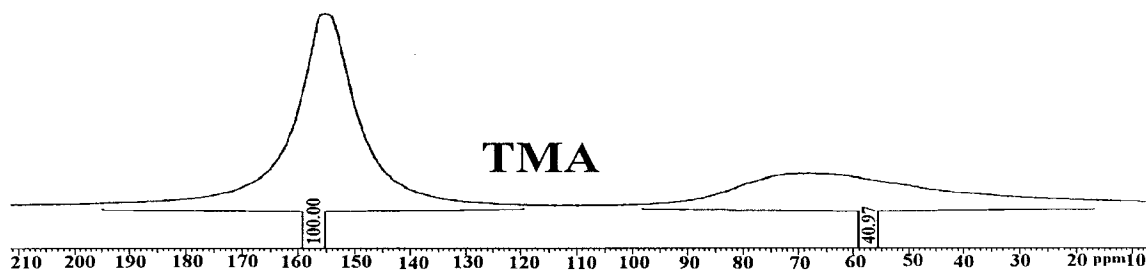


Figure 2 ^{27}Al -NMR spectrum of TMA ($[\text{Al}] = 0.475 \text{ M}$).

and the other one purchased from the ACROS Company (D), as shown in Figure 3.

All samples displayed a broad resonance at $\delta = -0.20 \text{ ppm}$ assigned to the methyl protons of the oligomeric $[\text{O}-\text{Al}(\text{CH}_3)-]$ compounds, confirming the result reported by Resconi et al.²

A sharp singlet at $\delta = -0.36 \text{ ppm}$ assigned to the free $\text{Al}_2(\text{CH}_3)$ (TMA) was observed in Figure 3(a), (b), and (d), whereas another singlet at $\delta = -0.58 \text{ ppm}$ was observed in Figure 3(b), (c), and (d), and its relative content was 4.41, 4.43, and 6.09%, respectively.

The resonance at $\delta = -0.58 \text{ ppm}$ has not been reported for MAO in previous literature.

Ueyama et al.⁸ first observed that the proton resonance of dimerized MAO at $\delta = -0.95 \text{ ppm}$, whereas Resconi et al.² reported that the resonance of MAO with high molecular weight was observed at $\delta = -0.20 \text{ ppm}$. The resonance at δ

$= -0.58 \text{ ppm}$ was intermediate between that of the protons of MAO with high molecular weight (-0.20 ppm) (1) and that of $\text{Me}_2\text{AlOAlMe}_2$ and thus was assigned to MAO with low molecular weight (2) (-0.95 ppm), corresponding to the middle stage of the reaction from low molecular weight to high molecular weight. The content of this intermediate compound varies with different samples.

^1H -NMR AND ^{27}Al -NMR STUDY OF THE *IN SITU* HYDROLYSIS REACTION OF TMA WITH WATER

^1H -NMR

As stated before, it will be very beneficial for the study of polymerization mechanism with metallocene catalysts if the process of TMA hydrolysis to prepare MAO is explored.

Influence of the Hydrolysis Concentration of TMA

The ^1H -NMR spectra of the *in situ* hydrolyzed products of TMA at two different TMA concentrations are shown in Figure 4.

At lower concentrations ($[\text{Al}] = 0.095 \text{ M}$), no broad resonance at $\delta = -0.20 \text{ ppm}$ typical of MAO

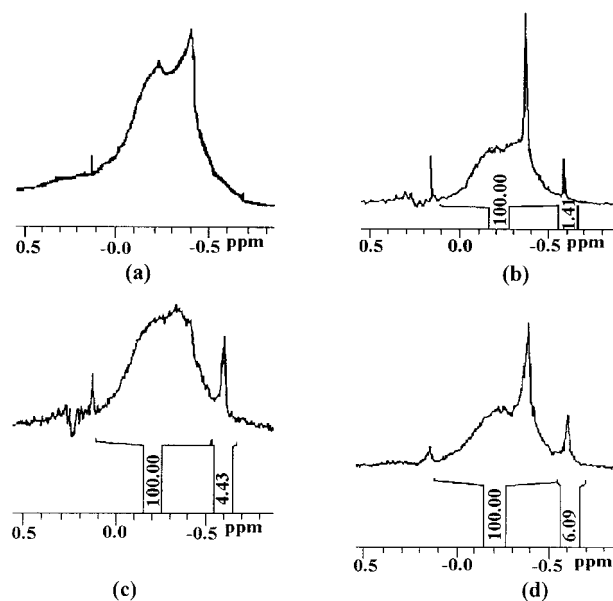


Figure 3 ^1H -NMR spectra of three MAO samples conventionally synthesized under different conditions (a, b, c) and a MAO sample commercially purchased (d).

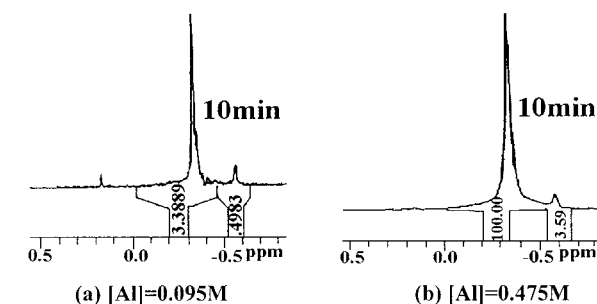


Figure 4 ^1H -NMR spectra of the *in situ* partially hydrolyzed products of TMA with water at different concentrations (40°C).

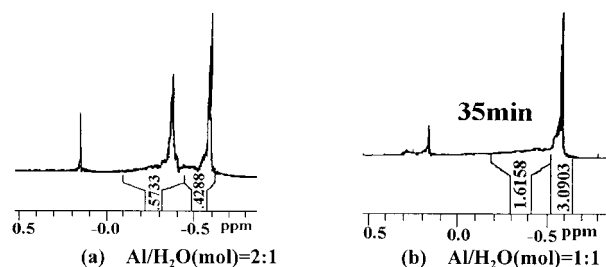


Figure 5 $^1\text{H-NMR}$ spectra of the *in situ* partially hydrolyzed products of TMA with water at different $\text{Al}/\text{H}_2\text{O}$ (mol) ratios ($[\text{Al}] = 0.095\text{ M}$, 40°C , 35 min).

with high molecular weight (**1**) is observed, but two sharp singlets at $\delta = -0.36\text{ ppm}$ and $\delta = -0.58\text{ ppm}$ are observed, assigned respectively to the methyl groups of the residual free TMA and MAO with low molecular weight (**2**). This is appreciably different from that of MAO conventionally synthesized [Fig. 2(a), (b), and (c)], owing to the fact that the hydrolysis reaction rate is slow and the molecular weight of the products is low, and thus the content of MAO with high molecular weight (**1**) is low and could not be observed at low concentration. The average molecular weight obtained with the cryscopic method of the *in situ* hydrolyzed product of TMA after 35 min is about 300 g/mol, while that of MAO(A) is about 1500 g/mol. This demonstrates that the molecular weight of the *in situ* hydrolyzed product of TMA is low.

At higher concentration ($[\text{Al}] = 0.475\text{ M}$), a relatively broad peak at $\delta = -0.36\text{ ppm}$, which is different from the sharp singlet of TMA [Fig. 1(b)], is observed. The broad band is due to the high concentration and the relatively high molecular weight. The down-field shift is due to its relatively higher molecular weight than the product at low concentration. On the other hand, the band at $\delta = -0.58\text{ ppm}$ is not obvious, which is perhaps because the hydrolysis rate is relatively fast and the molecular weight also grows fast and so the relative content of MAO with low molecular weight (**2**) is low at high concentration.

It may be concluded that at relatively lower concentration, the spectrum mainly displays the resonance of the residual TMA and MAO with low molecular weight (**2**), and at higher concentration it displays that of MAO with relatively high molecular weight (**3**). It can also be concluded that the hydrolysis concentration of TMA is important for the molecular weight of MAO after the same reaction time.

Influence of $\text{Al}/\text{H}_2\text{O}$ (mol) Ratios

The $^1\text{H-NMR}$ spectra of the *in situ* partially hydrolyzed products of TMA with water at different $\text{Al}/\text{H}_2\text{O}$ (mol) ratios are shown in Figure 5.

The $^1\text{H-NMR}$ spectra vary greatly with $\text{Al}/\text{H}_2\text{O}$ (mol) ratios. No resonance is observed when $\text{Al}/\text{H}_2\text{O}$ (mol) is 1 : 2.6, owing to the fact that TMA was overhydrolyzed, and thus, the contents of the residual TMA and MAO are low. The relative content of MAO with low molecular weight (**2**) is lower when $\text{Al}/\text{H}_2\text{O}$ (mol) is 2 : 1, compared to the one when $\text{Al}/\text{H}_2\text{O}$ (mol) is 1 : 1, because the content of the residual TMA is relatively higher when TMA is in excess.

So it may be concluded that the $\text{Al}/\text{H}_2\text{O}$ (mol) ratio is one of the main factors influencing the composition of the hydrolysis product.

Influence of Hydrolysis Reaction Time ($t_{\text{Al}+\text{H}_2\text{O}}$)

The $^1\text{H-NMR}$ spectra of the *in situ* partially hydrolyzed products of TMA with H_2O with different reaction times and at different concentrations are shown in Figure 6.

At $[\text{Al}] = 0.095\text{ M}$, the $^1\text{H-NMR}$ spectra are fairly different with different reaction times, owing to the change of the contents of the residual TMA and MAO with low molecular weight (**2**).

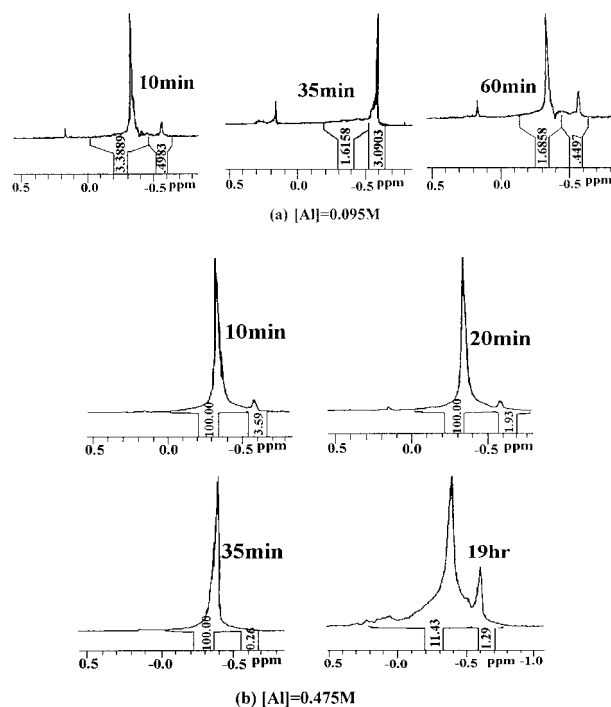


Figure 6 $^1\text{H-NMR}$ spectra of the *in situ* partially hydrolyzed products of TMA with water after different reaction time at different concentrations (40°C).

Table I Relative Contents of the Peak Area of $\delta = -0.58$ ppm ($\Delta 1$) to That of $\delta = -0.36$ ppm ($\Delta 2$) with Different Hydrolysis Reaction Times ($t_{\text{Al}+\text{H}_2\text{O}}$) at $[\text{Al}] = 0.475$ M

No.	$t_{\text{Al}+\text{H}_2\text{O}}$ (min)	$\Delta 1/\Delta 2$ (%)
1	10	3.59
2	20	1.93
3	35	0.26
4	60	0.16
5	120	0.37
6	19 h	8.05

At $[\text{Al}] = 0.475$ M, the $^1\text{H-NMR}$ spectra are nearly the same after different reaction times in 2 h, except that the relative content of (2) varied slightly. The relative contents of (2) after different reaction times are shown in Table I. It decreases with the reaction time within a short period of time while maintaining unchanged after 35 min, but after 19 h it increases again due to the undissolved products formed after a long reaction time.

So the composition of hydrolysis product varies greatly with reaction time at lower TMA concentrations while slightly at higher TMA concentration.

Influence of Hydrolysis Reaction Temperature (T)

The $^1\text{H-NMR}$ spectra of the *in situ* partially hydrolyzed products of TMA with water at $[\text{Al}] = 0.475$ M at different reaction temperatures are shown in Figure 7.

The relative content of (2) varies appreciably with the reaction temperatures. It is relatively lower at 10°C because the reaction rate is slow at lower temperatures. At 40°C , it increases due to the relatively fast reaction rate, while at 60°C it decreases again, perhaps because TMA reacts violently with water at high temperatures, thus leading to the formation of undissolved products. In the meantime, the molecular weight of (2) increases rapidly at higher temperatures, which is confirmed by the broad band at $\delta = -0.36$ ppm at 60°C .

It can thus be concluded that the compositions of MAO under different conditions are different, and that the peaks at -0.20 and -0.36 ppm in $^1\text{H-NMR}$ spectroscopy stand for MAO with different molecular weights. The hydrolysis concentration of TMA mainly influences the molecular weight of the product, while the $\text{Al}/\text{H}_2\text{O}$ (mol)

ratio, reaction time, and reaction temperature mainly influence its composition.

$^{27}\text{Al-NMR}$ Study of *In Situ* Hydrolysis Reaction of TMA with Water

Benn et al.⁹ reported that there was a simple correlation between the coordination number of Al atoms and $^{27}\text{Al-NMR}$ chemical shift δ (^{27}Al) in organoaluminum compounds. For the Al atom with four coordinated numbers, its $^{27}\text{Al-NMR}$ chemical shift is in 140–170 ppm.

Sugano et al.⁵ showed that the ^{27}Al chemical shift of MAO was approximately 154 ppm, which was due to the tetra-coordinated structure. They also found that the line width of MAO increased with the molecular weight of MAO.

The $^{27}\text{Al-NMR}$ spectra of the *in situ* partially hydrolyzed products of TMA with water after different reaction times are shown in Figure 8.

The broad resonance at approximately 70 ppm is assigned to that of the NMR tube. The chemical shifts of the *in situ* partially hydrolyzed products of TMA with water are nearly the same at approximately 155 ppm after different reaction times, which leads to the conclusion that it is also tetra-coordinated.

The line width (W) is shown in Table II.

The line widths of the *in situ* partially hydrolyzed products of TMA with water are narrower than that reported by Sugano et al.,⁵ and vary slightly with reaction time within a short period of time, which means that the molecular weights are low and nearly the same. But after 19 h, it increases a bit, mainly due to the increase of its molecular weight after a long time.

With the *in situ* partially hydrolyzed products of TMA as cocatalyst, the *in situ* ethylene polymerization activity of Cp_2ZrCl_2 is high,¹⁰ so it can be concluded that high activity can also be achieved with MAO of which proton resonance is at -0.58 ppm. This means that the proton resonance at -0.58 ppm is valuable for ethylene polymerization.

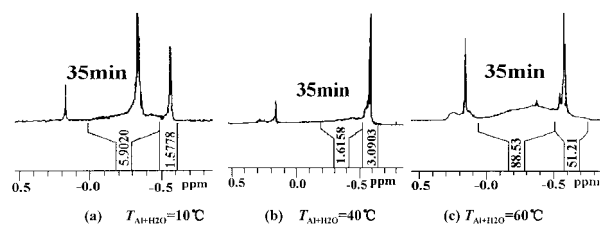


Figure 7 $^1\text{H-NMR}$ spectra of the *in situ* partially hydrolyzed products of TMA with water at different temperature ($[\text{Al}] = 0.095$ M, 35 min).

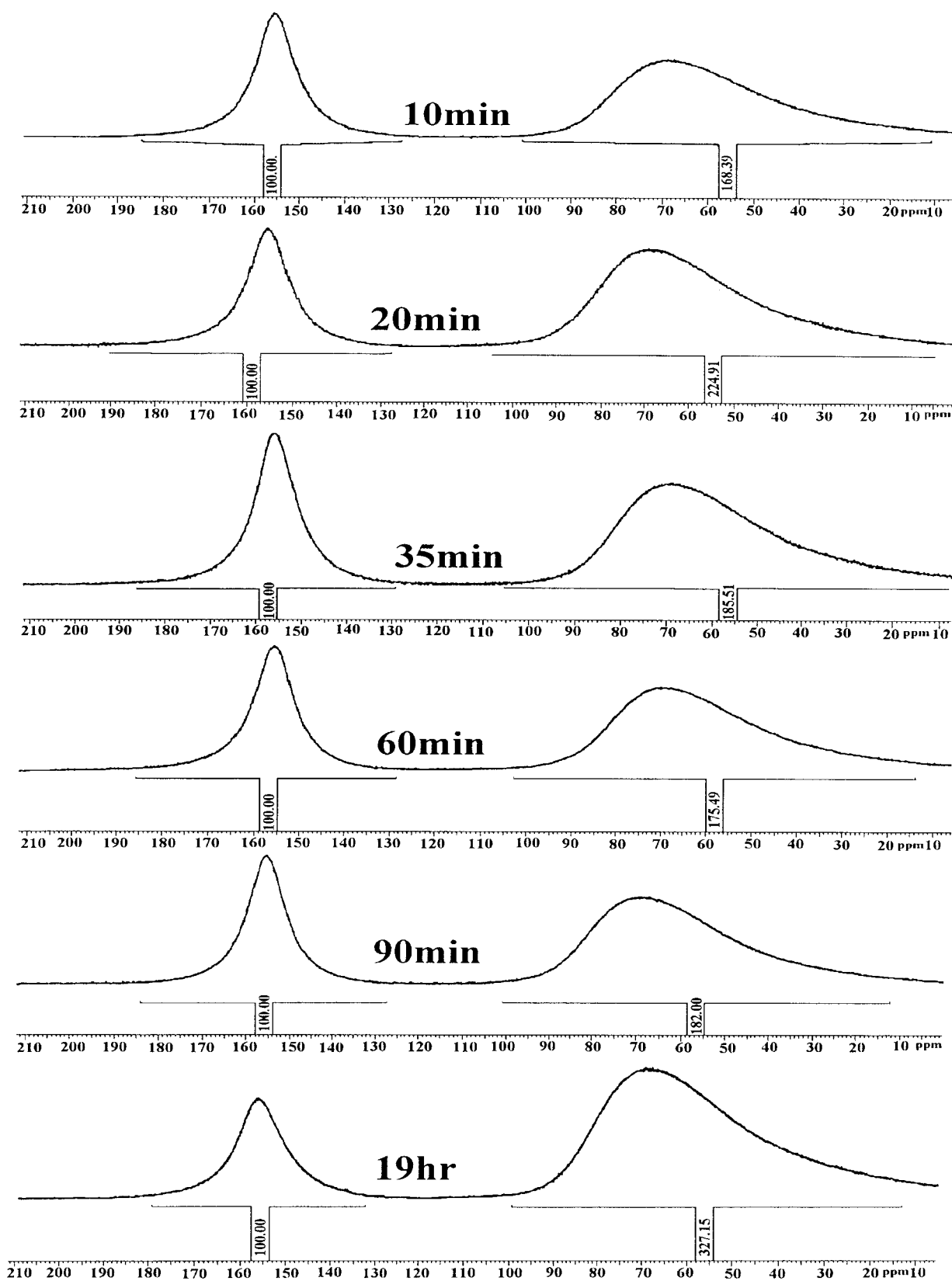


Figure 8 ^{27}Al -NMR spectra of the *in situ* partially hydrolyzed products of TMA with water after different reaction time ($[\text{Al}] = 0.475 \text{ M}$, 40°C).

Table II ^{27}Al -NMR Parameters of TMA, MAO, and the *In Situ* Partially Hydrolyzed Products of TMA with Water Under Different Conditions ($[\text{Al}] = 0.475\text{ M}$)

No.	Conditions ($[\text{Al}]$, $t_{\text{Al}+\text{H}_2\text{O}}$)	δ (ppm)	$W_{1/2}$ (Hz) (at 130.3 MHz)	$W_{1/2}$ (Hz) (at 70.4 MHz)	A_{155}/A_{70}
1	TMA (2.5M)	154	1358	734	18.87
2	TMA (0.475M)	155	1509	815	2.44
3	TMA + H ₂ O (0.475M, 10 min)	155	1660	897	0.59
4	TMA + H ₂ O (0.475M, 20 min)	155	1660	897	0.44
5	TMA + H ₂ O (0.475M, 35 min)	155	1660	897	0.54
6	TMA + H ₂ O (0.475M, 60 min)	155	1660	897	0.57
7	TMA + H ₂ O (0.475M, 90 min)	155	1660	897	0.55
8	TMA + H ₂ O (0.475M, 19 hr)	156	1886	1019	0.35
Ref. 5	TMA	153		750	
	MAO ($n = 14$) ^a	154		1400	
	MAO ($n = 20$) ^a	154		1650	
	MAO ($n = 21$) ^a	154		1690	

^a n is the oligmerization degree of MAO.

^1H -NMR STUDIES ON THE INTERACTIONS OF Cp_2ZrCl_2 WITH TMA, MAO, AND THE *IN SITU* HYDROLYZED PRODUCTS OF TMA WITH WATER

Cp_2ZrCl_2 + TMA

The ^1H -NMR spectrum, after mixing of TMA and Cp_2ZrCl_2 benzene solution, is shown in Figure 9.

Besides the signal of the starting material (Cp_2ZrCl_2) at $\delta = 5.89$ ppm, two new singlets at $\delta = 5.75$ ppm and $\delta = 0.43$ ppm are observed, assigned respectively to the cyclopentadienyl and methyl groups of Cp_2ZrMeCl . A sharp resonance at $\delta = -0.33$ ppm was also observed. This resonance was slightly shifted with respect to that of TMA, perhaps owing to the presence of a mixture of TMA and $\text{Al}_2(\text{CH}_3)_4\text{Cl}_2$.

These results lead to the assumption that Cp_2ZrCl_2 can be partially monoalkylated by TMA.

Cp_2ZrCl_2 + MAO

As shown in Figure 10, the sharp singlet of Cp_2ZrCl_2 at $\delta = 5.89$ ppm is also split into two singlets at $\delta = 5.89$ ppm and 5.75 ppm on com-

plexing with MAO; in the meantime, a new small singlet at $\delta = 0.43$ ppm is observed.

The sharp resonance of the free TMA in MAO at $\delta = -0.36$ ppm, is practically missing, while on the contrary, the broad signal at $\delta = -0.20$ ppm of MAO, does appear.

These results lead to the assumption that Cp_2ZrCl_2 is partially monoalkylated by the free TMA in MAO, as already reported by Cam et al.¹¹

Cp_2ZrCl_2 + *In Situ* Hydrolyzed Products of TMA with Water

As shown in Figure 11, the sharp singlet at $\delta = 5.89$ ppm of Cp_2ZrCl_2 is also split into two singlets at $\delta = 5.89$ ppm and 5.75 ppm on complexing with the *in situ* partially hydrolyzed products of TMA with water, and a new singlet at $\delta = 0.44$ ppm was also observed.

The sharp singlet of the free TMA initially present at $\delta = -0.36$ ppm disappears and a new singlet at $\delta = -0.33$ ppm is observed, while the singlet at $\delta = -0.58$ ppm corresponding to the methyl group of (2) remains unchanged.

These results lead to the assumption that Cp_2ZrCl_2 is also partially monoalkylated by the *in*

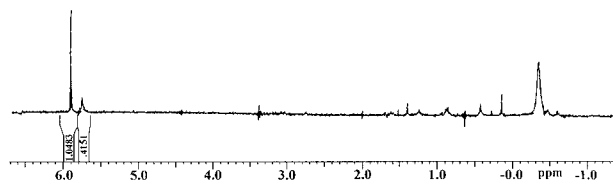


Figure 9 ^1H -NMR spectrum of Cp_2ZrCl_2 + TMA ($\text{Al}/\text{Zr} = 24$).

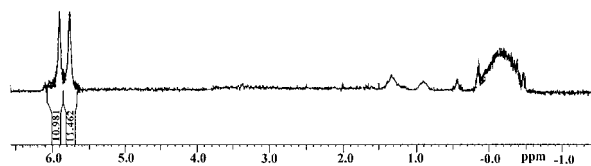


Figure 10 ^1H -NMR spectrum of Cp_2ZrCl_2 + MAO ($\text{Al}/\text{Zr} = 120$).

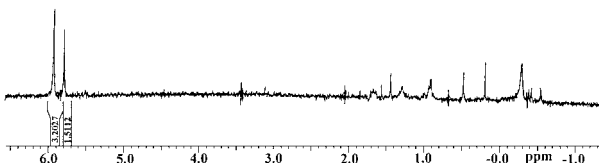


Figure 11 $^1\text{H-NMR}$ spectrum of Cp_2ZrCl_2 + *in situ* partially hydrolyzed products of TMA with water ($\text{Al/Zr} = 24$).

situ partially hydrolyzed products of TMA with water, and the actual alkylating agent is free TMA in it.

From the $^1\text{H-NMR}$ studies on the interactions of Cp_2ZrCl_2 with TMA, MAO, and the *in situ* partially hydrolyzed products of TMA with water above, it is verified that Cp_2ZrCl_2 can be partially monoalkylated by each of them, but the actual alkylating agent is TMA.

But with TMA as the cocatalyst, the olefin polymerization activity of Cp_2ZrCl_2 was very low, so it could be concluded that methylation was not the rate-determining step for olefin polymerization.

CONCLUSION

1. A new peak at $\delta = -0.58$ ppm corresponding to the methyl protons of MAO with low molecular weight in $^1\text{H-NMR}$ is observed. Along with the resonance at -0.20 ppm for MAO with high molecular weight reported in the literature and Sinn's proposition,¹² it will be useful to control the MAO production and exploit the mechanism investigation.
2. The $^1\text{H-NMR}$ spectra of four MAOs are different, which means that the compositions of MAO under different conditions are different.
3. The $^1\text{H-NMR}$ spectra of the *in situ* partially hydrolyzed products of TMA with water under different conditions are different, of which the molecular weights are low. High

polymerization activity can also be achieved with MAO, which displayed resonance at -0.58 ppm, so the observed peak at -0.58 ppm is important.

4. $^{27}\text{Al-NMR}$ investigations show that the *in situ* hydrolyzed products of TMA with H_2O are tetra-coordinated, and their molecular weights are low. High polymerization activity could also be achieved with MAO with low molecular weight as the cocatalyst, which is different from the result reported by Giannetti et al.³
5. Cp_2ZrCl_2 can be partially monoalkylated by TMA, MAO, and the *in situ* partially hydrolyzed products of TMA with water. The TMA in them is the actual alkylating agent, which confirms the result reported by Cam et al.,⁷ and methylation was not the rate-determining step for olefin polymerization.

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