NMR studies on the reactivity of aluminium compounds with an unsaturated alcohol

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Abstract

The interaction of an unsaturated alcohol, 10-undecen-1-ol ($CH_2=CH(CH_2)_8CH_2OH$), with aluminium compounds $AlEt_3$ and MAO (30% toluene solution) has been studied. The reactions were investigated at room and elevated temperatures and followed by ^1H, ^{13}C and ^{27}Al NMR-spectroscopy. The alcohol end group of 10-undecen-1-ol reacts quantitatively with aluminium alkyls ($AlEt_3$ as well as $AlMe_3$ present in MAO), liberating alkane gas and forming in the first step the dimeric complexes $[R'_2AlOR]_2$ and $[R'Al(OR)_2]_2$ (R' = Me, Et; R = 10-undecen). In the presence of excess 10-undecen-1-ol the alkyl aluminium alkoxides are found to generate tetrameric aluminium compounds, $Al_4(R')_n(OR)_{12-n}$ (n = 6,4) containing six-coordinated central aluminium surrounded by six oxygen atoms. The structural assignment is based on ^{13}C as well as ^{27}Al NMR, where narrow resonances at 8.21 and 7.3 ppm are observed for $Al_4Me_6(OR)_6$ and $Al_4Et_6(OR)_6$, respectively. Besides the above reaction between the alcohol moiety and AlR_3 another effect was also visible in the reaction of 10-undecen-1-ol with MAO. Broad carbon resonances were observed in ^{13}C NMR at the downfield side of the normal olefinic and alkoxy carbon resonances, indicating some kind of interaction of methylaluminoxane with the corresponding carbon atoms.

Keywords: Aluminum alkyl; Methylaluminoxane; Unsaturated alcohol; NMR

1. Introduction

Aluminium compounds are of great importance since they are widely used as cocatalysts in a variety of important industrial processes catalyzed by transition metals, such as Ziegler–Natta and metallocene alkene polymerizations [1]. The ability of aluminium alkyl compounds, such as methylaluminoxane (MAO), to alkylate, to reduce and to function as a Lewis acid, is the main reason for their use in the chemical industry.

Aluminium compounds react very easily with electron donors, such as alcohols [2], diols [3], ethers [4], ketones [5] and silyl ethers [6,7]. We have studied reactivity of aluminium compounds $AlEt_3$ and MAO with an unsaturated alcohol, 10-undecen-1-ol, containing besides the alcohol moiety an alkene group. These two functional groups are separated by a spacer of a $(CH_2)_9$ chain.

We have previously studied synthesis of

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functional polyolefins through direct poly-merization of ethylene and 10-undecen-1-ol with a soluble metallocene–MAO catalyst [8]. The polymers obtained from the copolymerizations possess broad molar mass distributions. At a moderate alcohol concentration the molar mass distribution curve becomes bimodal, indicating the presence of two or more catalytically active sites. The incorporation of the polar comonomer in the polyethylene backbone can be deduced from the results of the melt flow indices of the copolymers, which increase on the addition of the polar compounds.

For the interpretation of the results from the copolymerization of ethene and 10-undecen-1-ol we planned a study aiming at the resolution of the interaction mechanism between the polar olefin, 10-undecen-1-ol and MAO. Triethylalu-minium was used first as the aluminium reagent in order to understand the reaction between 10-undecen-1-ol and an aluminium alkyl, since the toluene solution of MAO contains besides the various methylaluminoxane oligomers trimethylaluminium [9]. The alcohol/aluminium molar ratio of the starting materials is an impor-tant factor in the reaction. When the molar ratio is proper, a tetramer containing a six-coordi-nated aluminium surrounded by six oxygen atoms is formed.

2. Experimental

All the solvents were purified and dried with the standard techniques [10]. The polar olefin, 10-undecen-1-ol (Aldrich), and aluminium alkyls, $AlEt_3$ (Aldrich) and MAO (30% solution in toluene, Witco), were used as received.

All the reactions were studied straight in 10 mm NMR-tubes specially designed for sealing. Aluminium alkyls are both air and moisture sensitive, so all the NMR samples were pre-pared under nitrogen in a glove box. Weighed amounts of aluminium alkyl compounds were added dropwise to a solution of 10-undecen-1-ol (weighed) in toluene-D_8. The tubes were closed

with NMR Tube Tip-Off Manifold (Wilmad) and sealed outside the glove box using a butane flame.

The ^1H, ^{13}C and ^{27}Al spectra were recorded on a Bruker AM-250 spectrometer operating at 62.9 MHz for ^{13}C-NMR and at 65.18 MHz for ^{27}Al-NMR. The reaction solution was measured at ambient temperature. Quantitative proton-de-coupled ^{13}C spectra were measured with the gated decoupling technique. The ^1H and ^{13}C chemical shifts were referenced to the residual CH_3 peak of toluene (δ 2.09 ppm for ^1H and δ 21.4 ppm for ^{13}C). The ^{27}Al chemical shifts were referenced to an external 1.5 M solution of $Al(NO_3)_3$ in D_2O. The multinuclear probehead used in the ^{27}Al NMR measurements gave a broad background signal at 62 ppm. The heating of samples was done in a water thermostat. After the heating, the NMR spectra were mea-sured as soon as the samples were cooled down to room temperature. The dissolved gas was not removed from the NMR samples and therefore for the reactions of 10-undecen-1-ol with $AlEt_3$ the sharp signals due to ethane were observed in ^1H and ^{13}C NMR at 0.75 ppm and 6.95 ppm, respectively.

3. Results and discussion

The reactions between 10-undecen-1-ol and aluminium alkyls, $AlEt_3$ and MAO, were stud-ied at room and elevated temperatures and fol-lowed by ^1H, ^{13}C and ^{27}Al NMR-spectroscopy. The structure proposals for the products were done with combination of ^1H and ^{13}C NMR as well as with ^{27}Al NMR, where the chemical shifts of ^{27}Al resonances give an indication of the number of alkoxy ligands and the coordina-tion number of aluminium atoms [11].

3.1. Reaction between Et_3Al and 10-undecen-1-ol

Triethylaluminium was used first as the alu-minium compound in order to understand the

reaction between aluminium alkyls and 10-undecen-1-ol. The reaction was studied using three different mole ratios ($ROH/AlEt_3 = 1{:}3$, 1:1 and 2:1). The rapid and vigorous reaction occurred immediately when a toluene solution of the aluminium alkyl was added to the toluene solution of alcohol. Addition of $AlEt_3$ was done as fast as the evolution of ethane gas permitted (ca. 5 min).

The reaction between 10-undecen-1-ol and Et_3Al in toluene in a 1:3 stoichiometry produced $[Et_2AlOR]_2$ (R = 10-undecene) as the main product (Eq. (1)):

$$Al_2Et_6 + 2ROH \rightarrow [Et_2AlOR]_2 + 2EtH \qquad (1)$$
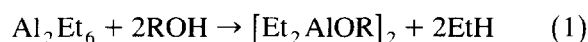
R = 10-undecene

All of the alcohol had reacted since there was no OH signal (at 4.46 ppm) visible in the ^1H-spectrum and the signal at 62.4 ppm due to the CH_2OH-group of the parent alcohol in the ^{13}C-spectrum was no longer present (Table 1). Instead, in the ^{13}C-spectrum of this reaction solution two new CH_2O signals at 63.9 and 65.8 ppm could be observed. The first of these two signals can be assigned to $[Et_2AlOR]_2$ on the basis of the integrated intensity ratio of the ^{13}C signals of CH_2O and EtAl. The resonance

at 65.8 ppm is assumed to be due to $[EtAl(OR)_2]_2$, the formation of which could be explained by the disproportionation reaction (Eq. (2)). This reaction is facilitated by the formation of the triethylaluminium dimer [12]:

$$2[Et_2AlOR]_2 \rightleftharpoons [EtAl(OR)_2]_2 + Al_2Et_6 \qquad (2)$$
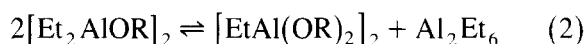
R = 10-undecene

In the 1:3 molar ratio the amount of $[EtAl(OR)_2]_2$ is rather small when compared to that of $[Et_2AlOR]_2$ ($[Et_2AlOR]_2/[EtAl(OR)_2]_2 = 5.8{:}1$). Moreover, on prolonged heating at 60°C the amount of $[EtAl(OR)_2]_2$ decreased significantly ($[Et_2AlOR]_2/[EtAl(OR)_2]_2 = 21{:}1$). Dialkoxyalkylaluminium reacts with alcohol with much greater difficulty than the first alkoxy derivate, $[Et_2AlOR]_2$ [13]. There was no evidence of this reaction observed in the NMR-spectra measured from this sample.

The ^{27}Al-spectrum of the 1:3 reaction solution shows only one broad signal at 157 ppm due to $[Et_2AlOR]_2$ and the excess $AlEt_3$. This broad resonance prevents an accurate structural proposal for $[Et_2AlOR]_2$. The chemical shift range would indicate the dimeric nature of $[Et_2AlOR]_2$ [13,14].

Table 1

NMR characterization of reactions of AlEt3 with 10-undecen-1-ol [a]

Sample	10-undecen-1-ol (mmol)	AlEt_3 (mmol)	^1H NMR		^{13}C NMR					^{27}Al NMR [b]	
			OCH_2	CH=CH	C_1	C_2	C_3	Al-CH_2CH_3	Al-CH_2	δ(Al)	ω_{1/2} (Hz)
10-undecen-1-ol			3.58(m)	139.10 114.62,114.43	62.43	33.20	26.93				
AlEt_3								8.97, 8.86	0.51	170	3000
ROH:AlEt_3 = 1:3	1.73	5.32	3.48(t) 3.45(m)	139.20 114.42	65.76 63.94	33.20 32.71	26.01 25.92	9.05, 8.93 8.82	0.50 −0.56	158	3900
ROH:AlEt_3 = 1:1	3.31	3.11	3.50(t) 3.75(m)	139.1, 139.06 114.45	65.76 64.41 63.91	33.44 33.17	26.24 25.96	10.04, 9.07	1.56 −0.57	155 7.29	broad 150
ROH:AlEt_3 = 2:1	4.12	2.04	3.75(m) 3.89(m)	139.11, 139.05 114.46	64.40 63.00	33.43 33.09	26.48 26.23	10.05, 10.02	1.56	7.20	210

[a] The NMR spectra were measured in toluene-D8 at room temperature.

[b] The background signal of the probehead at 62 ppm has been omitted.
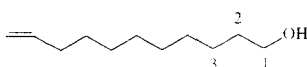
The amount of alcohol was increased in the next two samples. The ROH/AlEt$_3$ molar ratio in the second reaction was increased to 1:1. This showed remarkable changes in all recorded NMR spectra. The most significant change could be seen in the ^{27}Al-spectrum. The broad signal at 157 ppm was now very weak and one very sharp signal had appeared at 7.3 ppm. The last resonance gave a reason to propose that in solution there is six-coordinated aluminium species present, the formation of which could be explained by Eq. (3) [13]:

$$3[Et_2Al(OR)]_2 + [Al(OR)_3]_2$$
$$\rightarrow 2[Al_4Et_6(OR)_6] \qquad (3)$$
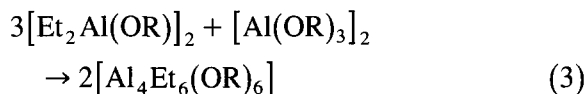
R = 10-undecene

Formation of a stable compound containing a central six-coordinated aluminium atom is the driving force for this reaction. There may be
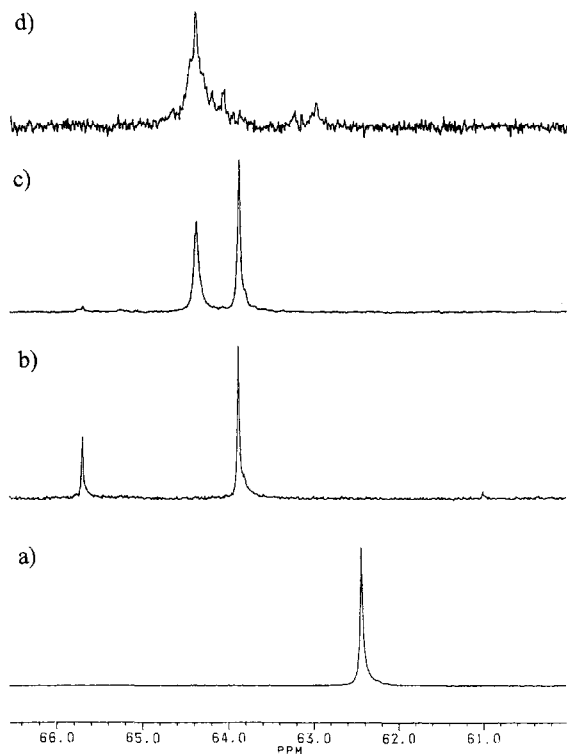

Fig. 2. Structure of tetrameric Al$_4$Et$_6$(OR)$_6$ (R = 10-undecene).

other pathways for formation of [Al$_4$Et$_6$(OR)$_6$], since reorganization processes are well known for organoaluminium compounds. One possible path from [Et$_2$Al(OR)]$_2$ and [EtAl(OR)$_2$]$_2$ can be excluded on the basis of the observations made during the first reaction.

The produced stable tetramer, [Al$_4$Et$_6$(OR)$_6$], has one central aluminium surrounded by six oxygen atoms, which gives in ^{27}Al NMR a resonance typically around 7 ppm [14]. The ^{27}Al resonances associated with aluminium atoms of the Et$_2$Al moieties were not observed at the temperature used for recording the NMR spectrum (25°C).

In the ^{13}C-spectrum of the 1:1 reaction solution three kinds of CH$_2$O-groups present were observed. The signals at 65.76, 64.6 and 63.9 ppm most likely originate from [EtAl(OR)$_2$]$_2$, [Al$_4$Et$_6$(OR)$_6$] and [Et$_2$AlOR]$_2$, respectively. The resonance due to [EtAl(OR)$_2$]$_2$ is very weak. The changes in this area are shown in Fig. 1. New resonances are also found at the downfield side of those of the second and third carbon from the alkoxy oxygen of [Et$_2$AlOR]$_2$ and [EtAl(OR)$_2$]$_2$. Similarly, in the ^{1}H-spectrum of the 1:1 solution a new broad resonance at 3.75 ppm due to the protons of the OCH$_2$ group can be observed.

The assignment of Al$_4$Et$_6$(OR)$_6$ for this new product is based on the ^{1}H, ^{13}C and ^{27}Al NMR data presented above. The relative intensities (1:1:1) of the ^{13}C resonances of the OCH$_2$ group and AlCH$_2$ and AlCH$_2$CH$_3$ are in a good agreement with the proposed structure of tetrameric Al$_4$Et$_6$(OR)$_6$, which is shown in Fig. 2.

Fig. 1. ^{13}C NMR spectra of the reaction solutions of 10-undecen-1-ol and AlEt$_3$ in toluene-D$_8$ (66.5–60 ppm): (a) 10-undecen-1-ol, (b) 10-undecen-1-ol + AlEt$_3$ (1:3), (c) 10-undecen-1-ol + AlEt$_3$ (1:1), (d) 10-undecen-1-ol + AlEt$_3$ (2:1).
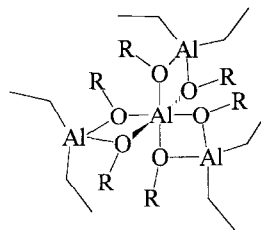
The amount of 10-undecen-1-ol was further increased in order to find more evidence for the proposed reaction (Eq. (3)). For a solution with a $ROH/AlEt_3$ molar ratio of 2:1 it was found that all of the alcohol reacted, generating tetrameric aluminium alkyl alkoxides, $Al_4Et_x(OR)_{12-x}$ ($x = 6,4$). In ^{13}C NMR two CH_2O resonances at 64.42 and 63.02 ppm as well as a weak CH_2O resonance at 63.91 ppm (due to $[Et_2AlOR]_2$) were detected. The first signal is assigned to $Al_4Et_6(OR)_6$ on the basis of its chemical shift. The new resonance at 63.02 ppm is proposed to originate from another aluminium alkyl alkoxide oligomer, $Al_4Et_n(OR)_{12-n}$. ^{27}Al NMR supports this proposal since there is only one sharp signal at 7.2 ppm (Fig. 3). A similar mixture of tetrameric oligomers $R_nAl_4(OR)_{12-n}$ ($R = Et$, $n = 1–6$) has been obtained in a reaction between $AlEt_3$ and EtOH [11].

As a conclusion 10-undecen-1-ol reacts quantitatively with $AlEt_3$ forming $[Et_2AlOR]_2$. This undergoes a disproportionation reaction already at an early stage of the reaction to give $[EtAl(OR)_2]_2$ and Al_2Et_6. As soon as the $ROH/AlEt_3$ molar ratio is proper $[Et_2AlOR]_2$ can undergo reaction with excess ROH to give $[EtAl(OR)_2]_2$ and further the tetramer $Al_4Et_6(OR)_6$. The higher $ROH/AlEt_3$ molar ratios facilitate formation of other oligomers $Al_4Et_n(OR)_{12-n}$ ($n = 4,2$).

3.2. Reaction between 30% MAO and 10-undecen-1-ol

The reaction between 10-undecen-1-ol and MAO (30% toluene solution) was studied in two molar ratios ($ROH/Al_{total} = 1:3$ and $1:2$), which were selected on the basis of the polymerization studies described in the introduction. On a slow addition of the MAO solution to the toluene-D_8 solution of 10-undecen-1-ol a similar fast reaction with evolution of gas occurred as in the case of alcohol and $AlEt_3$. The MAO was added dropwise as fast as the evolution of methane gas allowed (ca. 5 min).
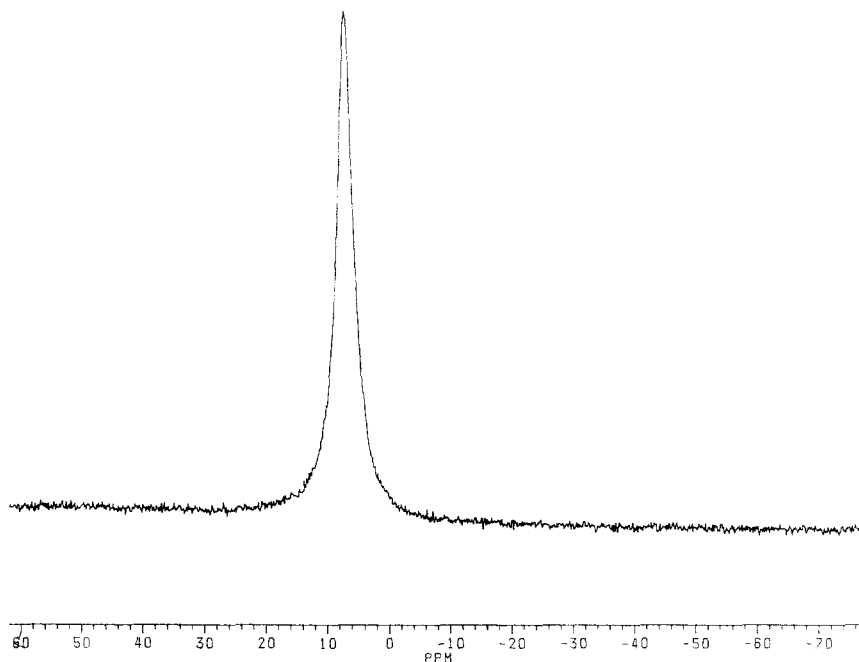

Fig. 3. ^{27}Al NMR spectrum of the reaction solution of 10-undecen-1-ol and $AlEt_3$ in toluene-D_8 (2:1).
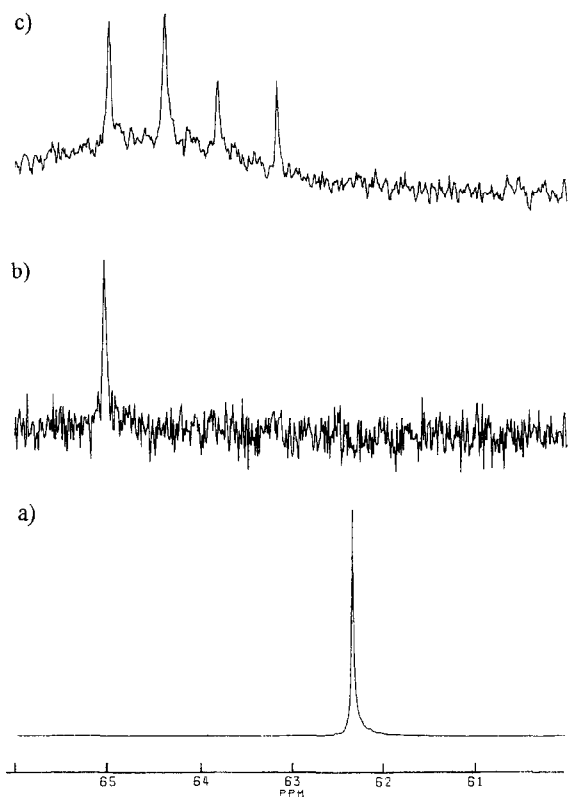
c)

b)

a)

Fig. 4. ^{13}C NMR spectra of the reaction solutions of 10-undecen-1-ol and MAO in toluene-D$_8$ (66.5–60 ppm): (a) 10-undecen-1-ol, (b) 10-undecen-1-ol+MAO (1:3), (c) 10-undecen-1-ol+MAO (1:2).

The reaction between alcohol and MAO was studied first in a 1:3 stoichiometry. The absence of alcohol OH signal at 4.46 ppm in the ^{1}H-spectrum of the reaction solution indicates that all the alcohol had reacted with aluminium. This can also be seen in the ^{13}C-spectrum where the signal at 62.43 ppm due to the (CH$_2$–OH)-group is no longer observed (Fig. 4). Instead in the ^{13}C spectrum two signals are found at 65.16 and 63.30 ppm (Table 2), which are tentatively assigned to [MeAl(OR)$_2$]$_2$ and [Me$_2$AlOR]$_2$, respectively. The relative intensities of the OCH$_2$ and AlMe signals support this assignment. Moreover, new changes in the ^{13}C spectrum are detected. Broad signals can be observed by the side of the sharp signals of olefinic carbons (Fig. 4). Similar broad resonances are also found at the carbon signals of OCH$_2$, OCH$_2$CH$_2$ and OCH$_2$CH$_2$CH$_2$ groups. These broad signals can be explained by the interaction of a quadrupolar nucleus like aluminium $(I = 5/2)$ with the olefinic and alkoxy carbon atoms. It is proposed that the presence of especially methylaluminoxane in the close proximity of these groups of 10-undecene is the origin of the broad carbon resonances. The absence of this type of interac-

Table 2
NMR characterization of reactions of MAO with 10-undecen-1-ol [a]

Sample	10-undecen-1-ol (mmol)	Al$_{total}$ (mmol)	AlMe$_3$ (mmol)	^{1}H NMR		^{13}C NMR			^{27}Al NMR [b]		
				OCH$_2$	CH=CH	C$_1$	C$_2$	C$_3$	Al-CH$_3$	δ(Al)	$\omega_{1/2}$ (Hz)
10-undecen-1-ol				3.58(m)	139.10	62.43	33.20	26.93			
					114.62, 114.43						
MAO									−7.00	158	1900
ROH:MAO = 1:3	1.73	5.21	1.1	3.75(m)	139.20	65.16	32.90	25.96	−7.25	[c]	
					114.72, 114.52	63.33	32.71	25.69	−8.93		
									−10.36		
ROH:MAO = 1:2	2.60	5.29	1.1		139.91	65.07	33.18	26.34	−7.50	8.21	370
					114.44	64.47	32.82	26.18	−8.00		
						63.89	32.62	25.89	−9.00		
						63.24		25.61			

[a] The NMR spectra were measured in toluene-D$_8$ at room temperature.
[b] The background signal of the probehead at 62 ppm has been omitted.
[c] Only the background signal visible.

c)

b)

a)

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         139.0                    114.0
         PPM                      PPM
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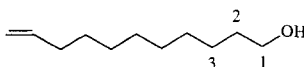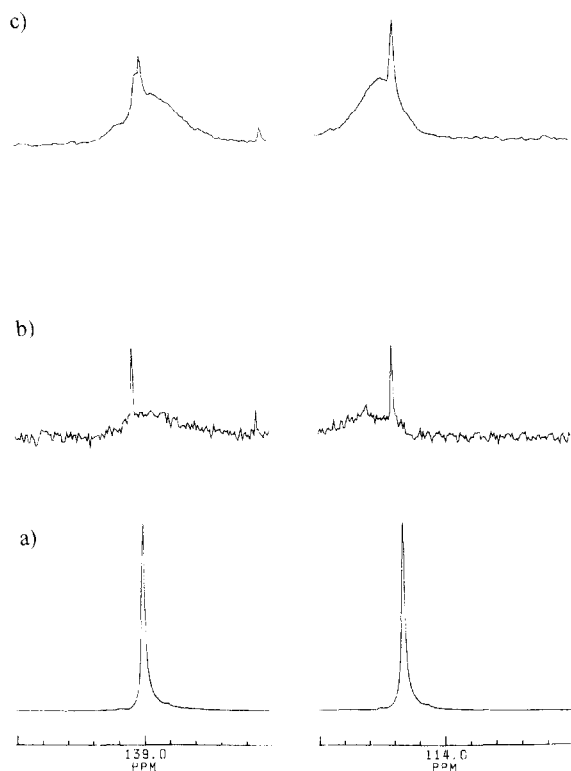
Fig. 5. ^{13}C NMR spectra of the reaction solutions of 10-undecen-1-ol and MAO in toluene-D_8 (140–138 ppm and 115–113 ppm). (a) 10-undecen-1-ol, (b) 10-undecen-1-ol + MAO (1:3), (c) 10-undecen-1-ol + MAO (1:2).
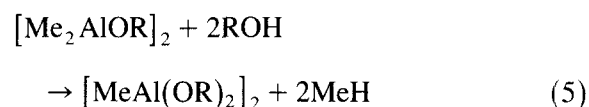
tion in the reaction solutions of 10-undecen-1-ol and AlEt$_3$ supports this proposal.

In ^{27}Al NMR one broad signal at 158 ppm is detected for a MAO solution (in toluene-D_8). This aluminium resonance originates from methylaluminoxane and $AlMe_3$ present in 30% MAO. In the 1:3 alcohol/MAO sample the 158 ppm signal has disappeared, indicating that the alcohol has reacted with Me_3Al to give $[Me_2AlOR]_2$ and $[MeAl(OR)_2]_2$ according to a similar mechanism (Eqs. (4) and (5)) as that proposed for the reaction of 10-undecen-1-ol with Et_3Al:

$$Me_6Al_2 + 2ROH \rightarrow [Me_2AlOR]_2 + 2MeH \quad (4)$$

R = 10-undecene

$$[Me_2AlOR]_2 + 2ROH$$

$$\rightarrow [MeAl(OR)_2]_2 + 2MeH \quad (5)$$

R = 10-undecene

A prolonged heating at 60°C and 80°C does not change the relative ratio of $[MeAl(OR)_2]_2$ and $[Me_2AlOR]_2$ remarkably.

When the amount of alcohol in the reaction solution is increased to 1:2, the changes in NMR become more obvious. In the [27]Al spectrum a new sharp signal at 8.2 ppm (Fig. 6) is observed. In the ^{13}C spectrum four OCH_2 signals at 65.07, 64.47, 63.89 and 63.24 ppm are found. The chemical shifts of the first and last resonances are close to those assigned to $[MeAl(OR)_2]_2$ and $[Me_2AlOR]_2$. We propose


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   200                100                     0              -100
                              PPM
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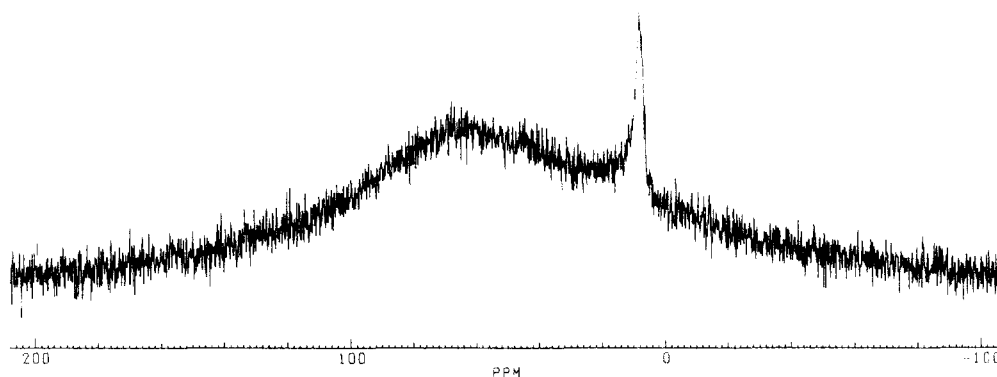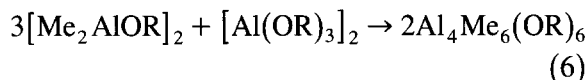
Fig. 6. ^{27}Al NMR spectrum of 10-undecen-1-ol and MAO in toluene-D_8 (1:2).

that the two middle resonances (64.47 and 63.89 ppm) belong to tetrameric aluminium alkoxides. Based on the ^{27}Al and ^{13}C NMR results the molar ratio of 10-undecen-1-ol and $AlMe_3$ is assumed to be proper for the formation of tetrameric $Al_4Me_n(OR)_{12-n}$ ($n = 6,4$) according to Eq. (6):

$$3[Me_2AlOR]_2 + [Al(OR)_3]_2 \rightarrow 2Al_4Me_6(OR)_6 \quad (6)$$

R = 10-undecene

As for the previous reaction solution (1:3) similar broad carbon resonances are also observed by the side of olefinic and alkoxy resonances, indicating some kind of interaction between aluminium of most probably methylaluminoxane, MAO, and these carbon atoms (Figs. 4 and 5.) Aging of the reaction solution was found to weaken this interaction. For the preceding reaction (ROH/MAO = 1:3) the ^{13}C spectrum shown in Fig. 5 was measured after 10 days from the preparation of the solution and the relative intensities of the broad signals are smaller than those of the latter reaction solution although the total aluminium content is higher than that in the latter reaction solution (ROH/MAO = 1:2).

Based on the ^{13}C NMR results the alcohol functional group of 10-undecen-1-ol reacts quantitatively with the aluminium alkyl species present in the MAO solution forming the analogous products as in the reactions with $AlEt_3$. At the same time the both olefinic and alcohol moieties of 10-undecen-1-ol simultaneously experience an interaction from methylaluminoxane. The mechanism of this interaction is not evident but it probably involves some kind of Lewis base–Lewis acid interaction between the functional groups of 10-undecen-1-ol and the aluminium species of MAO.

4. Conclusions

The interaction of methylaluminoxanes with 10-undecen-1-ol can have an effect on the mechanism according to which MAO functions as a cocatalyst in the olefin polymerization catalyzed with metallocenes. The resolution of the interaction mechanism of MAO is difficult because of the ambiguous nature of commercial MAO, which contains, besides methylaluminoxane oligomers, $AlMe_3$ in two forms: free as Al_2Me_6 and complexed with MAO MAO · $AlMe_3$ [9,15]. A comprehensive study on this interaction mechanism is in progress.

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