An Alternative Route to Methylalumoxane: Synthesis, Structure, and the Use of Model Methylalumoxanes as Cocatalysts for Transition Metal Complexes in Polymerization Reactions

Yury V. Kissin*,† and Anita J. Brandolini‡

Department of Chemistry, Rutgers University, 610 Taylor Road, Piscataway, New Jersey 08854-8087, and Department of Chemistry and Physics, William Paterson University, 300 Pompton Road, Wayne, New Jersey 07470

Received December 26, 2001; Revised Manuscript Received October 10, 2002

ABSTRACT: Methylalumoxane (MAO) is commonly produced by controlled hydrolysis of $AlMe_3$; it is widely used as a cocatalyst for metallocene complexes and complexes of late transition metals in polymerization reactions of alkenes and styrene. This article explores alternative routes to MAO synthesis in reactions of $AlMe_3$ with bis(trialkyltin)oxides $R_3Sn-O-SnR_3$ or with Me_3SnOH. The products of these reactions, when prepared at molar ratios $[AlMe_3]$:[Sn compound] > 1, are efficient cocatalysts for metallocene complexes in alkene polymerization reactions and for various Ti compounds in syndiospecific styrene polymerization reactions. A multinuclear NMR study of the reaction products in both cocatalyst mixtures prepared at different reactant ratios provided information about the chemical structure of the MAO analogues and MAO itself.

Introduction

Methylalumoxane $[Al(Me)O]_n$ (MAO) is widely used as a cocatalyst in two types of polymerization reactions: the polymerization of alkenes with various metallocene and multidentate late-transition metal complexes (see review 1) and the syndiospecific polymerization of styrene with various Ti and Zr complexes.[2,3] MAO is conventionally synthesized by the controlled hydrolysis of $AlMe_3$,[4−7] by reacting $AlMe_3$ either with water (as a vapor, a liquid or a solid[1,6−10]) or with hydrates of inorganic salts such as $CuSO_4 \cdot 5H_2O$ or $Al_2(SO_4)_3 \cdot 15H_2O$.[7,10,11] From 10 to 30% of all Al atoms in commercially manufactured MAO belong to residual $AlMe_3$, the starting material for the MAO synthesis.[5] Pure MAO is a white amorphous solid soluble in aromatic solvents and partially soluble in aliphatic hydrocarbons.[12] NMR data[7,13−17] show that virtually all aluminum atoms in MAO solutions are four-coordinated and all oxygen atoms are three-coordinated. This conclusion was recently supported by quantum-mechanical calculations.[18−20]

The exact structure of MAO is the subject of significant controversy. It is generally accepted that MAO is a mixture of oligomeric compounds $[Al(Me)O]_n$ with n ranging from 4 to 30.[7,9,19−21,23] Some of the oligomers apparently have three-dimensional cage structures composed of hexagonal and square faces,[19,20,23,24] similarly to *tert*-butylalumoxane, which cage structure was determined experimentally by Barron.[14,22] Solutions of MAO in aromatic solvents are opaque, relatively viscous and easily form gels; both these features suggest a significant degree of intermolecular association. Sinn, who prepared the first samples of MAO essentially free of $AlMe_3$, proposed an MAO structure in which four linear MAO tetramers, $Al_4O_3Me_6$, form a half-open dodecahedron structure, $Al_{16}O_{12}Me_{24}$.[23,24] This model was later challenged (see discussion in refs 19 and 20). DFT calculations suggest that $[Al(Me)O]_n$ species may exist as an equilibrium between several cage structures, with the hexagonal-faced $[Al(Me)O]_{12}$ being the most abundant oligomer at room temperature.[19,20] However, several experimental measurements (see discussion in ref 24) showed that the $[CH_3]$:[Al] ratio in MAO is always substantially higher than 1 suggesting the presence of Me_2AlO- groups in its structure. Additionally, free $AlMe_3$ can be coordinated to MAO molecules. Its concentration affects the n value in the MAO formula.[13,20]

In the 1960s, Racanelli and Porri studied polymerization of butadiene and isoprene with cobalt acetylacetonate. They found that this complex can be activated with several cocatalysts including $AlEt_2Cl$, $AlEtCl_2$, and chloroalkylaluminum compounds containing $Al-O-Al$ bonds, i.e., chloroalkylalumoxanes. The latter were produced by the same method that is currently used for MAO synthesis, by reacting $AlEt_2Cl$ with water.[25,26] However, Racanelli and Porri discovered that the chloroalkylalumoxanes could be also prepared by reacting $AlEt_2Cl$ with bis(triethyltin)oxide, $(Et_3Sn)_2O$, at an [Al]:[O] molar ratio of 2.[27]

We used the latter approach as a starting point in our search for alternative cocatalysts capable of activating metallocene catalysts in alkene and styrene polymerization reactions. Some early results of this research were briefly described in refs 28 and 29. This article discusses two subjects: (a) the effectiveness of the products formed in reactions between trialkylaluminum compounds and some organotin compounds as activators for transition metal complexes in alkene and styrene polymerization reactions and (b) an NMR study of these reaction products and its relevance for a better understanding of the MAO structure.

Experimental Section

Solid MAO and MAO Analysis. Solid MAO was prepared from a commercial MAO sample supplied by Schering Berlin Polymers Co. as a solution in toluene (total Al content 5.23

---

* Corresponding author. E-mail: ykissin@rutchem.rutgers.edu.
† Rutgers University.
‡ William Paterson University.

10.1021/ma012234o CCC: $25.00

wt %; MAO concentration ~10 wt %, free $AlMe_3$ ~30% of the total Al content). The solid material was prepared by precipitation of MAO from this solution in a 10-fold excess of *n*-hexane. The insoluble material was separated by centrifuging; it was repeatedly washed with hexane and dried at 70 °C in a nitrogen flow. The number of methyl groups attached to Al atoms in MAO and MAO analogues was determined by reacting the organoaluminum compounds with protic compounds and by measuring the volume of evolved methane. The protonolysis reaction was usually carried out in three steps, first with excess of 2-propanol or *n*-butanol, then with water, and as the last stage, with concentrated HCl solution. The fully dissolved hydrolysis products were then analyzed for Al content.

NMR Spectra. Four types of NMR spectra were recorded with a JEOL GX400 NMR spectrometer: ^1H at 400 MHz, ^{13}C at 100 MHz, ^{27}Al at 104.4 MHz, and ^{119}Sn at 149.2 MHz. $SnMe_4$ was used as an internal standard in ^{119}Sn NMR spectra, and ethylbenzene in ^{13}C NMR spectra. The solid-state ^{27}Al NMR spectra of the hexane-insoluble MAO fraction were recorded using a Bruker 500 MHz NMR spectrometer. The solid-state ^{27}Al NMR spectra of 30% MAO solution in toluene were recorded with a 93.6 MHz (^{27}Al) NMR spectrometer. A sealed tube containing the solution was placed into a 7.5 mm MAS rotor and spun at a speed of 3−4 kHz.

IR Spectra. IR spectra were recorded with a Perkin-Elmer 1600 FTIR spectrophotometer. MAO samples were either deposited from the toluene solution onto KBr windows and sealed between two KBr windows or were prepared as mulls in dry Nujol and also sealed between two KBr windows. All these operations were carried out in a nitrogen box and the spectra (accumulation time of ~1 min) were recorded within a few seconds after removing the samples from the box.

Polymerization Reactions. Polymerization reactions of alkenes were carried out in a 0.5-L Autoclave Engineers polymerization reactor following procedures described earlier[30,31] using toluene, hexane, or heptane as solvents. Polymerization reactions of styrenes were carried out in 50-mL glass vials capped with septa and flushed with nitrogen. Mixtures of toluene, monomers, and catalyst components were agitated with magnetic stirrers at different temperatures for periods of time ranging from 2 to over 20 h; then the vial contents were mixed with a 5-fold excess of 2-propanol. Crystalline syndiotactic polystyrene was recovered by filtration.

Polymer Characterization. DSC data were recorded with a DuPont 9900 thermal analyzer. Samples of ethylene polymers were premelted at 150 °C and cooled from 150 to 40 °C at a rate of 0.5 °C/min. DSC melting curves were recorded by heating the crystallized samples at a rate of 2 °C/min from 30 to 140 °C. Samples of syndiotactic polystyrenes were melted at a rate of 10 °C/min from 30 to 300 °C. Contents of crystalline syndiotactic polystyrene fractions were determined by extraction with boiling MEK. Molecular weights and molecular weight distributions of polymers were determined by GPC analysis performed with a Waters 150C liquid chromatograph at 145 °C (two columns 10^6, 10^4, and 10^3 Å) using 1,2,4-trichlorobenzene as a solvent. Resolution of GPC curves into Flory components was carried out with the Scientist program (MicroMath Scientific Software), as described earlier.[32]

Results and Discussion

1. Alkene Polymerization Reactions. $AlMe_3$−(n-$Bu_3Sn)_2O$ Cocatalyst System.

Our first goal was to identify organoaluminum compounds for which reaction products with bis(trialkyltin)oxides are effective as cocatalysts for metallocene complexes in ethylene polymerization reactions. These experiments were carried out both in toluene and in *n*-hexane with Cp_2ZrCl_2 as a catalyst and with mixtures of bis(tri-*n*-butyltin)oxide, (n-$Bu_3Sn)_2O$, as the first cocatalyst component and several organoaluminum compounds. Preliminary experiments showed that neither (n-$Bu_3Sn)_2O$ itself nor any of the tested organoaluminum compounds, $AlMe_3$, $AlEt_3$, Al*i*-Bu_3, and $AlMe_2Cl$, when used alone, activate the metallocene complex. Combinations of (n-$Bu_3Sn)_2O$ with $AlEt_3$, Al*i*-Bu_3, or $AlMe_2Cl$ were ineffective as well. However, combinations of $AlMe_3$ and (n-$Bu_3Sn)_2O$ at a molar $[AlMe_3]$:[(n-$Bu_3Sn)_2O$] ratio (abbreviated below as [Al]:[O] ratio) higher than 1 were found to be potent cocatalysts for Cp_2ZrCl_2. Polyethylene yields varied from 1.6×10^5 g/(mmol Zr) (in toluene at 80 °C for 1 h) to 6.8×10^4 g/(mmol Zr) (in hexane).

Table 1. Effect of $[AlMe_3]$:[(n-$Bu_3Sn)_2O$] Molar Ratio on the Activity of Cp_2ZrCl_2 in Ethylene Homopolymerization[a]

[Al]:[O]	2.0	1.5	1.2	1.1	1.0	0.71
av rate, g/(mmol Zr min)	29	35	43	47	~3	low

[a] Polymerization in hexane at 70 °C, $P_E = 1.24$ MPa, $[Cp_2ZrCl_2] = 1.4 \times 10^{-5}$ M, [Al]:[Zr] = 860.

Mixing $AlMe_3$ and (n-$Bu_3Sn)_2O$ in toluene solution results in a rapid exothermic reaction with the formation of soluble products. We assumed that both Sn−O bonds in the $R_3Sn-O-SnR_3$ molecule can react with $AlMe_3$ to form an MAO analogue containing Al−O−Al groups (see discussion in part 4). The products formed in the reaction between $AlMe_3$ and (n-$Bu_3Sn)_2O$ are kinetically stable. They activate metallocene complexes even if the cocatalyst components are premixed long before use. If solutions of metallocene complexes are contacted with one of the components of the $AlMe_3$−(n-$Bu_3Sn)_2O$ system under polymerization conditions (no reaction ensues), addition of the second component immediately starts the polymerization reaction. The same is true for ternary cocatalyst mixtures containing (n-$Bu_3Sn)_2O$ and two different organoaluminum compounds. For example, the system containing Al*i*-Bu_3, (n-$Bu_3Sn)_2O$, and Cp_2ZrCl_2 is inactive in ethylene polymerization, as mentioned above. When an excess of $AlMe_3$ was added to this mixture, it resulted in a rapid onset of high polymerization activity. Stability of the catalysts systems containing metallocene complexes and the $AlMe_3$−(n-$Bu_3Sn)_2O$ cocatalyst manifests itself also in very stable kinetic behavior in the polymerization reactions: after a short activation stage, the ethylene consumption in these reactions remains nearly constant for several hours. Only the Sn−O−Sn group is suitable for converting $AlMe_3$ into an active cocatalyst. The sulfur analogue, (n-$Bu_3Sn)_2S$, was tested with $AlMe_3$ and Cp_2ZrCl_2; it was found to be completely ineffective in the polymerization reactions.

The effect of the [Al]:[O] ratio on the reactivity of Cp_2ZrCl_2 was tested in ethylene polymerization reactions at a constant [Al]:[Zr] ratio of 860 (Table 1). The cocatalyst is effective at [Al]:[O] ratios higher than 1. The $AlMe_3$ concentration was kept constant in these experiments; therefore, as the [Al]:[O] ratio decreases, the ratio between the real cocatalyst, the product of the $AlMe_3$−(n-$Bu_3Sn)_2O$ reaction, and Cp_2ZrCl_2 increases. This increase results in an increase of the reaction rate. It is well known[1] that the activity of the MAO−Cp_2ZrCl_2 system also increases with an increase of the [Al]:[Zr] ratio when the concentration of the metallocene complex is kept constant.

When the polymerization reaction with the $AlMe_3$−(n-$Bu_3Sn)_2O$ mixture is carried out at [Al]:[O]<1, the reaction rate is very low. However, after an additional amount of $AlMe_3$ is introduced, the reaction rate rapidly increases. In one experiment with stepwise addition of the cocatalyst components, a mixture of $AlMe_3$ and (n-

Table 2. Ethylene Polymerization with Various MetalloceneComplexes Activated with $AlMe_3-(n\text{-}Bu_3Sn)_2O$ Mixture[a]

metallocene complex	[Al]:[transition metal], mol/mol	time, min	yield, kg/(mmol metal)
Cp_2ZrCl_2	1410	60	12.9
$MeCp_2ZrCl_2$	3550	60	17.5
Cp_2TiCl_2	615	120	2.1
Cp_2HfCl_2	600	90	9.2

[a] Polymerization in hexane/1-hexene 80/20 mixture at 70 °C, $P_E = 1.24$ MPa, [Al]:[O] = 2.5.

$Bu_3Sn)_2O$ prepared at [Al]:[O] = 1.4 was used to activate Cp_2ZrCl_2 at [Al]:[Zr] = 2750. This combination produced a highly active catalyst, which indicates that the two principal stages of the active species formation, alkylation of Cp_2ZrCl_2 and the formation of the Cp_2ZrMe^+ cationic species, have been accomplished. After 20 min, an additional 0.88 mmol of $(n\text{-}Bu_3Sn)_2O$ was introduced into the reactor, which decreased the [Al]:[O] ratio to 0.98. This change resulted in an immediate deactivation of the working catalyst system. When 1.4 mmol of fresh $AlMe_3$ was added to the inactive system to bring the [Al]:[O] ratio up to 1.5, the polymerization activity was rapidly restored.

Combinations of $AlMe_3$ and $(n\text{-}Bu_3Sn)_2O$ can activate other metallocene complexes as well. Table 2 lists the results of ethylene/1-hexene copolymerization reactions with several metallocene compounds. Although these reactions were carried out at approximately the same [Al]:[O] ratios, the final [Al]:[transition metal] ratios were different due to variations in the activities of metallocenes of different transition metals. In qualitative terms, zirconocenes exhibit the highest activity whereas hafnocenes and titanocenes are less active.

Molecular weights of polyethylene produced with the $AlMe_3-(n\text{-}Bu_3Sn)_2O$ cocatalyst and zirconocene complexes depend strongly on the reaction conditions (solvent, temperature) and on the alkene concentration in a reactor. The ethylene homopolymer produced in toluene at 80 °C had a low molecular weight, M_w = 27 500, whereas the same reaction in hexane produced polymers with M_w = 93 000 at 80 °C and with M_w = 307 000 at 70 °C. Ethylene/1-hexene copolymerization reactions at 80 °C produced copolymers with low molecular weights, $M_w \sim$ 18 000–20 000, whereas the same reactions at 70 °C yielded copolymers with M_w in the 40 000–45 000 range. Molecular weights of copolymers produced with other metallocene complexes under the same reaction conditions (Table 2) reflect both their 1-hexene-copolymerization ability and relative rates of chain termination reactions. The observed patterns, in terms of both the relative activities of various metallocenes and the molecular weights of the polymers, are similar to those observed for metallocene complexes activated with MAO.[1,5]

A comparison of the relative activities of MAO and the $AlMe_3-(n\text{-}Bu_3Sn)_2O$ mixture as cocatalysts for Cp_2ZrCl_2 was carried out in a series of ethylene/1-hexene copolymerization reactions at 70 and 60 °C in *n*-heptane. Both systems exhibit a very stable kinetic behavior at these temperatures: the polymerization rates remain virtually constant for over 1 h. Table 3 gives the [Al]:[Zr] and [O]:[Zr] ratios and the polymerization rates. Under similar [cocatalyst]:[Zr] ratios, the $AlMe_3-(n\text{-}Bu_3Sn)_2O$ combination affords slightly higher reaction rates than MAO. This cocatalyst produces ethylene/1-hexene copolymers with approximately the same comonomer composition and with higher molecular weights compared to MAO.

The binary $AlMe_3-(n\text{-}Bu_3Sn)_2O$ cocatalyst can be also used for activating supported metallocene complexes. One such catalyst was prepared by depositing Cp_2ZrCl_2 from THF solution onto silica calcined at 600 °C, followed by drying the slurry at 60 °C. The catalyst was active in ethylene polymerization, both in the presence of MAO and the $AlMe_3-(n\text{-}Bu_3Sn)_2O$ cocatalyst. When the latter cocatalyst, at [Al]:[O] = 2.0 and [Al]:[Zr] = 306, was used in ethylene/1-hexene copolymerization reaction at 70 °C, the catalyst system had a productivity of 500 g/(g cat h), which translates into a productivity of ~3.6 kg of PE/(mmol Zr h).

$AlMe_3-Me_3SnOH$ Cocatalyst System. The principal idea in using the $AlMe_3-(n\text{-}Bu_3Sn)_2O$ system as a cocatalyst for metallocene complexes is to make use of the ability of the Sn–O bond to react with $AlMe_3$, resulting in the formation of the Al–O bond. Another organotin compound that is suitable for this purpose is Me_3SnOH. Me_3SnOH is a solid insoluble in aromatic and aliphatic hydrocarbons. When this compound is slurried in toluene and mixed with $AlMe_3$, it reacts violently with the liberation of a large quantity of gas, apparently in a reaction between the OH group of Me_3SnOH and $AlMe_3$. The final products of this reaction (see part 4) also activate metallocene complexes in ethylene polymerization reactions. Some details of these reactions are given in Table 4. The reactions are similar to the polymerization reactions using the $AlMe_3 - (n\text{-}Bu_3Sn)_2O$ cocatalyst. The $AlMe_3-Me_3SnOH$ mixture is an effective cocatalyst for Cp_2TiCl_2 as well: when this mixture, at [Al]:[O] = 1.4, was used in a slurry ethylene–hexene copolymerization reaction at 70 °C, the productivity of the catalyst system was ~2 kg/(mmol Ti).

2. Structure and Properties of Ethylene Polymers Prepared with Binary Cocatalysts. The properties of ethylene polymers prepared with both binary cocatalysts were compared with the properties of the polymers prepared with MAO.[32] The molecular weight distributions of ethylene polymers prepared with the zirconocene/MAO catalysts depend on the [Al]:[Zr] ratio. If this ratio is sufficiently high (several thousands), the M_w/M_n values for the polymers are in the range 2.0–2.5, irrespective of molecular weights of the polymers. These narrow molecular weight distributions suggest that only one population of active centers exists in these catalysts. However, the M_w/M_n ratios increase as the [Al]:[Zr] ratio decreases.[32] Molecular weight distributions of the polymers prepared with both binary cocatalysts, $AlMe_3-(n\text{-}Bu_3Sn)_2O$ and $AlMe_3-Me_3SnOH$, also vary depending on the [O]:[Zr] and [Al]:[O] ratios. In the case of ethylene polymers prepared at [Al]:[O] = 2.0 and $[(n\text{-}Bu_3Sn)_2O]$:[Zr] = 3000–3500, the M_w/M_n values range from 2.2 to 2.8. The latter value suggests the presence of two types of active centers with similar kinetic characteristics. However, M_w/M_n values increase to 14–22 for the homopolymers and to 5–10 for the copolymers prepared at relatively low $[(n\text{-}Bu_3Sn)_2O]$:[Zr] ratios, 1000–1500.

Results of the GPC curve analysis of several polymers produced at low $[(n\text{-}Bu_3Sn)_2O]$:[Zr] ratios are given in Table 5. This analysis separates GPC curves into Flory components, polymer components produced by a single type of active center, with M_w/M_n = 2.0. The copolymer prepared at $[(n\text{-}Bu_3Sn)_2O]$:[Zr] = 590 can be represented by three Flory components with the low molecular

Table 3. Ethylene/1-Hexene Copolymerization Reactions with Cp_2ZrCl_2 activated with $AlMe_3-(n\text{-}Bu_3Sn)_2O$ Mixture or with MAO[a]

temp, °C	cocatalyst	[Al]:[Zr]	[O]:[Zr]	rate, g/(mmol Zr min)	C_{Hex}, mol %[b]	M_w
70	$AlMe_3-(n\text{-}Bu_3Sn)_2O$	5200	3300	980	2.0	81 000
70	MAO	4600	3200	840	1.8	45 700
60	$AlMe_3-(n\text{-}Bu_3Sn)_2O$	5100	3200	590	2.6	121 000
60	MAO	4600	3200	320	1.6	62 700

[a] Polymerization in hexane/1-hexene 80/20 mixture, $P_E = 1.24$ MPa. [b] Content of 1-hexene in ethylene/1-hexene copolymer.

Table 4. Ethylene Polymerization with $Cp_2ZrCl_2-Me_3SnOH/AlMe_3$ Catalyst[a]

type of reaction	temp, °C	[Al]:[O], mol/mol	time, min	productivity, kg/mmol Zr	M_w
homopolymerization	80	2.8	50	9.1	108 000
copolymerization with 1-hexene	70	3.0	60	142	47 400

[a] Polymerization in hexane at $P_E = 1.24$ MPa.

Table 5. Analysis of Molecular Weight Distribution of Ethylene/1-Hexene Copolymers Prepared with $Cp_2ZrCl_2-AlMe_3/(n\text{-}Bu_3Sn)_2O$ System at Low $[(n\text{-}Bu_3Sn)_2O]:[Cp_2ZrCl_2]$ Ratios

$[(n\text{-}Bu_3Sn)_2O]:[Cp_2ZrCl_2]$	temp, °C	Flory component	M_w	fract, %
590	70	I	8400	64
		II	20000	24
		III	56000	12
290	80	I	2800	6
		II	7400	26
		III	25400	48
		IV	65100	13
		V	155000	5

weight component as the largest; the $(M_w/M_n)_{av}$ value is ~3.0. The second product in Table 5 is a mixture of five Flory components; its $(M_w/M_n)_{av}$ value is ~5.0. This effect of the $[(n\text{-}Bu_3Sn)_2O]$:[Zr] ratio on the molecular weight distribution parallels the effect of the [MAO]:[Zr] ratio in the case of the $MAO-Cp_2ZrCl_2$ system.[1,32]

Ethylene/1-alkene copolymers prepared with metallocene/MAO systems have relatively narrow compositional distributions and low melting points, irrespective of the type of the reaction medium, aromatic or aliphatic solvent.[1] The same compositional uniformity was found in ethylene/1-hexene copolymers prepared with $AlMe_3-(n\text{-}Bu_3Sn)_2O$ and $AlMe_3-Me_3SnOH$ cocatalysts and various metallocene catalysts. DSC analysis of carefully annealed copolymers shows that their melting points decrease sharply with an increase of the 1-hexene content, from ~134 °C for the ethylene homopolymer to 116.0−116.5 °C for the copolymers containing 2.6−3.1 mol % of 1-hexene. Both these features indicate a high degree of compositional uniformity.

3. Styrene Polymerization Reactions. Combinations of $AlMe_3$ and organotin compounds with Sn−O bonds, when used at [Al]:[O] > 1.0, are also effective cocatalysts in the syndiospecific polymerization of styrene with a variety of Ti(IV) compounds, both monometallocene complexes $CpTiX_3$ and tetraalkoxides $Ti(OR)_4$. Table 6 lists several examples of such polymerization reactions. They were all performed in toluene at a styrene concentration of 1.74 M. Styrene polymers prepared with monotitanocene complexes activated with $AlMe_3-(n\text{-}Bu_3Sn)_2O$ mixtures at relatively high $[(n\text{-}Bu_3Sn)_2O]$:[Ti] ratios are low molecular weight, single-Flory materials. The polymer produced with $CpTiCl_3$ at 25 °C (the first line in Table 6) has $M_w = 6350$ and $M_w/M_n = 1.96$; the polymer prepared with $CpTi(OPh)_3$ has $M_w = 3500$ and $M_w/M_n = 2.03$.

The products of all these reactions contain a high fraction, ~90%, of MEK-insoluble syndiotactic polystyrene. The melting points of the extracted materials (which reflect their steric purity) are 265.3 °C in the case of the $Ti(O\textit{i}\text{-}Pr)_4-[AlMe_3-(n\text{-}Bu_3Sn)_2O]$ system (reaction at 25 °C) and 259.8 °C in the case of the $CpTiCl_3-[AlMe_3-(n\text{-}Bu_3Sn)_2O]$ system whereas the material prepared with $CpTiCl_3$ at 60 °C has a melting point of 248.6 °C. These cocatalyst systems can be also used for polymerization and copolymerization of ring-substituted styrenes. Polymerization of *p*-methylstyrene with the $CpTiCl_3-[AlMe_3-(n\text{-}Bu_3Sn)_2O]$ system at 25 °C and a monomer concentration of 2.1 M produced, after 20 h, an amorphous polymer with a 32% yield. Copolymerization of styrene and *p*-methylstyrene under the same conditions produced a semicrystalline copolymer with a softening point of 122 °C.

4. NMR Analysis and Structure of MAO and MAO Analogues. NMR Spectra of MAO. NMR analysis of the reaction products formed in the mixtures of $AlMe_3$ and the organotin compounds was carried out in conjunction with the NMR study of MAO itself. As was mentioned earlier, all commercial MAO solutions contain free $AlMe_3$. NMR spectra of these materials have been studied very thoroughly[7,13−16] and our study was restricted to MAO separated from $AlMe_3$ by solvent fractionation. Most of MAO components in its toluene solutions are soluble in aliphatic hydrocarbons as well; only 7−12% of the total [Al] amount is precipitated in *n*-hexane. On the basis of our titration results (alcohols, water), the alkane-insoluble MAO fraction still has a quite high $[CH_3]$:[Al] ratio, 1.4−1.6. The absence of narrow resonances for $AlMe_3$ in its NMR spectra (at 153 ppm in ^{27}Al NMR, −7.8 ppm in ^{13}C NMR, −0.4 ppm in ^{1}H NMR) indicates that the precipitate does not contain free $AlMe_3$.

Interpretation of the NMR spectra of $AlMe_3$-free MAO, after it was redissolved in toluene, proved to be difficult under the NMR experimental conditions typically used for solutions. The ^{27}Al NMR spectrum of this MAO shows only one weak broad signal at +53 ppm (Figure 1A), its ^{13}C NMR spectrum does not exhibit any signals at all (except for those of the solvent), and its ^{1}H NMR spectrum has only a very small resonance at −0.07 ppm. The scant NMR information on the $AlMe_3$-free MAO structure is contrasted with the results of its IR analysis. The IR spectrum of the solid MAO (Figure 2) exhibits all the bands expected for the MAO structure: C−H stretching bands at 2940, 2897, and 2855 cm^{-1} and very strong bands at 811, 696, ~660, and 600 cm^{-1} which were previously[8,33] assigned to the overlap of Al−O and Al−C stretching modes. The medium-intensity band at 1219 cm^{-1} in the MAO IR spectrum can be attributed to a combination of the Al−O stretching mode and one of the low-frequency deformation (Al−

Table 6. Polymerization of Styrene with Transition-Metal Complexes Activated by Combinations of $AlMe_3$ and Organotin Compounds[a]

catalyst	Sn compound	[Al]:[O], mol/mol	[O]:[M], mol/mol	temp, °C	time, h	yield, %	insoluble[b] fraction, %
$CpTiCl_3$	$(n\text{-}Bu_3Sn)_2O$	2.0	630	25	22	29.3	90.0
$CpTiCl_3$	$(n\text{-}Bu_3Sn)_2O$	4.3	360	60	2	9.0	
$CpTiCl_3$	Me_3SnOH	2.1	370	25	24	7.0	
$CpTiCl_3$	Me_3SnOH	3.1	270	25	22	11.6	
$CpTi(OPh)_3$	$(n\text{-}Bu_3Sn)_2O$	2.0	510	25	22	39.2	89.7
$Ti(Oi\text{-}Pr)_4$	$(n\text{-}Bu_3Sn)_2O$	2.0	420	25	22	18.2	90.5

[a] Styrene concentration 1.74 M. [b] Yield of syndiotactic polystyrene insoluble in MEK.

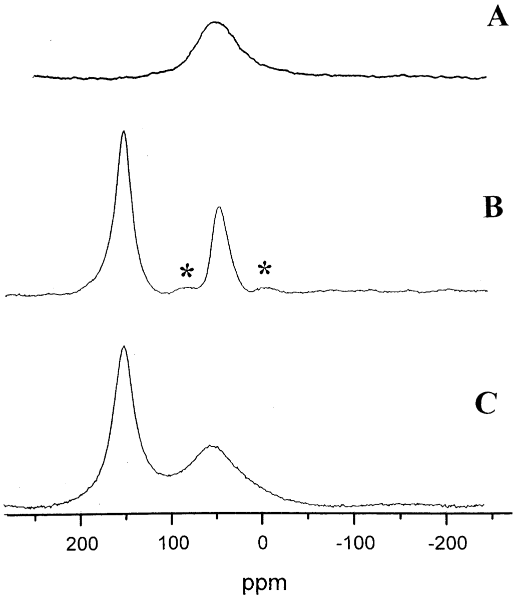


Figure 1. ^{27}Al NMR spectra of MAO: (A) spectrum of $AlMe_3$-free MAO; (B and C) "solid-state" spectra of 30 wt % MAO solution in toluene (contains free $AlMe_3$). Key: (B) MAS spectrum (asterisks indicate spinning sidebands); (C) static spectrum.

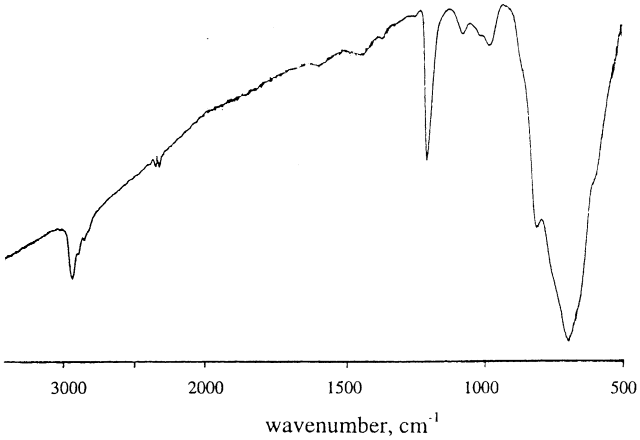


Figure 2. IR spectrum of $AlMe_3$-free MAO.

C-related) modes in the MAO molecule (this band disappears in the spectrum of hydrolyzed MAO).

Reasons for the failure to observe any ^{13}C NMR features of the $AlMe_3$-free MAO fraction are not obvious. The presence of the Al−O bond next to the CH_3 group in MAO is not the only reason: ^{13}C NMR signals of carbon atoms attached to Al atoms in $AlMe_2OMe$ and $AlEt_2OEt$ are easily observed; although the proximity of the Al−O bond broadens them, their half-widths increase from ~25 to 120−140 Hz. The most pertinent information about the unusual NMR behavior of MAO came from recording "solid-state" ^{27}Al NMR spectra of 30 wt % solution of MAO in toluene (the solution contains free $AlMe_3$). A sealed ampule with the solution was placed in a magic-angle (MAS) rotor spinning at a speed of 3−4 kHz at a 54.7° angle with respect to the magnetic field vector. Parts B and C of Figure 1 show two spectra of this MAO solution, one recorded with spinning and the other without spinning. The static spectrum (Figure 1C) is virtually identical to the MAO spectra solutions reported in the literature.[7,13−16] It shows two peaks, the narrow peak of free $AlMe_3$ at 153 ppm, and the same broad resonance of MAO itself (58 ppm) as that seen in the NMR spectrum of $AlMe_3$-free MAO in Figure 1A. Judging by the peak position, these MAO species contain four-coordinated Al atoms with at least three coordination positions occupied by O atoms.[34,35] Recording the "solid-state" spectrum of this solution allows the identification of those MAO components whose molecular motions are too restricted to be observed in solution. Magic-angle spinning (Figure 1B) does not affect the $AlMe_3$ resonance at 153 ppm; this indicates that the molecular motion of $AlMe_3$ in this concentrated MAO solution is not significantly anisotropic. However, the broad resonance of MAO exhibits a ~8 ppm upfield shift and significant narrowing when the spinning is applied. These changes indicate that Al atoms in MAO molecules in solution exhibit more anisotropy and/or restriction in molecular motion than in $AlMe_3$. High-resolution ^{27}Al and ^{13}C NMR spectra of the MAO solution recorded at a low-temperature (−120 °C) indicated no changes in peak positions or relative intensities, suggesting that $AlMe_3$ and MAO molecules are not in a state of chemical equilibrium.

In chemical terms, the similarity between the spectra in Figure 1, parts B and C suggests that the MAO species which produce the broad NMR signal in the static ^{27}Al NMR spectrum have the same chemical structure as those with a narrower signal in the spinning spectrum. Our inability to observe carbon atom signals from MAO molecules is most likely attributable to very strong Al−C coupling in the $(O)_3Al{-}CH_3$ moiety. Overall, all these NMR features support the model of MAO as a strongly aggregated network with pseudocolloidal features.

$AlMe_3$-free MAO, after it is redissolved in toluene, reacts with protic compounds in two distinct stages. A smaller fraction of its $Al{-}CH_3$ bonds, from 7 to 20%, is decomposed with 2-propanol whereas most of the remaining $Al{-}CH_3$ bonds do not react with 2-propanol but are hydrolyzed with water. This behavior agrees with the general notion about the MAO structure: most $Al{-}CH_3$ bonds in MAO molecules are strongly associated and have low reactivity with alcohols.

NMR Spectra and the Structure of MAO Analogues. Mixtures of $AlMe_3$ and $(n\text{-}Bu_3Sn)_2O$ are quite suitable for NMR studies because both the initial

Table 7. $[CH_3]$:[Al] Ratios in the Products of Reaction between $AlMe_3$ and $(n\text{-}Bu_3Sn)_2O$[a]

	$[CH_3]$:[Al], after decompn		
[Al]:[O], mol/mol	2-propanol	water	total
0.35	0.81	0.48	1.29
0.91	0.84	0.75	1.59

[a] Toluene solution, 20 °C, $(n\text{-}Bu_3Sn)_2O = 8.03$ mmol.

compounds and the reaction products are soluble in toluene. Obviously, the composition of the products formed in these mixtures strongly depends of the ratio between the components. We assumed, as a starting hypothesis, that the following overall reaction takes place:

$$x\ AlMe_3 + y\ (n\text{-}Bu_3Sn)_2O \rightarrow z\ n\text{-}Bu_3SnMe + R{-}[Al(Me){-}O]_n{-}R \quad (1)$$

Reaction 1 produces MAO analogues which are capped either with $Me_2Al{-}O$ groups, if $x > 2y$, or with n-Bu_3-Sn−O groups, if $x < y$. As shown above, only the products of reaction 1 at [Al]:[O] > 1 activate transition metal complexes for polymerization reactions.

The $[CH_3]$:[Al] ratio was measured in two of the products of reaction 1, at [Al]:[O] = 0.33 and 0.91, by reacting them, in succession, with 2-propanol and water (Table 7). In both cases, the [Al]:[O] ratio was kept lower than 1 to ensure the absence of free $AlMe_3$. Interaction of the MAO analogues with protic solvents proceeds in two distinct steps, similar to the same reactions with MAO. Some of the $Al{-}CH_3$ bonds, ∼0.8 CH_3/Al, easily react with 2-propanol whereas the remaining $Al{-}CH_3$ bonds are decomposed only with water. The relative content of the latter bonds increases from ∼0.5 to 0.75 as the [Al]:[O] ratio increases (Table 7). The data for the second mixture in Table 7 can be interpreted, in qualitative terms, as indicative of the existence of two methyl groups attached to an Al atom. One methyl group reacts with 2-propanol, and the second methyl group, which becomes the $CH_3{-}Al(Oi\text{-}Pr)O{-}$ group after the reaction with the alcohol, reacts only with water.

We recorded NMR spectra of $AlMe_3{-}(n\text{-}Bu_3Sn)_2O$ mixtures at [Al]:[O] ratios ranging from 0.25 to 2.1. Interpretation of the spectra is easiest when the [Al]:[O] ratio is either quite high or quite low. $(n\text{-}Bu_3Sn)_2O$ has easily distinguishable features both in the ^{119}Sn NMR spectrum (Figure 3A, the signal at +83.0 ppm with respect to $SnMe_4$) and in the ^{13}C NMR spectrum: its signals are at 13.9 (CH_3), 16.7 (α-CH_2 to Sn), 28.6 (β-CH_2), and 27.6 ppm (γ-CH_2). When reaction 1 is carried out at [Al]:[O] < 1, the ^{119}Sn NMR spectra (Figure 3A) exhibit, in addition to the peaks due to unreacted $(n\text{-}Bu_3Sn)_2O$, four other resonances:

1. The signal of the main product of reaction 1, n-Bu_3SnMe, is observed at −5.1 ppm. The signal was assigned based on literature data about the chemical-shift effects of substituents on ^{119}Sn.[36]

2. Two smaller resonances are observed at 103.7 and 107.8 ppm. A strong downfield shift suggests that the Sn atoms in these two compounds are attached to strongly electron-withdrawing moieties, more electronegative than in $(n\text{-}Bu_3Sn)_2O$ itself. The ratio between the yields of these products and that of n-Bu_3SnMe depends on the [Al]:[O] ratio (Table 8A). Assignments for these two signals are proposed below.

3. A very small peak is observed at +46.4 ppm, which can be tentatively assigned to $Sn{-}CH_2{-}Sn$ species.

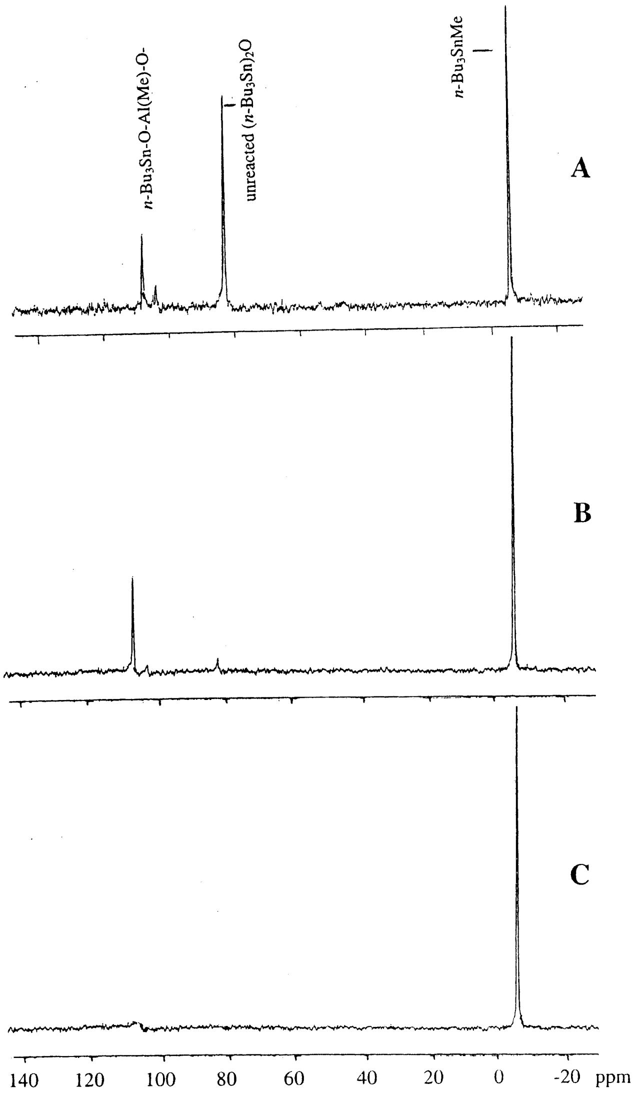


Figure 3. ^{119}Sn NMR spectra of reaction products in the mixtures of $AlMe_3$ and $(n\text{-}Bu_3Sn)_2O$: (A) [Al]:[O] = 0.5; (B) [Al]:[O] = 1.0; (C) [Al]:[O] = 2.0.

Table 8. ^{119}Sn NMR Data for Reactions between Organoaluminum Compounds and $(n\text{-}Bu_3Sn)_2O$

A. Products Formed in $AlMe_3{-}(n\text{-}Bu_3Sn)_2O$ Mixtures (Signal Areas Normalized Relative to n-Bu_3SnMe)

[Al]:[O]	0.25	0.4	0.5	0.5	1.0
$(n\text{-}Bu_3Sn)_2O$	2.83	∼1.0	1.04	0.45	0.04
signal at 107.8 ppm	0.17	0.51	0.34	0.16	0.32
signal at 103.7 ppm	0.17	0.24	0.14	0.04	0.05

B. Observable vs Unobservable Sn Compounds

conditions					products		
			$(n\text{-}Bu_3Sn)_2O$			[Sn], mmol	
AlR_3	temp, °C	[Al]:[O], mol/mol	mmol	convn, %	Bu_3SnR, mmol	obsd	NMR invisible
$AlMe_3$	0	0.33	6.70	35	2.13	0.87	1.66
$AlMe_3$	40	0.54	1.57	52	1.01	0.45	0.16
$AlMe_3$	25	0.34	2.66	35	0.75	0.44	0.66
$AlEt_3$	0	0.34	2.72	38	0.76	0.39	1.02

Quantitative analysis of the ^{119}Sn NMR spectra (using $SnMe_4$ as an internal standard) provided crucial information about the distribution of Sn atoms in the products formed at different [Al]:[O] ratios (Table 8B). When reaction 1 is carried out at [Al]:[O] = 0.3 and at a low temperature, each mole of $AlMe_3$ consumes slightly over 1 mol of $(n\text{-}Bu_3Sn)_2O$ and generates approximately 1 mol of $n\text{-}Bu_3SnMe$ (such mixtures do not activate metallocene complexes). These data clearly indicate that the first stage of reaction 1 at low [Al]:[O] ratios is

$$AlMe_3 + (n\text{-}Bu_3Sn)_2O \rightarrow n\text{-}Bu_3SnMe + Me_2Al{-}O{-}Sn(n\text{-}Bu)_3 \quad (2)$$

A similar compound, $Me_2Al{-}O{-}SnPh_3$, was synthesized earlier by Oliver et al.;[37] it crystallizes as a dimer with both the Al and the Sn atoms in a pseudotetrahedral environment. Judging by Figure 3A and the data in Table 8, the $Me_2Al{-}O{-}SnBu_3$ species formed in reaction 2 participate in further reactions, e.g.:

$$Me_2Al{-}O{-}Sn(n\text{-}Bu)_3 + (n\text{-}Bu_3Sn)_2O \rightarrow n\text{-}Bu_3SnMe + n\text{-}Bu_3Sn{-}O{-}Al(Me){-}O{-}Sn(n\text{-}Bu)_3 \quad (3)$$

$$2Me_2Al{-}O{-}Sn(n\text{-}Bu)_3 \rightarrow n\text{-}Bu_3SnMe + Me_2Al{-}O{-}Al(Me){-}O{-}Sn(n\text{-}Bu)_3 \quad (4)$$

$$Me_2Al{-}O{-}Al(Me){-}O{-}Sn(n\text{-}Bu)_3 + (n\text{-}Bu_3Sn)_2O \rightarrow n\text{-}Bu_3SnMe + n\text{-}Bu_3Sn{-}O{-}Al(Me){-}O{-}Al(Me)\text{-}O{-}Sn(n\text{-}Bu)_3, \text{ etc.} \quad (5)$$

Analysis of relative areas of all signals in the ^{119}Sn spectra of $AlMe_3{-}(n\text{-}Bu_3Sn)_2O$ mixtures prepared at different [Al]:[O] ratios (Table 8-A) suggests that the signal at 103.7 ppm (Figure 3A) belongs to $Me_2Al{-}O{-}Sn(n\text{-}Bu)_3$ (the product of reaction 2), and the signal at 107.8 ppm can be attributed to oligomeric methylalumoxane molecules capped with the $Sn(n\text{-}Bu)_3$ group, $Me_2Al{-}O{-}[Al(Me){-}O]_n{-}Sn(n\text{-}Bu)_3$ and $n\text{-}Bu_3Sn{-}O{-}[Al(Me){-}O]_n{-}Sn(n\text{-}Bu)_3$, formed in reactions 3−5. The fraction of these products reaches a maximum at [Al]:[O] ~ 0.4 and then gradually decreases at high [Al]:[O] ratios (compare Figure 3 parts A and B). Reaction 5 is significantly slower than reactions 2 and 3. For example, the initial consumption of $(n\text{-}Bu_3Sn)_2O$ in the reaction with $AlMe_3$ at [Al]:[O] ~ 0.25, ~40%, is completed within a few minutes, but its subsequent consumption in reaction 5 (in competition with reaction 4) at 20 °C continues for several days.

Similarly to the ^{119}Sn spectra, the ^{13}C NMR spectra of the $AlMe_3{-}(n\text{-}Bu_3Sn)_2O$ mixtures at low [Al]:[O] ratios contain numerous peaks belonging to unreacted $(n\text{-}Bu_3Sn)_2O$ and to the main product, $n\text{-}Bu_3SnMe$, as well as small peaks arising from other oligomeric $n\text{-}Bu_3\text{-}Sn{-}O$-capped products. Judging from the data on the catalytic activity of $AlMe_3{-}(n\text{-}Bu_3Sn)_2O$ mixtures in experiments using stepwise addition of the components (see part 1), none of the $n\text{-}Bu_3Sn{-}O$-capped MAO analogues is an active cocatalyst for zirconocene complexes.

When reaction 1 is carried out at [Al]:[O] ~ 2, the ^{119}Sn NMR spectrum is simple (Figure 3C): all $(n\text{-}Bu_3Sn)_2O$ and all the intermediate products are consumed, and the spectrum contains only the signal of $n\text{-}Bu_3SnMe$. The ^{13}C NMR spectrum of this mixture also shows only a set of signals for $n\text{-}Bu_3SnMe$; in particular, the signal at −12.7 ppm belongs to $CH_3(Sn)$ (the peak is assigned based on the coupled ^{13}C NMR spectrum).

All resonances in the ^{119}Sn spectra of $AlMe_3{-}(n\text{-}Bu_3Sn)_2O$ mixtures are narrow and their integrations with respect to that of the added internal standard, $SnMe_4$, affords precise accounting of all Sn atoms in the mixtures. These measurements produced an unexpected result. When the [Al]:[O] ratio is significantly higher than 1, all $(n\text{-}Bu_3Sn)_2O$ is accounted for; it is converted to Bu_3SnMe. However, when the [Al]:[O] ratio is lower than 1, only a fraction of the Sn atoms are observable, as unreacted $(n\text{-}Bu_3Sn)_2O$, Bu_3SnMe, and the two minor products discussed above (signals at 107.8 and 103.7 ppm in Figure 3A). The remaining Sn atoms become NMR invisible. Their amounts, listed in Table 8B, depend on the [Al]:[O] ratio and reaction temperature. For example, when reaction 1 is carried out at [Al]:[O] ~ 0.3 at 0 °C, only ~35% of all Sn atoms in the product mixture, apart from those in unreacted $(n\text{-}Bu_3Sn)_2O$ and $n\text{-}Bu_3SnMe$, are observed, while the remaining Sn atoms are NMR invisible. When the same reaction is carried out at [Al]:[O] = 0.5 at 40 °C, 74% of all remaining Sn atoms are NMR observable and only 26% of them remain NMR invisible. Several such reactions were carried out under slightly different conditions at [Al]:[O] < 1. In all of them, a significant fraction, from 40 to 60%, of Sn atoms other than in $n\text{-}Bu_3SnMe$ and unreacted $(n\text{-}Bu_3Sn)_2O$ are NMR-unobservable. However, after additional $AlMe_3$ is introduced into such systems, all Sn atoms again become observable, in the form of $n\text{-}Bu_3SnMe$. The reason for the "disappearance" and reappearance of some Sn species is discussed below.

As was mentioned earlier, $(n\text{-}Bu_3Sn)_2O$ readily reacts with various trialkylaluminum compounds AlR_3 with the formation of respective alkylalumoxanes $(AlRO)_n$ capped with different end groups. One such reaction using $AlEt_3$ at [Al]:[O] = 0.33 was also studied by NMR. The spectra of the mixture show the following signals:

1. The signals due to unconverted $(n\text{-}Bu_3Sn)_2O$ in the ^{119}Sn and ^{13}C NMR spectra.
2. The signals due to the main product, $n\text{-}Bu_3SnEt$, at −8.2 ppm in the ^{119}Sn NMR spectrum and a series of resonances in the ^{13}C NMR spectrum; in particular, the $\alpha\text{-}CH_2$ signal of the $Sn{-}C_2H_5$ group at +1.00 ppm.
3. Signals of two types of $n\text{-}Bu_3Sn{-}O$-capped ethylalumoxane molecules in the ^{119}Sn NMR spectrum at 107.4 ppm and at 103.1 ppm (most probably, $n\text{-}Bu_3Sn{-}O{-}AlEt_2$).
4. The signals of the $Al{-}C_2H_5$ group in $n\text{-}Bu_3Sn{-}O$-capped ethylalumoxane: a weak broad signal of the Al atom in the ^{27}Al NMR spectrum at ~+45 ppm and the $\alpha\text{-}CH_2$ signal in the ^{13}C NMR spectrum at +2.55 ppm. Each mole of $AlEt_3$ in this mixture converts ~1 mol of $(n\text{-}Bu_3Sn)_2O$ and produces 0.8 mol of $n\text{-}Bu_3SnEt$. Again, only 28% of the remaining Sn atoms are NMR observable (Table 8B).

Several MAO analogues were prepared in two steps, first reacting $AlMe_3$ and $(n\text{-}Bu_3Sn)_2O$ at a particular [Al]:[O] ratio and then adding either fresh $AlMe_3$ or $(n\text{-}Bu_3Sn)_2O$ to the formed MAO analogues. This procedure can lead to the formation of methylalumoxane molecules capped with different end groups. For example, one such reaction mixture was prepared starting at [Al]:[O] ~ 2.1. The mixture did not contain any unreacted $(n\text{-}Bu_3Sn)_2O$ but contained a small quantity of free $AlMe_3$. The absence of any $Al{-}O{-}Sn$ species, as seen from the ^{119}Sn and ^{13}C NMR spectra, indicates that all oligomeric MAO molecules in the mixture are capped with the $Me_2Al{-}O$ groups. The mixture was then treated with additional $(n\text{-}Bu_3Sn)_2O$ to bring the [Al]:[O] molar ratio to 1.0. The ensuing reaction consumed all the remaining $AlMe_3$ and most of the added ($(n\text{-Bu}_3\text{Sn})_2\text{O}$: on the basis of the ^{119}Sn NMR spectrum, only ~30% of it remained unreacted. These data show that $(n\text{-Bu}_3\text{Sn})_2\text{O}$ reacted with the preformed $\text{Me}_2\text{Al}-\text{O}$-capped methylalumoxane molecules, similarly to reactions 3 and 5.

Interpretation of ^{27}Al NMR spectra of the products of reaction 1 shows, in terms of complexity, a trend opposite to that of the ^{119}Sn NMR spectra. When reaction 1 is carried out at low [Al]:[O] ratios, the ^{27}Al spectra are simple, showing only a small broad signal at ~50 ppm (Figure 4A), despite a significant Al atom concentration in the mixture. This signal, which can be assigned to $n\text{-Bu}_3\text{Sn}-\text{O}-\text{Al(Me)}-\text{O}-\text{Sn}(n\text{-Bu})_3$, is similar to that observed in the ^{27}Al spectrum of AlMe_3-free MAO (Figure 1A). A similar weak signal at ~45 ppm was observed in the ^{27}Al NMR spectrum when AlEt_3 was used instead of AlMe_3 at [Al]:[O] = 0.33 (see above). On the other hand, the ^{27}Al NMR spectrum of the $\text{AlMe}_3-(n\text{-Bu}_3\text{Sn})_2\text{O}$ mixture at [Al]:[O] ~ 2.2 is quite complex (Figure 4B); it exhibits, in addition to the narrow resonance at 153 ppm due to free AlMe_3 and the same broad asymmetric signal at ~45−50 ppm, a small broad signal at ~100 ppm, and a signal in the 160−170 ppm range. The latter feature strongly overlaps with the AlMe_3 resonance but is clearly observable at [Al]:[O] ~ 1. Unfortunately, quantitative analysis of the various Al species in $\text{AlMe}_3-(n\text{-Bu}_3\text{Sn})_2\text{O}$ mixtures based on their ^{27}Al NMR spectra is unreliable because some of these species are unobservable by NMR, similarly to the NMR spectra of MAO itself. Quantitative analysis of the ^{27}Al NMR spectra is less reliable because all signals are quite broad. For example, one semiquantitative measurement of the $\text{AlMe}_3-(n\text{-Bu}_3\text{Sn})_2\text{O}$ mixture at [Al]:[O] ~ 2.1 gave a ratio between free AlMe_3 and NMR-observable Al species of ~1 whereas, based on simple stoichiometric considerations, one would expect a much higher yield of the MAO analogues.

The second MAO analogue we examined is formed in the reaction between AlMe_3 and Me_3SnOH. When toluene slurry of solid Me_3SnOH is mixed with AlMe_3, it reacts vigorously with the release of a large volume of gaseous products and dissolution of the solid:

$$\text{Me}_3\text{SnOH} + \text{AlMe}_3 \rightarrow \text{Me}_2\text{Al}-\text{O}-\text{SnMe}_3 + \text{CH}_4 \quad (6)$$

$$\text{Me}_2\text{Al}-\text{O}-\text{SnMe}_3 + \text{AlMe}_3 \rightarrow \text{Me}_2\text{Al}-\text{O}-\text{AlMe}_2 + \text{SnMe}_4 \rightarrow (+\text{Me}_3\text{SnOH} + \text{AlMe}_3) \rightarrow \text{MAO analogue} \quad (7)$$

As described above, only mixtures of AlMe_3 and Me_3SnOH with [Al]:[O] > 1 activate transition metal compounds for polymerization reactions. ^{119}Sn and ^{13}C NMR spectra of the reaction mixture prepared at [Al]:[O] = 2 contain only signals due to SnMe_4. No free AlMe_3 was observed in the ^{13}C spectrum, suggesting that virtually all AlMe_3 was spent in reactions 6 and 7. The ^{27}Al NMR spectrum of the reaction products exhibits four signals. One is a broad resonance at 51 ppm [~65% of all observable Al atoms]; it is the same signal as in the spectrum of MAO (Figure 1A) and the first MAO analogue (Figure 3). The other three signals are a broad peak at ~150 ppm with a shoulder at ~170 ppm (together they account for ~30% of Al atoms), and a small peak at 110 ppm (~5% of Al atoms).

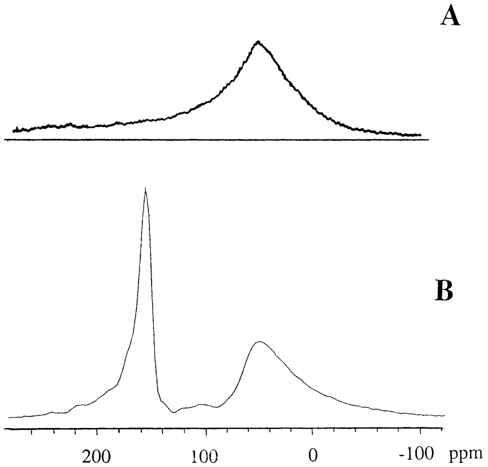
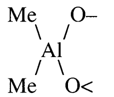


Figure 4. ^{27}Al NMR spectra of reaction products in the mixtures of AlMe_3 and $(n\text{-Bu}_3\text{Sn})_2\text{O}$: (A) [Al]:[O] = 0.25; (B) [Al]:[O] = 2.1.

Discussion

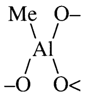
The biggest problem encountered in NMR spectroscopic studies of MAO is the ^{13}C NMR undetectability of most of its components, although they are clearly observed in IR (Figure 2). This phenomenon suggests that ^{13}C dipolar broadening in MAO molecules is quite large. Judging by the experimental data produced under solid-state conditions, most of MAO ingredients, although formally dissolved in aromatic hydrocarbons (and some in aliphatic hydrocarbons as well), remain “quasi-solid” in the sense that their molecular motion is severely restricted. Judging from the NMR invisibility of Sn atoms in Sn-capped MAO analogues $n\text{-Bu}_3\text{Sn}-\text{O}-[\text{Al(Me)}-\text{O}]_n-\text{Sn}(n\text{-Bu})_3$, the NMR invisibility encompasses both the central part of these oligomeric molecules and their Sn-capped chain ends. A change of solvent (toluene vs aliphatic solvents) does not affect this aspect of the MAO structure.

On the basis of the combined NMR spectroscopic data on MAO and its analogues produced in reactions 1 and 7, conventional MAO has Al species of two types. Their signals in the ^{27}Al NMR spectrum are at 150−170 ppm and 50−70 ppm, respectively. Literature data[12,23,24] and our own studies of several organoaluminum compounds suggest that both these types of Al atoms are tetracoordinated and may have the following structures:



(A)

(150-170 ppm)



(B)

(50-70 ppm)

The ratio between the two Al coordination types depends on the method of MAO preparation and reflects its molecular weight. MAO fractions of the highest molecular weight (which are insoluble in aliphatic hydrocarbons) do not have any Al atoms of type A, whereas MAO analogues with low molecular weights, which are prepared from AlMe_3 and the organotin compounds, contain both types of Al atoms in comparable amounts.

As discussed earlier, only a relatively small fraction of the $\text{Al}-\text{CH}_3$ bonds in AlMe_3-free MAO and in MAO analogues reacts with alcohols. On the other hand, the MAO analogues prepared at [Al]:[O] < 1 have one $\text{Al}-\text{CH}_3$ bond which readily reacts with alcohols. This $\text{Al}-\text{CH}_3$ bond apparently belongs to small molecules, such as $\text{Me}_2\text{Al}-\text{O}-\text{Sn}(n\text{-Bu})_3$ (see Table 8 and related discussion). One can assume that the readily reacting $\text{Al}-\text{CH}_3$ bonds in the MAO analogues prepared at high [Al]:[O] ratios (the second line in Table 7) and in MAO itself occupy similar environments (structure A) and belong to molecules such as $Me_2Al-O-Al(Me)-O-Al(Me)-O-AlMe_2$, etc. These structures are present in the $AlMe_3$-free MAO fraction in a very small amount (Figure 1A). On the other hand, the $Al-CH_3$ bonds that can only be decomposed with water apparently belong to MAO components that exist in a quasi-solid form and have structure B. Not only is the reactivity of such Al−C bonds with protic compounds low, but their accessibility to metallocene derivatives (the active species in polymerization reactions) can be restricted as well due to their shielding by the network of Al−O−Al−O chains.

The reason zirconocene complexes, when reacted either with conventional MAO or with the reaction products of $AlMe_3$ and the organotin compounds described in this article, require very high [cocatalyst]:[Zr] ratios to become active in alkene polymerization reactions remains the central unresolved question.[38,39] These high [cocatalyst]:[transition metal] ratios contrast with the data for early metallocene-based catalysts such as $Cp_2TiCl_2-AlEt_2Cl$ and $Cp_2Ti(Me)Cl-AlEtCl_2$, which normally operate at [Al]:[Ti] ratios on the order of 1−10.[40,41] Although the detailed answer to this question is beyond the scope of this study, we can speculate that the high [Al]:[Zr] ratios required for the metallocene−MAO catalysts may be related to the physical state of MAO. Our NMR data suggest that most MAO molecules are aggregated in dense intermolecular complexes and that only a small fraction of MAO molecules is available in a nonassociated form suitable for interaction with metallocene complexes.

MAO analogues produced in reactions between $AlMe_3$ and various organotin compounds containing Sn−O bonds are a convenient replacement for MAO in all catalytic polymerization reactions of alkenes and styrenes. The investigation of the [Al]:[O] ratio effect on the catalytic activity, in particular, a significant increase in the cocatalyst efficiency even after a small incremental increase in the [Al]:[O] ratio above 1 (Table 1), the effects of stepwise addition of cocatalyst components on polymerization rates, and the NMR results all suggest that only MAO analogues with Me_2Al-O chain ends are active cocatalysts for metallocene complexes. The main advantages of the MAO analogues used in this work compared to commercial MAO are (a) simplicity and safety of synthesis, (b) the possibility (to some degree) of manipulating the MAO structure, and (c) the ability to control chain ends in MAO and the amount of free $AlMe_3$ by titration with small quantities of the tin compounds. This synthetic route is also convenient for the synthesis of alkylalumoxanes with various alkyl groups and their mixtures, as well as for the synthesis of alkylalumoxanes with different alkyl groups in the core of their chains and in the end groups.

Acknowledgment. Solid-state NMR spectra were recorded by H. K. C. Timken and S. E. Schramm (Mobil Research and Development Corp.).

References and Notes

(1) Krentsel, B. A.; Kissin, Y. V.; Kleiner, V. I.; Stotskaya, L. L. *Polymers and Copolymers of Higher* α*-Olefins*; Hanser: New York, 1997; Chapter 8.

(2) Ishihara, N.; Kuramoto, M.; Uoi, M. (Idemitsu Kosan, Japan) Eur. Patent Appl. 210,615, 1987.

(3) Ishihara, N.; Kuramoto, M.; Uoi, M. *Macromolecules* **1988**, *21*, 3356.

(4) Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* **1980**, *18*, 99.

(5) Sinn, H., Kaminsky, W., Hoker, H., Eds. *Alumoxanes*; Macromolecular Symposium 97; Huthig & Wepf: Heidelberg, Germany, 1995.

(6) Sinn, H.; Bliemeister, D.; Clausnitzer, D.; Tikwe, L.; Winter, H.; Zarncke, O. In *Transition Metals Organometallics as Catalysts for Olefin Polymerization*; Kaminsky, W., Sinn, H., Eds.; Springer: Berlin, 1988; p 257.

(7) Pasynkiewicz, S. *Polyhedron* **1990**, *9*, 429,.

(8) Winter, H.; Schnuchel, W.; Sinn, H. *Makromol. Chem., Symp.* **1995**, *97*, 119.

(9) Lasserre, S.; Derouault, J. *Nouv. J. Chem.* **1983**, ***7***, 659.

(10) Chien, J. C. W.; Wang, B.-P. *J. Polym. Sci., Polym. Chem. Ed.* **1988**, *26*, 3089.

(11) Resconi, L.; Bossi, S.; Abis, L. *Macromolecules* **1990**, *23*, 4489.

(12) Gianetti, E.; Nicoletti, G. M.; Mazzocchi, R. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 2117.

(13) Tritto, I.; Mealares, C.; Sacchi, M. C.; Locatelli, P. *Macromol. Chem. Phys.* **1997**, *198*, 3963.

(14) Mason, M. R.; Smith, J. M.; Bott, S. G.; Barron, A. R. *J. Am. Chem. Soc.* **1993**, *115*, 4971.

(15) Tritto, I.; Sacchi, M. C.; Locatelli, P.; Li, S.-X. *Macromol. Chem. Phys.* **1996**, *197*, 1573.

(16) Babushkin, D. E.; Semikolenova, N. V.; Panchenko, V. N.; Sobolev, A. P.; Zakharov, V. A.; Talsi, E. P. *Macromol. Chem. Phys.* **1997**, *198*, 3845.

(17) Sugano, T.; Matsubara, K.; Fujita, T.; Takahashi, T. *J. Mol. Catal.* **1993**, *82*, 93.

(18) Zakharov, I. I.; Zakharov, V. I.; Potapov, A. G.; Zhidomirov, G. M. *Macromol. Theory Simul.* **1999**, *8*, 272.

(19) Zurek, E.; Woo, T. K.; Firman, T. K.; Ziegler, T. *Inorg. Chem.* **2001**, *40*, 361.

(20) Zurek, E.; Ziegler, T. *Inorg. Chem.* **2001**, *40*, 3279.

(21) Cam, D.; Albizzati, E.; Cinguina, P. *Makromol. Chem.* **1990**, *191*, 1641.

(22) Harlan, C. F.; Mason, M. R.; Barron, A. R. *Organometallics* **1994**, *13*, 2957.

(23) Sinn, H. *Makromol. Chem., Symp.* **1995**, *97*, 27.

(24) Sinn, H.; Schimmel, I.; Ott, M.; von Thienen, N.; Harder, A.; Hagendorf, W.; Heitmann, B.; Haupt, E. In *Metalorganic Catalysts for Synthesis and Polymerization*; Kaminsky, W., Ed.; Springer: Berlin, 1999; p 105.

(25) Porri, L.; diCorato, A.; Natta, G. *Eur. Polym. J.* **1969**, *5*, 1.

(26) Racanelli, P.; Porri, L. *Eur. Polym. J.* **1970**, *6*, 751.

(27) Racanelli, P.; Porri, L. Italian Patent 745741, 1965.

(28) Kissin, Y. V. U.S. Patent 5,326,837, 1994.

(29) Kissin, Y. V. U.S. Patent 5,397,757, 1995.

(30) Kissin, Y. V.; Mink, R. I.; Nowlin, T. E. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 4255.

(31) Kissin, Y. V. *J. Mol. Catal.* **1989**, *56*, 220.

(32) Kissin, Y. V. *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33*, 227.

(33) Sakharovskaya, G. B.; Korneev, N. N.; Popov, A. F.; Kissin, Y. V.; Mezhikovski, S. M.; Kristalnyi, E. A. *Zh. Obshch. Khim.* **1969**, *39*, 788.

(34) Benn, R.; Rufinska, A.; Lehmkuhl, H.; Janssen, E.; Kruger, C. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 779.

(35) Akitt, J. W.; Farthing, A. *J. Chem. Soc., Dalton Trans.* **1981**, *1617*, 1624.

(36) Harris, R. K.; Mann, B. E. *NMR and the Periodic Table*; Academic Press: London, 1978.

(37) Ghazi, S. U.; Kumar, R.; Heeg, M. J.; Oliver, J. P. *Inorg. Chem.* **1994**, *33*, 411.

(38) Zurek, E.; Ziegler, T. *Organometallics* **2002**, *21*, 83.

(39) Srinavasa Reddi, S.; Shashidhar, G.; Sivaram, S. *Macromolecules* **1993**, *26*, 1180.

(40) Chien, J. C. W. *J. Am. Chem. Soc.* **1959**, *81*, 86.

(41) Henrichi-Olive, G.; Olive, S. *Adv. Polym. Sci.* **1969**, *6*, 421.

MA012234O