ORIGINAL ARTICLE

The preparation of boron-containing aluminoxanes and their application as cocatalysts in the polymerization of olefins

Ryo Tanaka, Takaaki Hirose, Yuushou Nakayama and Takeshi Shiono

Boron-moiety-containing aluminoxanes (BMAOs) were prepared from the partial protonolysis of Me_3Al using various arylboronic acids. Compared with methylaluminoxane (MAO) generated from the hydrolysis of Me_3Al , BMAO prepared from $\text{C}_6\text{F}_5\text{B}(\text{OH})_2$ and Me_3Al induced a higher activity at the same Al/Ti ratio in the Ti-based olefin polymerization catalyst (*ansa*- $\text{Me}_2\text{Si}(\text{Flu})(\text{N}^t\text{Bu})\text{TiMe}_2$; **5**). The time course of propylene consumption when using BMAO showed the deactivation of the catalyst, whereas the 5-dMAO system promoted a living polymerization. Among the BMAOs, only those derived from arylboronic acids with electron-withdrawing groups were observed to act as efficient cocatalysts.

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INTRODUCTION

Aluminoxanes are an important class of Lewis acids, frequently used in the activation of olefin polymerization catalysts. The versatile activation properties of methylaluminoxane (MAO),^{1–3} which is the condensation product of Me_3Al and H_2O , toward transition metal-based coordination-polymerization catalysts have attracted enormous research interest since the discovery of the remarkable potential of MAO as a cocatalyst in metallocene-mediated ethylene polymerization by Kaminsky and Sinn.⁴ However, systematic studies on modifications of MAO remain scarce. This is most likely because MAO usually exists in an equilibrium between linear and cyclic oligomers of varying degrees of polymerization, all of which contain $-\text{Al}(\text{Me})-\text{O}-$ repeating units.⁵ The elucidation of MAO's precise structure and the mechanistic investigation of polymerizations involving MAO are highly complex, although fragmental information has been gathered over time from nuclear magnetic resonance (NMR),^{6–12} x-ray photoelectron,¹³ infrared (IR)¹⁴ and ultraviolet–visible,^{15,16} and mass-spectrometry.¹⁷

Examples of modified MAOs (MMAO) can be categorized into two classes depending on the synthetic route by which they are generated. The first is based on the hydrolysis of alkylaluminum precursors, and the best-known example is probably the commercially available MMAO, which is obtained from the hydrolysis of a mixture of $t\text{Bu}_3\text{Al}$ and Me_3Al .¹⁸ The limited solubility of MAO in hydrocarbons can be improved by the introduction of branched alkyl groups in the corresponding MMAO precursor. Barron was able to isolate compounds with distorted cage structures, such as **1** (Figure 1), from the hydrolysis of $t\text{Bu}_3\text{Al}$.^{19–23} Conversely, the protonolysis of

$t\text{Bu}_3\text{Al}$ with a bulky arylboronic acid resulted in the formation of a uniform cage structure (**2**) in very high yield. Compounds **1** and **2** were found to promote Cp_2ZrMe_2 -mediated ethylene polymerization, although the induced polymerization activity was much lower

than in the presence of an excess of MAO. Eventually, the active species derived from Cp_2ZrMe_2 and **1** was identified by ^1H NMR analysis as **3** (Figure 1).^{19–23} Recently, the synthesis of an oxo-bridged Zr/Al binuclear complex from a mononuclear aluminum complex with a β -diketimide ligand (**4**) was reported, and this complex can promote the polymerization of ethylene in the presence of MAO.²⁴

The second class of examples of MMAOs is based on the incorporation of elements other than Al, O, C and H in the aluminoxanes. For example, the introduction of tin into MAO led to an enhanced activation ability, by 20–80%, even though the structure of the resultant compounds could not be precisely determined.²⁵ Increased polymerization activities (three to sevenfold) were also observed for modifications of MAO by the reaction with trimethylboroxin (MeBO)₃²⁶ or $\text{B}(\text{C}_6\text{F}_5)$ ₃.²⁷

These previously reported results prompted us to investigate why the addition of elements other than Al, O, C and H improved the cocatalyst performance of MAO. For that purpose, we prepared a series of aluminoxanes from Me_3Al and arylboronic acids with varying electronic parameters. Herein, we describe the synthesis and spectroscopic characterization of aluminoxanes and compare the prepared aluminoxanes' activation properties toward prototypical titanium-based olefin polymerization catalysts.

Figure 1 Chemical structures of the well-defined aluminoxanes **1–4**.

EXPERIMENTAL PROCEDURE

General

All manipulations were performed under a nitrogen atmosphere using standard Schlenk line techniques. MAO was generously donated by Tosoh-Finechem (Yamaguchi, Japan). Dry toluene was purchased from Kanto Chemical (Tokyo, Japan), and traces of residual water were removed by reaction with sodium metal. *ansa*-Me₂Si(Flu)(N^tBu)TiMe₂ (**5**) and tris(pentafluorophenyl)boroxine were synthesized according to procedures in the literature.^{28,29} Trace amounts of water and O₂ were removed from propylene gas (Sumitomo Seika, Osaka, Japan) by passing the gas stream through GC-RP and DC-A4 columns (Nikka Seiko, Tokyo, Japan) prior to use. Other materials were used without further purification. ¹H, ¹⁹F, ¹¹B and ²⁷Al NMR spectra were recorded in THF-*d*₈ on a Varian 500 NMR spectrometer or LA-500 spectrometer (JEOL, Tokyo, Japan). The obtained ¹H NMR spectra were referenced to the signals of the residual traces of the partially protonated solvent (δ_{H} (THF) = 3.58 and 1.73 p.p.m.). The calibration was performed using external standards for the other nuclei (δ_{F} (CFCl₃ in CDCl₃) = 0 p.p.m.; δ_{B} (BF₃·OEt₂ in CDCl₃) = 0 p.p.m.; δ_{Al} (Al(NO₃)₃ in D₂O) = 0 p.p.m.). The ¹³C NMR spectrum of the polypropylene was measured using a JEOL-LA-500 spectrometer at 130 °C, using 1,1,2,2-tetrachloroethane-*d*₂ as a solvent. The obtained spectrum was referenced to the signals of the residual traces of the partially protonated solvent (δ = 74.47 p.p.m.). IR spectra were recorded on a FT/IR-300E spectrometer (JASCO, Tokyo, Japan) using KBr pellets. The molecular weight of the obtained polymer was determined by GPC on a Viscotec 350B HT-GPC (Viscotec systems, Malvern, UK; *T* = 150 °C; eluent: *o*-dichlorobenzene) chromatograph calibrated with polystyrene standards. The concentration of polymers in the injecting solutions was ca. 2 mg ml^{−1}, and the injection volume was 0.2 ml. Synthetic protocols are identical for all boron-containing aluminoxanes (**BMAO1–BMAO7**). In the following two sections, representative examples are described in detail for **BMAO1**.

Preparation of the boron-containing aluminoxane **BMAO1**

Pentafluorophenylboronic acid (211 mg, 1.0 mmol) suspended in toluene (20 ml) was added dropwise to a solution of Me₃Al (1.05 mmol in hexane, 0.95 ml, 1.0 mmol) at 0 °C. After the addition was complete, the mixture was heated to 50 °C and stirred for 12 h. The obtained solution was subsequently used for polymerization experiments without any further purification.

Polymerization of propylene using **BMAO1**

Fresh **BMAO1** prepared from Me₃Al (0.50 mmol) and C₆F₅B(OH)₂ (0.50 mmol) was suspended in toluene (29 ml). Nitrogen in the headspace of the flask was removed and replaced with propylene at 0 °C until saturation was achieved. The polymerization was initiated by the addition of **5** (3.7 mg, 10 μmol) in toluene (1.0 ml) under a steady stream of propylene. After the solution had been stirred for 10 min at 0 °C, the resultant mixture was poured into MeOH (200 ml) containing concentrated HCl (4 ml), and the precipitated

Table 1 Preparation of **BMAO1–BMAO7**

$n \text{ R}_3\text{Al} + \text{ArB(OH)}_2 \xrightarrow[\text{12 h}]{\text{toluene, 50 }^\circ\text{C}} \text{BMAO}$			
BMAO	<i>R</i>	<i>Ar</i>	<i>n</i>
1	Me	C ₆ F ₅	1
2	Me	C ₆ F ₅	2
3	Me	C ₆ H ₅	1
4	Me	C ₆ H ₅	2
5	Me	2,6-Me ₂ C ₆ H ₃	1
6	Me	2,6-Me ₂ C ₆ H ₃	2
7	^t Bu	C ₆ F ₅	2

Abbreviation: BMAO, boron-moiety-containing aluminoxane.

polymer was collected by filtration. The obtained polymer was washed with MeOH, and dried for 6 h at 60 °C under reduced pressure until a constant weight was measured. Likewise, 963 mg of polypropylene was obtained as a white solid.

RESULTS AND DISCUSSION

The boron-containing aluminoxanes **BMAO1–BMAO7** were prepared by the reaction of trialkylaluminum with arylboronic acids in toluene (Table 1). After incubation for 12 h at 50 °C, a cloudy solution was obtained. The colorless solids that were obtained after all the volatiles had been removed *in vacuo* were soluble in THF, partially soluble in benzene and toluene, and insoluble in hexane.

Although these aluminoxanes were complex mixtures, spectroscopic analyses of **BMAO1** and **BMAO2** were attempted. In the hydride region of the ¹H NMR spectrum in THF-*d*₈, **BMAO1** showed a broad signal at approximately δ_{H} = −1.5 to 0 p.p.m. with small sharp peaks, whereas **BMAO2** showed an additional three sharp peaks, at δ_{H} = −0.65, −0.60 and −0.35 p.p.m. (Figure 2). According to the assignment of the ¹H NMR spectrum of MAO in THF-*d*₈,³⁰ the broad signal corresponds to the polymeric aluminoxane structure, and the sharp peaks correspond to the mononuclear alkylaluminums. The observed chemical shift of each sharp peak in **BMAO2** differed from that of the peak corresponding to Me₃Al in THF-*d*₈ (δ_{H} = −1.08 p.p.m.) but was rather close to that of the peak corresponding to unreacted and unbridged Me₃Al (δ_{H} = −0.53 p.p.m.), indicating the presence of monomeric alkylaluminum species with a different structure. The integration ratios of the sharp peaks with respect to the broad signal were 1.5% (δ_{H} = −0.65 p.p.m.), 1.6% (δ_{H} = −0.60 p.p.m.) and 1.8% (δ_{H} = −0.35 p.p.m.), showing that the total content of monomeric alkylaluminum species in **BMAO2** was ca. 5%.

The ²⁷Al NMR spectra of **BMAO1**, **BMAO2** and dried MAO (dMAO) each showed a single broad signal at approximately δ_{Al} = 60 p.p.m., for which the chemical shifts were identical to that of aluminoxane (Figure 3).⁷ The half widths of the signals of **BMAO1** ($\Delta_{1/2}$ = 8600 Hz) and **BMAO2** ($\Delta_{1/2}$ = 6800 Hz) were broader than that of dMAO ($\Delta_{1/2}$ = 3700 Hz), most likely because of the heterogeneity of aluminum in the **BMAOs** as a result of the incorporation of boron atoms. The peak position of **BMAO1** (47.4 p.p.m.) was located at a higher field than for **BMAO2** (69.0 p.p.m.) and dMAO (67.0 p.p.m.), indicating that the aluminum center of **BMAO1** was more shielded than the aluminum centers of **BMAO2** and dMAO. This result implies a stronger coordination of the THF solvent to the aluminum centers in **BMAO1** relative to **BMAO2** and dMAO, most

Figure 2 ^1H NMR spectrum of **BMAO1** and **BMAO2** (500 MHz, $\text{THF}-d_8$) between -2.0 and 0 p.p.m.

likely because of the stronger Lewis acidity of the **BMAO1** aluminum center.

The ^{11}B and ^{19}F NMR spectra of **BMAO1** and **BMAO2** were so complex that precise assignment of the individual signals was impossible (see Supplementary Information). However, three broad signals were observed between -110 and -160 p.p.m. in the ^{19}F NMR spectra, and several sharp peaks were observed at approximately 5 – 25 p.p.m. and 50 – 60 p.p.m. in the ^{11}B NMR spectra, indicating the incorporation of the pentafluorophenyl groups and boron atoms into the polymeric structure. The chemical shift of the former in the ^{11}B NMR spectra was almost identical to that of $(\text{C}_6\text{F}_5\text{BO})_3$ (boroxin; $\delta_{\text{B}} = 18.6$ p.p.m. in Et_2O),³¹ suggesting the presence of a B–O–B moiety. The chemical shift of the latter, on the other hand, was significantly low-field shifted compared with the starting materials, $\text{C}_6\text{F}_5\text{B}(\text{OH})_2$ ($\delta_{\text{B}} = 26.2$ p.p.m. in Et_2O) and boroxin, and was close to the chemical shifts of boric acids, $\text{R}_2\text{B}(\text{OH})$.

In the fingerprint region of the IR spectrum, both **BMAO1** and **BMAO2** exhibited absorption peaks indicative of O–Al–O asymmetric vibrations (802 cm^{-1} in **BMAO1** and 801 cm^{-1} in **BMAO2** (see Supplementary Information), and C–H vibrations at $\sim 2960\text{ cm}^{-1}$, which was similar to MAO.¹⁴ Apart from the peaks assigned to aluminosilane, a peak was observed at 1312 cm^{-1} in **BMAO1** and at 1306 cm^{-1} in **BMAO2**, and both of these were assigned to the B–O bond stretch. The O–Al–O peaks were shifted to lower wavenumbers than those previously reported for MAO ($\nu_{\text{asym}} = 808\text{ cm}^{-1}$), thus suggesting longer O–Al bonds in **BMAO1** and **BMAO2**.

Figure 3 ^{27}Al NMR spectrum of **BMAO1**, **BMAO2** and **dMAO** (130 MHz, 2.0 M in $\text{THF}-d_8$).

Next, we examined the ability of **BMAO1**–**BMAO7** to activate prototypical titanium-based olefin polymerization catalysts (Table 2). Polymerizations were performed at 0°C under a propylene pressure of 1 atm using a titanium complex with a fluorenylamide ligand (**5**), which promotes a syndiotactic-specific polymerization of propylene. Among the BMAOs examined, only **BMAO1** and **BMAO2** gave an analyzable amount of polypropylene in the range of an Al/Ti ratio of 50 – 100 , whereas **BMAO3**–**BMAO7** did not activate the catalyst. The activities of **BMAO1** were higher than those of **dMAO** and **MAO** at the same Al/Ti ratio (run 1 vs 7 and 4 vs 9). In order to achieve the same catalyst activity, the amount of **dMAO** required was 8 times higher than the amount of **BMAO1** (run 1 vs 10). The stereotriad distribution of polypropylene obtained using **5**–**BMAO1** as determined by ^{13}C NMR spectroscopy ($rr = 61\%$, Figure 4) was almost the same as that obtained using **5**–**dMAO** ($rr = 63\%$).³² The molecular weight of the polymer obtained using **BMAO1** was higher than that

Table 2 Ti-catalyzed polymerization of propylene using BMAOs as cocatalysts

Run	5 (μmol)	BMAO	Al:B:Ti	Time (min)	Yield (mg)	A^a	$M_n^b (10^3)$	PDI^b	$N^c (\mu\text{mol})$
1	10	1	50:50:1	10	963	578	748	1.8	1.3
2	10	1	50:50:1	20	1083	325	837	1.7	1.3
3 ^d	20	1	50:50:1	20	1454	218	289	1.5	5.0
4 ^d	20	1	100:100:1	10	1884	565	259	1.5	7.3
5	20	2	100:50:1	30	193	19	212	2.5	0.9
6	10	MAO	50:0:1	30	Trace	ND ^e	ND ^e	ND ^e	ND ^e
7	10	dMAO	50:0:1	10	68	41	26	10.5	2.6
8	20	MAO	100:0:1	10	34	10	7	1.7	4.7
9	10	dMAO	100:0:1	10	483	290	49	1.5	9.9
10	10	dMAO	400:0:1	10	756	454	81	1.2	9.3

Abbreviations: BMAO, boron-moiety-containing aluminoxane; dMAO, dried MAO; MAO, methylaluminoxane; ND, not determined; PDI, polydispersity index.

^aActivity in $\text{kg mol Ti}^{-1} \text{h}^{-1}$.

^bDetermined by GPC calibrated with polystyrene standards.

^cNumber of the polymer chain calculated from yield (g) and M_n (g mol^{-1}).

^dFurther polymerization cannot be continued because of the ineffective stirring.

^eNot determined, as no polymer was obtained.

Figure 4 ^{13}C NMR spectrum of the methyl region of polypropylene obtained from **5-BMAO1** (Table 2, run 1).

obtained using dMAO, indicating that the propagation rate of the **5-BMAO1** system is higher than that of **5-dMAO**. This is most likely because of the presence of the C_6F_5 groups, which are electron-withdrawing and should enhance the Lewis acidity of the aluminum center. However, the number of polymer chains obtained using **BMAO1** was lower than that obtained using dMAO, indicating that the number of strong Lewis acidic sites in **BMAO1** is lower than in dMAO. The polydispersity indexes of the polymers obtained by using **BMAO1** were close to 2, and the **BMAO1** activity decreased in longer reactions, most likely because of the deactivation of the catalyst (run 1 and 2). The use of $(\text{C}_6\text{F}_5\text{BO})_3$ instead of $\text{C}_6\text{F}_5\text{B}(\text{OH})_2$ as the catalyst system resulted in the formation of a trace amount of the polymeric

Figure 5 Rate-time profiles of propene polymerization using **5** activated with **BMAO1**, **BMAO2** or dMAO (Table 2, Run 1, 5 and 9, respectively). Table 2. Ti-catalyzed polymerization of propylene using BMAOs as cocatalysts.

product, indicating that the protonolysis of Me_3Al is important in the formation of an active cocatalyst. An increase in the Al/Ti ratio increased the number of polymer chains, which is explained by the improvement in the initiation efficiency (run 3 and 4). **BMAO2** showed a comparable activity to MAO (run 5 vs 8), indicating that the amount of incorporated boron greatly influences the cocatalyst ability. The steric demand of the arylboronic acid was not observed because **BMAO3–BMAO6** gave only a trace amount of polymer. **BMAO7**, which was prepared from $^i\text{Bu}_3\text{Al}$ and $\text{C}_6\text{F}_5\text{B}(\text{OH})_2$, showed no cocatalyst ability. This behavior may arise because the aluminum center is sterically hindered by the isobutyl groups.

Rate-time profiles from the amount of propylene consumed in the **5-BMAO1/BMAO2/dMAO** systems are shown in Figure 5. When **BMAO1** and **BMAO2** were used, the polymerization rate reached a maximum within several minutes and gradually decreased, whereas continuous polymerization proceeded in the **5-dMAO** system. Previously, we investigated the effect of the cocatalyst on propylene polymerization by **5** and proposed that the counteranion from dMAO

and $\text{B}(\text{C}_6\text{F}_5)_3$ may form less active, but more stable, ion pairs with the active cationic Ti species and promote a living polymerization.³² On the other hand, non-interacting $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ resulted in the deactivation of the catalyst, even at -50°C . As with $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$, anions from the BMAOs are stable enough and do not interact with the generated Ti cation, thereby resulting in high polymerization rates and a gradual deactivation.

CONCLUSION

Boron-containing aluminoxanes **BMAO1**–**BMAO7** were prepared from the reaction of Me_3Al and arylboronic acids. The NMR and IR analyses of the products indicated polymeric structures containing both aluminum and boron atoms. **BMAO1** exhibited a higher activation activity toward the Ti-based olefin polymerization catalyst **5** than did MAO or dMAO at the same Al/Ti ratio; this is most likely due to the higher Lewis acidity of the aluminum centers in the Al–O–B structure. These results demonstrate the potential of boronic acids, especially those with electron-withdrawing groups, to act as protonolysis reagents for the preparation of MMAOs, which show desirable activation properties as cocatalysts in olefin polymerizations.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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