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Ligand exchange and abstraction reactions involving titanium isopropoxide with tris(pentafluorophenyl)borane and -alane: ramifications for ring-opening polymerization of propylene oxide [☆]

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Dedicated to Professor T.J. Marks on the occasion of his 60th birthday

Abstract

In situ mixing of $Ti(O'Pr)_4$ and $B(C_6F_5)_3$ generates a very efficient catalyst system for ring-opening polymerization (ROP) of propylene oxide (PO) with a turnover frequency (TOF) >1350/h, whereas the mixture of $Ti(O^{i}Pr)_{4}$ and $Al(C_{6}F_{5})_{3}$ is inactive for the same polymerization. The inactivity of the $Ti(O^{i}Pr)_{4}/Al(C_{6}F_{5})_{3}$ mixture is due to the formation of the stable isopropoxy-bridged bimetallic species $Ti(O'Pr)_3(\mu-O'Pr)Al(C_6F_5)_3$ (1), the structure of which has been confirmed by X-ray diffraction. The products of the $Ti(O^{j}Pr)_{4} + B(C_{6}F_{5})_{3}$ reaction, however, depend on the $Ti(O^{j}Pr)_{4}$: $B(C_{6}F_{5})_{3}$ ratio. The 1:1 ratio reaction in toluene at ambient temperature is rapid and produces the ligand exchange products: $Ti(O^{i}Pr)_{3}C_{6}F_{5}$ and ${}^{i}PrOB(C_{6}F_{5})_{2}$ (2), along with a small amount of $(^{1}\text{PrO})_{2}\text{BC}_{6}\text{F}_{5}$. The two resulting boranes are inseparable by recrystallization or vacuum distillation, and the formation of the undesired $(^{\prime}PrO)_2BC_6F_5$ is either significantly enhanced upon heating the reaction in toluene to 80 °C or nearly exclusive by carrying out the reaction in THF. By employing 1.2 equiv. of $B(C_6F_5)_3$ in the reaction with $Ti(O^iPr)_4$, however, the formation of $(^iPrO)_2BC_6F_5$ is suppressed, enabling the isolation of the new borane 2 in its pure state. The excess of $B(C_6F_5)_3$ added to the reaction apparently slows down the exchange reaction by stabilizing the intermediate $Ti(O^{i}Pr)_{3}(\mu-O^{i}Pr)B(C_{6}F_{5})_{3}$ (4), as shown by the 1:2 $Ti(O^{i}Pr)_{4}:B(C_{6}F_{5})_{3}$ reaction which initially forms the ligand abstraction product 4 followed by subsequent slow ligand exchange to give the final products $Ti(O'Pr)_3C_6F_5$ and 2. The studies of these individual reactions, in combination with control polymerization runs, reveal that the active species responsible for the catalytic activity of the Ti($O^{i}Pr$)₄/B($C_{6}F_{5}$)₃ mixture is the isopropoxy borane 2. Thus, the isolated 2, in the absence or presence of a hydroxylic initiator, serves as a very effective catalyst for the ROP of PO, producing PPOs with $M_{\rm n} = 2000-3000, M_{\rm w}/M_{\rm n} = 1.30-1.43$, and TOF >1400/h. The MALDI-TOF MS analyses of the PPOs formed show the linear PPO structures having the initiator and water molecules as end groups, demonstrating the control over the PPO structure. © 2004 Elsevier B.V. All rights reserved.

Keywords: Polymerization of propylene oxide; Titanium isopropoxide; Tris(pentafluorophenyl)borane; Tris(pentafluorophenyl)alane; Ligand exchange; Ligand abstraction; Poly(propylene oxide)

1. Introduction

Poly(propylene oxide) (PPO) is a useful material in a number of applications [1]. In particular, low to medium

molecular weight PPOs of a few thousand Da are key intermediates in polyurethane production [2] in which primary-hydroxyl-terminated polyols undergo polycondensation reactions with diisocyanates in certain rapid processes such as polyurethane reaction injection molding (Eq. (1)),

$$HO \sim R \sim OH + OCN - R' - NCO \longrightarrow \left\{ O \sim R \sim O - C - NH - R' - NH - C \right\}$$

$$(1)$$

 $^{^{\}star}$ Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2004.05.015.

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Base, acid, and coordination catalyses are three mechanistically distinct chemical processes commonly used for the production of PPOs through ring-opening polymerization (ROP) of propylene oxide (PO). In the base-catalyzed, anionic ROP process, PO is combined with a hydroxylic initiator and a strongly basic catalyst (e.g., potassium hydroxide) [1], whereby the initiator compound determines the functionality of PPO. Ethylene oxide is often added in a subsequent step at the end of the polymerization of PO to afford the reactive, primary-hydroxyl-terminated PPOs. A side reaction of concern in this process is the formation of allyl alcohol that leads to a terminally unsaturated, monofunctional polyol [3].

PPOs produced by acidic catalysts such as boron trifluoride diethyl etherate and HBF₄ [1,4] typically contain considerable amounts of byproducts, including dimethyldioxane and various concurrent cyclic oligomers [5] due to "backbiting" reactions. To substantially reduce the formation of such byproducts, Penczek and co-workers [6] have developed cationic "activated monomer" ring-opening polymerization where a heterocyclic monomer is activated via protonation by Brønsted acids such as HBF₄ and the growing chain end is the neutrally charged hydroxyl group, instead of the highly reactive, electrophilic oxonium ion (i.e., activechain end). To suppress the reactions proceeding with the active-chain end mechanism, the "activated monomer" ROP is typically carried out under monomer starving conditions.

Coordination catalysis typically produces PPOs having high molecular weight or with controlled structures [7]. For example, discrete (porphyrin)Al–X (X = Cl, OR, SR) complexes promote living or immortal coordination polymerization of PO [8]. Other examples of the discrete coordination catalysts investigated for PO polymerization include (Salen)Al–X [9] bulky bisphenoxide aluminum chloride dimers [10], isobutylalumoxane/PO complex [11]. The proposed bimetallic nature [12] of the PO polymerization by Lewis acidic metal complexes has been recently confirmed with the microstructure analysis of PPOs [10] and with the synthetic and polymerization study that PO polymerization by neutral aluminum Lewis acid/anionic aluminate pair is much faster and more controlled than that by the neutral catalyst alone [13].

We previously reported the PO polymerization catalyzed by strong organo-Lewis acids such as $M(C_6F_5)_3$ (M = B, Al) and initiated by hydroxylic initiators such as 1,4-butanediol [14]. Because of the instability of the alane catalyst in the presence of a hydroxylic initiator, we sought to explore the possibility of combining the Lewis acid catalysts $M(C_6F_5)_3$ with an organometallic complex carrying an initiating ligand such as $Ti(O'Pr)_4$. We report here the PO polymerization behavior of the $Ti(O'Pr)_4/M(C_6F_5)_3$ catalyst systems, the ligand exchange and abstraction reactions involved in these sys-



tems, as well as the implications of these reactions for PO polymerization (Scheme 1).

2. Experimental

2.1. Materials and methods

All syntheses and manipulations of air- and moisturesensitive materials were carried out in flamed Schlenktype glassware on a dual-manifold Schlenk line, on a high vacuum line $(10^{-5}-10^{-7} \text{ Torr})$ or in an argon-filled glovebox (<1.0 ppm oxygen and moisture). NMR scale reactions were conducted in Teflon-valve-sealed sample J. Young-type NMR tubes. Anhydrous or HPLC-grade organic solvents were first saturated with nitrogen during filling of the solvent reservoir and then dried by passage through activated alumina and Q-5 supported copper catalyst in stainless steel columns prior to use. Benzene-d₆ and toluene-d₈ were dried over Na/K alloy and distilled and/or filtered prior to use, whereas CDCl₃ was dried over activated Davison 4 A molecular sieves. NMR spectra were recorded on a Varian Inova 300 (FT 300 MHz, ¹H; 75 MHz, ¹³C; 282 MHz, ¹⁹F; and 96 MHz, ¹¹B) spectrometer. Chemical shifts for ¹H and ¹³C spectra were referenced to internal solvent resonances and are reported as parts per million relative to tetramethylsilane. ¹⁹F NMR and and ¹¹B spectra were referenced to CFCl₃ and BF₃ · OEt₂ external standards, respectively. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

Propylene oxide (PO), titanium isopropoxide, anhydrous isopropanol, 1,4-butanediol, and glycerin were purchased from Aldrich Chemical Co. and used as received unless otherwise indicated. PO and 1,4-butanediol were first degassed and dried over CaH_2 overnight and then vacuum-distilled before use.

Tris(perfluorophenyl)borane, B(C₆F₅)₃, was obtained as a research gift from Boulder Scientific Company and further purified by recrystallization from hexanes at -35 °C. Tris(pentafluorophenyl)alane, Al(C₆F₅)₃, as a $0.5 \cdot$ toluene adduct, was prepared according to the literature procedure [15], which is the modified synthesis of the alane first disclosed by Biagini et al. [16] *Extra caution should be exercised when handling this material because of its thermal and shock sensitivity*.

2.2. Synthesis of $Ti(O^iPr)_3(\mu - O^iPr)Al(C_6F_5)_3$ (1)

In an argon-filled glovebox, a 20-mL glass reactor was equipped with a magnetic stir bar and charged with Al(C₆F₅)₃ \cdot 0.5 toluene (0.24 g, 0.42 mmol) and 10 mL of toluene. To this reactor was added Ti(O^{*i*}Pr)₄ (0.12 mL, 0.42 mmol) at ambient temperature. The resulting yellow clear solution was stirred for 45 min, the volatiles of which were removed in vacuo to obtain a pale yellow solid. The crude material was redissolved in a minimum amount of hexanes and the solution was cooled to -30 °C inside a freezer of the glovebox. Colorless needles formed were filtered and dried to give 0.22 g (75%) of the pure product 1. Single crystals suitable for X-ray diffraction were obtained from a solution of 1 in a 3:1 toluene/hexanes solvent mixture at -30 °C in 3 h.

¹H NMR (C₆D₆, 23 °C) for Ti(OⁱPr)₃(μ-OⁱPr)Al(C₆F₅)₃ (1): δ 4.71 (sept, J = 6.3 Hz, 1H, CHMe₂), 4.03 (sept, J = 6.0 Hz, 3H, CHMe₂), 1.26 (d, J = 6.0 Hz, 6H, CHMe₂), 1.26 (d, J = 6.0 Hz, 18H, CHMe₂). ¹⁹F NMR (C₆D₆, 23 °C): δ -121.41 (d, ³J_{F-F} = 16.9 Hz, 6F, o-F), -153.23 (t, ³J_{F-F} = 19.52 Hz, 2F, p-F), -161.93 (m, 6F, m-F). ¹³C NMR (C₆D₆, 23 °C): δ 152.17, 148.70, 138.92, 135.52 (C₆F₅), 82.57 (CHMe₂), 76.94 (CHMe₂), 25.45 (CHMe₂), 23.80 (CHMe₂). Anal. Calc. for C₃₀H₂₈AlF₁₅O₄Ti: C, 44.35; H, 3.47. Found: C, 43.95; H, 3.47%.

2.3. Reaction of $Ti(O^i Pr)_4$ with 1 equiv. of $B(C_6F_5)_3$

In a glovebox, a 60-mL glass reactor was equipped with a magnetic stir bar and charged with a 25 mL solution $B(C_6F_5)_3$ (2.00 g, 3.34 mmol) in toluene. To this reactor was added Ti(OⁱPr)₄ (0.95 g, 3.34 mmol) at ambient temperature. The resulting mixture was stirred for 45 min, upon which time the mixture turned to yellow. The volatiles were removed in vacuo to obtain a pale yellow oil, the ¹H and ¹⁹F NMR of which showed the formation of three species: $Ti(O^iPr)_3C_6F_5$ i PrOB(C₆F₅)₂ [17], (2),and $(^{i}PrO)_{2}BC_{6}F_{5}$ (3) [18]. The crude material was extracted with hexanes and filtered, and removal of the solvent of the filtrate produced 2 in $\sim 94\%$ purity, with a small amount of 3 still present. Vacuum distillation of the oily product twice at 120-130 °C/0.2 Torr gave the slightly purer 2, but it was still contaminated with a trace amount 3.

¹H NMR (C₆D₆, 23 °C) for ^{*i*}PrOB(C₆F₅)₂ (**2**): δ 4.14 (sept, J = 6.0 Hz, 1H, CHMe₂), 1.07 (d, J = 6.0 Hz, 6H, CHMe₂). ¹⁹F NMR (C₆D₆, 23 °C): δ –133.14 (br, 6F, o-F), –149.70 (t, ³J_{F-F} = 19.5 Hz, 3F, p-F), –161.26 (br, 6F, *m*-F). ¹³C NMR (C₆D₆, 23 °C): δ 149.02, 144.50, 139.32 (C₆F₅, C_{ipso} obscured), 74.42 (CHMe₂), 23.93 (CHMe₂). ¹¹B NMR (C₆D₆, 23 °C): δ 39.58.

2.4. Reaction of $Ti(O^iPr)_4$ and 1.2 equiv. of $B(C_6F_5)_3$: Isolation of the pure ^{*i*} $PrOB(C_6F_5)_2$ (2)

The reaction was carried out in the similar manner as the 1:1 ratio reaction shown above, except for the change of the amount of the borane to 1.2 equiv. and the reaction time to 24 h. The crude product of **2** (89.2 %) was vacuum-distilled at 100–110 °C/0.1 Torr. The first two minor fractions contained predominant **2** plus a trace amount of **3**, whereas the third fraction gave the spectroscopically pure **2**; yield 62.9 %. The ¹H, ¹⁹F, ¹³C, and ¹¹B NMR data of **2** are reported above.

2.5. Reaction of $Ti(O^{i}Pr)_{4}$ with 2 equiv. of $B(C_{6}F_{5})_{3}$: in situ generation of $Ti(O^{i}Pr)_{3}(\mu-O^{i}Pr)B(C_{6}F_{5})_{3}$ (4)

In an argon-filled glovebox, a 6-mL glass vial was charged with $B(C_6F_5)_3$ (20.4 mg, 0.04 mmol) and 0.7 mL of benzene-d₆. To this vial was added Ti(O^{*i*}Pr)₄ (5.8 µL, 0.02 mmol), and the resulting mixture was transferred to a Teflon-valve-sealed sample J. Young NMR tube via pipette. The reaction was then monitored by ¹H and ¹⁹F NMR spectroscopy at 23 °C. The formation of **4** was observed within 10 min, while the other minor species (Ti(O^{*i*}Pr)₃C₆F₅ and **2**) were also detected. After sitting in the NMR tube for 24 h, the reaction gave Ti(O^{*i*}Pr)₃C₆F₅ and **2**, plus a trace amount of **4**.

¹H NMR (C₆D₆, 23 °C) Ti(O^{*i*}Pr)₃(μ -O^{*i*}Pr)B(C₆F₅)₃ (4): δ 4.48 (sept, J = 6 Hz, 1H, CHMe₂), 4.11 (sept, J = 6.0 Hz, 3H, CHMe₂), 1.29 (br, 6H, CHMe₂), 0.91 (d, J = 6.0 Hz, 18H, CHMe₂). ¹⁹F NMR (C₆D₆, 23 °C): δ -130.41 (br, 6F, *o*-F), -156.76 (br, 2F, *p*-F), -164.27 (b, 6F, *m*-F).

2.6. Polymerization procedures and polymer characterizations

Polymerization of propylene oxide was carried out in 50-mL Schlenk flasks on a Schlenk line. A weighed, flame-dried flask equipped with a magnet stirrer and capped with a septum was charged with PO (5.00 mL, 4.15 g, 71.5 mmol). For polymerizations employing a hydroxylic initiator, to this flask was added via microsyringe the degassed hydroxylic initiator in the desired PO/initiator ratio (see Table 1). After a desired temperature (23 °C) was reached using the external temperature-controlled bath, 2.0 mL of the freshly prepared catalyst solution in toluene (14.3 μ mol, [PO]_o:[Cat]_o = 5000:1) was added into the rapidly stirred flask using a gastight syringe. The reaction was stirred for the measured time interval and unreacted monomer was quickly removed under reduced pressure. The residue was dried under 0.1–0.2 Torr at ambient temperatures for 2 h, yielding a viscous oil. After the polymer yield was measured, the residue was dissolved in 25 mL of methylene chloride and washed with 15 mL of 0.1 M HCl in a

Table 1 Crystal data and structure refinements for 1

E	
Empirical formula	$C_{30}H_{28}AIF_{15}O_4I1$
Formula weight	812.40
Temperature (K)	167(2)
Wavelength (A)	0.71073
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	10.0821(16)
b (Å)	10.9600(17)
<i>c</i> (Å)	16.715(3)
α (°)	77.904(3)
β (°)	89.719(3)
γ (°)	72.961(3)
Volume (Å ³)	1723.6(5)
Ζ	2
$D_{\text{calc}} (\text{mg/m}^3)$	1.565
Absolute coefficient (mm ⁻¹)	0.389
F(000)	820
Crystal size (mm ⁻³)	0.30 imes 0.30 imes 0.25
θ Range for data collection (°)	1.99 to 28.38
Index ranges	$-12 \leq h \leq 13, -14 \leq k \leq 14,$
-	$-21 \leqslant 1 \leqslant 22$
Reflections collected	15999
Independent reflections	8220 $[R_{int} = 0.0403]$
Absorption correction	SADABS
Data/restraints/parameters	8220/0/460
Goodness-of-fit on F^2	1.047
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0661, wR_2 = 0.1717$
R indices (all data)	$R_1 = 0.0831, wR_2 = 0.1866$
Largest difference peak and	1.439 and -0.601
hole $(e/Å^3)$	

separatory funnel. The organic layer was washed with 2×10 mL distilled water and dried over anhydrous MgSO₄. The mixture was filtered; the solvent of the filtrate was removed in vacuo to yield PPOs, typically as colorless, viscous oils.

All PPOs produced from this study have similar ¹H NMR spectra. ¹H NMR (CDCl₃, 23 °C): δ 3.8–3.2 (m, 3H, CHMe and CH₂), 1.2–1.0 (m, 3H, Me). The PPO samples were analyzed by Matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MAL-DI-TOF MS). MALDI-TOF MS was performed on a Voyager DE Pro (Perseptive Biosystems) mass spectrometer operated in linear, delayed extraction, positive ion mode using a N₂ laser at 337 nm and 20 kV accelerating voltage. Matrix dithranol in THF was mixed with NaI (aqueous solution), followed by mixing with PPO (THF solution) before this mixture was added to the target.

2.7. X-ray crystallographic analysis of 1

Single crystals suitable for X-ray diffraction studies were obtained by recrystallization from a saturated solution of **1** in a 3:1 toluene/hexanes solvent mixture at -30 °C inside of a freezer of the glovebox. The solvents were decanted in the glovebox and the crystals were quickly covered with a layer of Paratone-N oil (Exxon, dried and degassed at $120 \text{ °C}/10^{-6}$ Torr for 24 h). The crystals were then mounted on thin glass fibers and transferred into the cold-steam of a Siemens SMART CCD diffractometer. The structures were solved by direct methods and refined using the Siemens SHELXTL program library [19]. The structure was refined by full-matrix weighted least-squares on F^2 for all reflections. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in the structure factor calculations at idealized positions unless otherwise indicated. Selected crystal data and structural refinement parameters are collected in Table 1.

3. Results and discussion

3.1. PO polymerization catalyzed by $Ti(O^{i}Pr)_{4}/M(C_{6}F_{5})_{3}$ (M = B, Al)

In situ mixing of Ti(OⁱPr)₄ and B(C₆F₅)₃ generates an efficient catalyst system for ROP of PO. In a ratio of $[PO]_0:[Cat]_0 = 5000:1$, a PO conversion >80% in 3 h of polymerization time was achieved, reflecting a turnover frequency (TOF) >1350/h (entries 1–3, Table 2). The PPO obtained was analyzed by MALDI-TOF MS, giving a M_n of 2170 Da and a molecular weight distribution of $M_w/M_n = 1.41$. As can be seen from the table, the premixing time, which ranged from 2 min to 3 h, had virtually no effect on polymerization activity in terms of TOF numbers (entries 1–3), whereas increasing the Ti(OⁱPr)₄: B(C₆F₅)₃ ratio from 1 to 10 significantly reduced the polymerization activity (entries 4–6 versus 1–3).

In sharp contrast, the system derived from in situ mixing of Ti($O^{i}Pr$)₄/Al($C_{6}F_{5}$)₃ was completely inactive for PO polymerization (entry 7). Control runs using Ti($O^{i}Pr$)₄ or Ti($O^{i}Pr$)₃ $C_{6}F_{5}$ showed no activity for either reagent (entries 8 and 9), whereas the polymerization using B($C_{6}F_{5}$)₃ or Al($C_{6}F_{5}$)₃ alone produced only dimer, trimer, and other low molecular weight oligomers [14]. Thus, the substantially increased molecular weight of the resulting PPO with Ti($O^{i}Pr$)₄/B($C_{6}F_{5}$)₃ and the inactivity for Ti($O^{i}Pr$)₄/Al($C_{6}F_{5}$)₃ pointed to an important role of Ti($O^{i}Pr$)₄ in these two catalyst systems. To understand their catalytic behavior, individual reactions involved in these systems were investigated in detail, the results of which are discussed in the following two sections.

3.2. Reaction of $Ti(O^{i}Pr)_{4}$ with $Al(C_{6}F_{5})_{3}$ and X-ray structure of $Ti(O^{i}Pr)_{3}(\mu-O^{i}Pr)Al(C_{6}F_{5})_{3}$ (1)

The reaction of Ti(O^{*i*}Pr)₄ with Al(C₆F₅)₃ in toluene proceeds cleanly to produce the microcrystalline, isopropoxy-bridged bimetallic species: Ti(O^{*i*}Pr)₃(μ -O^{*i*}Pr)-Al(C₆F₅)₃ (1). As already shown in Table 2, the Ti(O^{*i*}Pr)₄/Al(C₆F₅)₃ mixture is inactive for PO poly-

Table 2 Summary of PO polymerization catalyzed by $Ti(O^{i}Pr)_{4}/M(C_{6}F_{5})_{3}{}^{a}$

Entry	Catalyst	Premixing time (min)	Polymerization time (h)	Conversion (%)	TOF ^b (/h)
1.	$Ti(O^iPr)_4/B(C_6F_5)_3$	2	3	82.4	1370
2.	$Ti(O'Pr)_4/B(C_6F_5)_3$	15	3	81.9	1365
3.	$Ti(O^{i}Pr)_{4}/B(C_{6}F_{5})_{3}$	180	3	81.4	1356
4.	$2 \operatorname{Ti}(O^{i}Pr)_{4}/B(C_{6}F_{5})_{3}$	180	3	38.6	640
5.	$3 \text{ Ti}(O'Pr)_4/B(C_6F_5)_3$	180	3	31.8	530
6.	$10 \text{ Ti}(O^{i}Pr)_{4}/B(C_{6}F_{5})_{3}$	180	3	12.8	210
7.	$Ti(O^{i}Pr)_{4}/Al(C_{6}F_{5})_{3}$	120 or 180	3	0	0
8.	Ti(O ⁱ Pr) ₄	N.A.	3	0	0
9.	Ti(O ⁱ Pr) ₃ C ₆ F ₅	N.A.	3	0	0

^a Carried out at 23 °C, 5.00 mL (4.15 g) of PO, $[PO]_0$: $[Cat]_0 = 5000$.

^bTurnover frequency (TOF) = moles of PO consumed per mole of catalyst per hour; calculations were based on polymer yield.

merization; likewise, the PO polymerization using the isolated complex **1** showed no activity, indicative of the high stability of this adduct.

The bimetallic complex 1 crystallizes in the triclinic space group $P\overline{1}$. The crystal structure of 1 (Fig. 1) features the tight ion pair in which one isopropoxy ligand is unsymmetrically bonded to the distorted tetrahedral titanium and aluminum centers with a Ti–O–Al vector angle of 116.58(9)°. This bridging isopropoxy ligand to Ti distance is ~0.238 Å longer than the distance of Ti to the rest of three terminal isopropoxy ligands. The average Al–C(aryl) distance (1.998 Å) compares well with those in other Al(C₆F₅)₃ complexes with metallocene alkyl [20], imidazole [21], toluene [22], THF [23], water [24], and methanol [24]; the Al–O distance (1.834(2) Å) is noticeably shorter than those observed in the adducts of Al(C₆F₅)₃ with THF (1.860(2) Å), water (1.857(3) Å), and methanol (1.858(3) Å).



Fig. 1. Molecular structure of 1. Selected bond lengths (Å) and angles (°): Ti–O(4) = 1.979(2), Al–O(4) = 1.834(2), Ti–O(1) = 1.741(2), Ti–O(2) = 1.739(2), Ti–O(3) = 1.741(2), Al–C(13) = 2.007(2), Al–C(19) = 1.997(3), Al–C(25) = 1.992(2); Ti–O(4)–Al = 116.58(9).

3.3. Reaction of $Ti(O^iPr)_4$ with $B(C_6F_5)_3$: isolation of ^{*i*}PrOB(C_6F_5)₂ (2) and observation of unstable intermediate $Ti(O^iPr)_3(\mu-O^iPr)B(C_6F_5)_3$ (4)

The reaction of $Ti(O^{i}Pr)_{4}$ with $B(C_{6}F_{5})_{3}$ is sensitive to the ratio of the two reactants and solvent. The 1:1 ratio reaction in toluene at ambient temperature undergoes fast ligand exchange producing a product mixture consisting of $Ti(O^{i}Pr)_{3}C_{6}F_{5}$ and ${}^{i}PrOB(C_{6}F_{5})_{2}$ (2), along with a small amount of the undesired $({}^{i}PrO)_{2}BC_{6}F_{5}$ (3) (Scheme 2). The boranes 2 and 3 can be readily separated from the titanium species by hexane extraction; however, all attempts to separate themselves using either recrystallization or vacuum distillation afforded 2 in \sim 94% purity based on ¹H NMR. The 1:1 ratio reaction at 80 °C substantially enhanced the formation of 3, reaching a 2:3 ratio of 3:1 in the product mixture, whereas the reaction in THF selectively produced 3, along with the co-product $Ti(O^{i}Pr)_{3}C_{6}F_{5}$ and a trace amount of **2** (Scheme 2).

Interestingly, employing 1.2 equiv. of $B(C_6F_5)_3$ in the reaction with $Ti(O^iPr)_4$ in toluene considerably slows down the exchange reaction, and more significantly, it suppresses the formation of the undesired **3**. Using this strategy, the pure borane **2** was finally isolated in 63% yield through the 1:1.2 ratio reaction (Scheme 3), followed by recrystallization and vacuum distillation of the crude reaction products. Addition of $B(C_6F_5)_3$ to a **2**:3 mixture of a known ratio did not change the original ratio after more than 4 h of reaction time; this experiment suggests that the cleaner formation of **2** in the 1:1.2 reaction than in the 1:1 reaction is not due to the possible conversion of **3** to **2** by $B(C_6F_5)_3$ via ligand redistribution (Scheme 3).

To further probe the role of an excess of $B(C_6F_5)_3$ in suppressing the formation of **3** and in slowing down the ligand exchange reaction, we investigated the reaction of Ti(O^{*i*}Pr)₄ and $B(C_6F_5)_3$ in a 1:2 ratio. This reaction is fast, but it produces the ligand abstraction product Ti(O^{*i*}Pr)₃(μ -O^{*i*}Pr)B(C₆F₅)₃ (**4**), which eventually

$$Ti(O^{i}Pr)_{4} + B(C_{6}F_{5})_{3} \xrightarrow{toluene} (C_{6}F_{5})Ti(O^{i}Pr)_{3} + {}^{i}PrOB(C_{6}F_{5})_{2} (2) + ({}^{i}PrO)_{2}BC_{6}F_{5} (3) \\ 10 : 1 \\ 10 : 1 \\ toluene \\ 80 {}^{o}C, 14 h \\ \hline B0 {}^{o}C, 14 h \\ \hline C_{6}F_{5})Ti(O^{i}Pr)_{3} + {}^{i}PrOB(C_{6}F_{5})_{2} (2) + ({}^{i}PrO)_{2}BC_{6}F_{5} (3) \\ 3 : 1 \\ \hline THF \\ RT, 90min \\ Trace \\ \hline RT, 90min \\ \hline C_{6}F_{5})Ti(O^{i}Pr)_{3} + {}^{i}PrOB(C_{6}F_{5})_{2} (2) + ({}^{i}PrO)_{2}BC_{6}F_{5} (3) \\ \hline C_{6}F_{5})Ti(O^{i}Pr)_{3} + {}^{i}PrOB(C_{6}F_{5})_{2} (2) + ({}^{i}PrO)_{2}BC_{6}F_{5} (3) \\ \hline C_{6}F_{5})Ti(O^{i}Pr)_{3} + {}^{i}PrOB(C_{6}F_{5})_{2} (2) + ({}^{i}PrO)_{2}BC_{6}F_{5} (3) \\ \hline C_{6}F_{5})Ti(O^{i}Pr)_{3} + {}^{i}PrOB(C_{6}F_{5})_{2} (2) + ({}^{i}PrO)_{2}BC_{6}F_{5} (3) \\ \hline C_{6}F_{5})Ti(O^{i}Pr)_{3} + {}^{i}PrOB(C_{6}F_{5})_{2} (2) + ({}^{i}PrO)_{2}BC_{6}F_{5} (3) \\ \hline C_{6}F_{5})Ti(O^{i}Pr)_{3} + {}^{i}PrOB(C_{6}F_{5})_{2} (2) + ({}^{i}PrO)_{2}BC_{6}F_{5} (3) \\ \hline C_{6}F_{5})Ti(O^{i}Pr)_{3} + {}^{i}PrOB(C_{6}F_{5})_{2} (2) + ({}^{i}PrO)_{2}BC_{6}F_{5} (3) \\ \hline C_{6}F_{5})Ti(O^{i}Pr)_{3} + {}^{i}PrOB(C_{6}F_{5})_{2} (2) + ({}^{i}PrO)_{2}BC_{6}F_{5} (3) \\ \hline C_{6}F_{5})Ti(O^{i}Pr)_{3} + {}^{i}PrOB(C_{6}F_{5})_{2} (2) + ({}^{i}PrO)_{2}BC_{6}F_{5} (3) \\ \hline C_{6}F_{5} (2) + {}^{i}PrOB(C_{6}F_{5})_{2} (2) + {}$$

Scheme 2.

$$Ti(O^{i}Pr)_{4} + 1.2 B(C_{6}F_{5})_{3} \xrightarrow{\text{toluene}} (C_{6}F_{5})Ti(O^{i}Pr)_{3} + {}^{i}PrOB(C_{6}F_{5})_{2} (\mathbf{2}) + ({}^{i}PrO)_{2}BC_{6}F_{5} (\mathbf{3})$$

$$trace$$

$$B(C_{6}F_{5})_{2} + ({}^{i}PrO)_{2}BC_{6}F_{5} (\mathbf{3}) \xrightarrow{\text{toluene}} 2 {}^{i}PrOB(C_{6}F_{5})_{2} (\mathbf{2})$$

Scheme 3.



Scheme 4.

undergoes slow ligand exchange to give Ti(O'Pr)₃C₆F₅ and **2** (Scheme 4). This experiment suggests that the ligand exchange reaction observed for the 1:1 reaction occurs via the *unstable intermediate* **4**, and that in the 1:2 reaction the excess of B(C₆F₅)₃ *stabilizes* the bimetallic intermediate, allowing its direct detection in solution. This stabilization also renders the ligand exchange in the 1:1.2 Ti(O^{*i*}Pr)₄:B(C₆F₅)₃ reaction to occur in more controlled the fashion and suppress the formation of any further exchanged, undesired products such as (^{*i*}PrO)₂-BC₆F₅ (**3**).

3.4. PO polymerization catalyzed by ${}^{i}PrOB(C_{6}F_{5})_{2}$ (2) and the resulting PPO structures

We examined the PO polymerization behavior using the isolated 2 in the absence or presence of hydroxylic initiators, the results of which were summarized in Table 3. In the absence of any hydroxylic initiators, 2 effectively polymerizes PO to moderate molecular weight PPO ($M_n = 2550, M_w/M_n = 1.43$) with a TOF of 1438/h (entry 1, Table 3). This result is in sharp contrast to the PO polymerization result by $B(C_6F_5)_3$, which produced only dimer, trimer, and other low molecular weight oligomers [14]. This marked difference is originated from their substantially dissimilar reactivity patterns towards the PO monomer and the alcohol initiator: while $B(C_6F_5)_3$ forms stable adducts with the initiator and reacts vigorously with PO in the absence of the initiator to produce low molecular weight oligomers and the isomerization product – propionaldehyde [14], 2 does not form adducts with the initiator and reacts smoothly with PO in the absence of the initiator to produce only PPO. Nevertheless, the polymerization results by 2 compare well with - despite slightly better than - those obtained directly by the $Ti(O^{i}Pr)_{4}/B(C_{6}F_{5})_{3}$ mixture (entry 1, Table 2). The decreasing of polymerization activity with increasing the $Ti(O'Pr)_4:B(C_6F_5)_3$ ratio from 1 to 10 (entries 4-6, Table 2) correlates with the amount of 2 produced from the ligand exchange reaction; with an excess of $Ti(O^{i}Pr)_{4}$ employed, significant amounts of other species such as Ti(OⁱPr)₃C₆F₅, $({}^{i}PrO)_{2}BC_{6}F_{5}$, and $B({}^{i}PrO)_{3}$ are formed, along with the unreacted Ti(OⁱPr)₄, all of which exhibit negligible PO polymerization activity by control experiments. These

Table 3				
Summary of PO	polymerization	catalyzed	by	2 ^a

Entry	Catalyst/initiator	Polymerization time (h)	Conversion (%)	TOF ^b (/h)	$M_{\rm n}{}^{\rm c}~(M_{\rm w}/M_{\rm n})$
1.	2/none	3	86.3	1438	2550 (1.43)
2.	2 /120 ^{<i>i</i>} PrOH	3	91.3	1522	1830 (1.30)
3.	2/60 HO(CH ₂) ₄ OH	3	84.0	1400	2210 (1.32)
4.	2/40 HOCH(CH ₂ OH) ₂	3	85.4	1423	3060 (1.43)

^a Carried out at 23 °C, 5.00 mL (4.15 g) of PO, [PO]_o:[B]_o = 5000.

^b Turnover frequency (TOF) = moles of PO consumed per mole of catalyst per hour; calculations were based on polymer yield. ^c Determined by MALDI-TOF MS in dithranol matrix.



Fig. 2. MALDI-TOF MS spectrum of the PPO produced by with A and B representing the mass distributions for two primary PPO structures shown in Scheme 5.

observations, along with the individual reaction results discussed above, strongly suggest the real active species for the $Ti(O^iPr)_4/B(C_6F_5)_3$ mixture is the borane **2**.

Next, the PO polymerization behavior of the catalyst **2** in combination with hydroxylic initiators was also examined. Thus, addition of 120 equiv. mono-functional initiator ^{*i*}PrOH increased the polymerization activity and, as expected, significantly decreased the PPO molecular weight (entry 2 versus 1, Table 3). The use of 60 equiv. of bifunctional initiator HO(CH₂)₄OH did not affect the polymerization characteristics noticeably, whereas employing 40 equiv. of trifunctional initiator HOCH(CH₂OH)₂ increased M_n of the PPO to 3060 Da (entries 3 and 4, Table 3). These results show the advantage of using multifunctional initiators such as HOCH(CH₂OH)₂ for enhancing the PPO molecular weight in the acid-catalyzed ROP of PO.

Fig. 2 depicts an expanded range of the MALDI-TOF MS spectrum of the PPO prepared with $2/^{i}$ PrOH. There are two primary mass distributions, both of which have mass differences between the peaks representing the molar mass of PO (58.08 g/mol). The distribution with

higher intensities (A series) in Fig. 2 represents the linear PO structure A shown in Scheme 5, where $M_{end group}$ is the molar mass of isopropanol initiator (M = 60.10) and n is the degree of polymerization. The calculated mass values (e.g., $M_{27} = 1651.26$ Da) correlates well with the measured mass values (e.g., $M_{27} = 1651.93$ Da) listed in Fig. 2. The second PO structure is identified as linear structure **B**, where $M_{\text{end group}}$ is the molar mass of water molecule (M = 18.02), the mass distribution of which is labeled as **B** series in Fig. 2. The calculated (e.g., $M_{22} = 1318.77$ Da) and the found ($M_{22} = 1319.09$ Da) mass values match well. The formation of this secondary structure is presumably due to the initiation by water contained in the isopropanol initiator. The MALDI-TOF MS spectra of the PPO sample prepared with 2 in the presence of di- and tri-functional initiators features similarly two primary mass distributions for PPO structures **A** and **B** having the corresponding initiator end groups. These results are significant, because they show the borane 2-catalyzed PO polymerization can control over the PPO structure.

4. Conclusions

А:	RO—[(C ₃ п ₆ O) _n]—н	$M_n = (C_3 \Pi_6 O)_n + M_{end group} + M_{Na}$
	M ₂₇ = 1651.26 Da	= (58.08) x n + 83.10
B:	HO[(C ₃ H ₆ O) _n]H	$M_n = (C_3H_6O)_n + M_{end\ group} + M^+_{Na}$
	M ₂₂ = 1318.77 Da	= (58.08) x n + 41.01

Scheme 5.

The mixture of $Ti(O^{i}Pr)_{4}/B(C_{6}F_{5})_{3}$ is an effective catalyst system for ROP of PO, while the $Ti(O^{i}Pr)_{4}/Al(C_{6}F_{5})_{3}$ mixture is inactive; the inactivity of the latter mixture is due to the formation of a stable, catalytically inactive isopropoxy-bridged bimetallic species $Ti(O^{i}Pr)_{3}(\mu-O^{i}Pr)Al(C_{6}F_{5})_{3}$ (1). On the other hand, the reaction of $Ti(O^{i}Pr)_{4}$ and $B(C_{6}F_{5})_{3}$ produces the ligand exchange products via the unstable intermediate $Ti(O^{i}Pr)_{3}(\mu-O^{i}Pr)B(C_{6}F_{5})_{3}$ (4). The excess of $B(C_{6}F_{5})_{3}$ stabilizes this intermediate, thereby slowing down the ligand exchange reaction and rendering the reaction more selective. This strategy was used to successfully isolate the borane ${}^{i}PrOB(C_{6}F_{5})_{2}$ (2) in its pure state.

Control polymerization runs, in combination of the above studies on individual reactions, show that the active species responsible for the catalytic activity of the Ti(O^{*i*}Pr)₄/B(C₆F₅)₃ mixture is the neutral borane 2. When used in its pure form, isopropoxy borane 2, either by itself or when combined with hydroxylic initiators, is highly effective for PO polymerization, producing PPOs with $M_n = 2000-3000$ and TOF >1400/h. The MALDI-TOF MS analyses of the PPOs obtained by 2/initiator show the well-defined linear PPO structures having the initiator end groups. The effectiveness of this isopropoxy borane, when used alone for PO polymerization, is in sharp contrast to $B(C_6F_5)_3$; while $B(C_6F_5)_3$ forms stable adducts with alcohol initiators and reacts vigorously with PO in the absence of the initiator to produce only low molecular weight oligomers (dimer, trimer, etc.) and the isomerization product (propionaldehyde), 2 does not form adducts with the initiator and reacts with PO in the absence of any initiator in a controlled fashion to produce only PPO. These results show better polymerization control over the PPO structure demonstrated by the borane 2-catalyzed PO polymerization than that by $B(C_6F_5)_3$ -catalyzed polymerization.

5. Supplementary materials

Crystallographic data for the structural analysis of complex 1 have been deposited at the Cambridge Crystallographic Data Center (CCDC). CCDC reference number is 234877.

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