



Ethylene polymerization and ethylene/1-octene copolymerization with a titanium complex supported by a bis(indolyl) ligand

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Received: 17 July 2018 / Revised: 22 August 2018 / Accepted: 23 August 2018 / Published online: 19 September 2018
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Abstract

The synthesis of bis(diethylamido){di(3-methylindol-2-yl)phenylmethane}titanium (**1**) was achieved in high yield (85%) by the treatment of 2,2'-di(3-methylindolyl)phenylmethane with Ti(NEt₂)₄ in toluene at reflux for 18 h. The ethylene polymerization activity of the **1**/modified methylaluminoxane (MMAO) catalyst system was low (16.3 kg of polyethylene (PE)/mol of Ti•h), but pretreatment of **1** with ClSiMe₃ followed by activation with MMAO improved the activity up to 154 kg of PE/mol of Ti•h. An NMR-scale reaction of **1** with ClSiMe₃ in C₆D₆ at 80 °C for 22 h indicated the generation of an amido chlorido complex together with the formation of Et₂N–SiMe₃. Partial chlorination would facilitate methylation by MMAO. The polyethylenes obtained in this study are all monomodal by size exclusion chromatography and have linear structures by NMR spectroscopy. The catalyst system was also found to be active for ethylene/1-octene copolymerization (90 kg of copolymer/mol of Ti•h).

The polymerization of α -olefins with titanium(IV) complexes that contain a bulky bidentate diamide ligand is a part of the studies on post-metallocene catalysts [1]. The formal electron count of this catalyst system becomes lower than that of a metallocene, and thus, the cationic active species in the polymerization reactions can be more electrophilic. Figure 1 gives some examples of titanium complexes with chelating diamide ligands used for the α -olefin polymerization reactions. McConville et al. demonstrated the high activity of complex **A** in the polymerization of 1-hexene by activation with methylaluminoxane (MAO); [2] other examples of polymerizations with complex **A**, including the copolymerization of ethylene with 2-butene [3], synthesis of isotactic poly(propylene) [4], and living polymerization of propylene [5], are known. Nomura and

coworkers developed another type of complex **B**, which exhibited high catalytic activities for the polymerization of ethylene [6]. The catalytic activities of complexes **C** [7], **D** [8], **E** [9], and **F** [10] in ethylene polymerizations are also explored. Ethylene/1-octene copolymerization reactions with complexes **G** and **H** were studied by the Patton group [11, 12].

We are interested in the coordination chemistry of deprotonated 2,2'-bis(indolyl)methanes (henceforth: bis(indolyl)s) toward a titanium center and recently revealed that an indolyl nitrogen of these ligands adopts pyramidal geometry, which stands in sharp contrast to the typical planar geometry of amido nitrogen atoms when coordinated to early transition metals [13]. Bis(indolyl)-ligated titanium bis(diethylamido) complexes were also found to serve as catalysts for the intermolecular hydroamination of alkynes [13]. In this study, we report the catalytic features of bis(diethylamido){di(3-methylindol-2-yl)phenylmethane}titanium (**1**) for polymerization reactions. Although the polymerization of ethylene using the **1**/MAO catalyst system was preliminarily investigated by Mason et al. [14], we clarified here that pretreatment of **1** with ClSiMe₃ before activation with modified methylaluminoxane (MMAO) improved the activity. In addition, the copolymerization of ethylene with 1-octene was also examined. The obtained polymers were characterized by NMR spectroscopy, size

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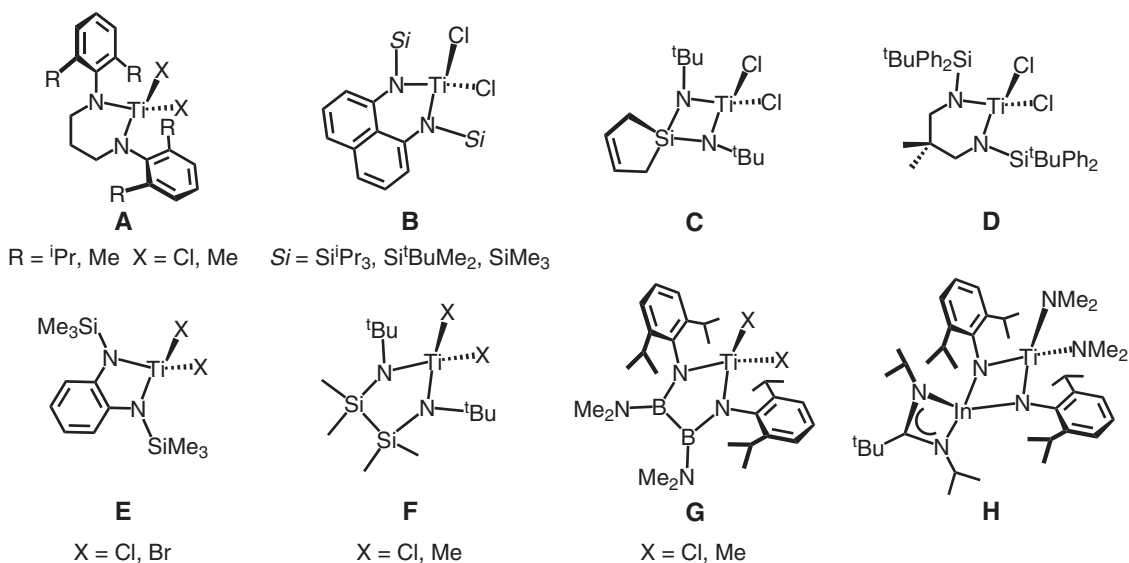
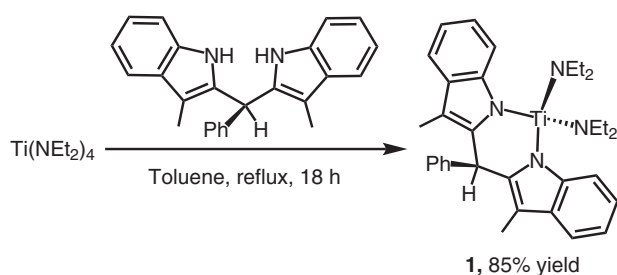


Fig. 1 Representative examples of titanium complexes bearing chelating diamide ligands used for the polymerization of α -olefins



Scheme 1 Synthesis of complex **1**

exclusion chromatography (SEC), and differential scanning calorimetry (DSC).

Complex **1** was originally synthesized by the Mason group; however, their isolated yield was low (23%) [14]. We isolated **1** as brown powder in 85% yield by a slight modification of Mason's procedure (Scheme 1). A mixture of Ti(NEt₂)₄ [15] and 2,2'-di(3-methylindolyl)phenylmethane [16] in a 1.2:1 molar ratio was heated to reflux in toluene for 18 h to give a reddish brown solution, from which **1** was obtained by evaporation, followed by washing with cold pentane to remove the small amount of unreacted Ti(NEt₂)₄. The identification was verified by comparison with the ¹H NMR spectrum reported in the literature [14].

Ethylene (1 atm) polymerization using **1** was carried out in toluene for 15 min at room temperature using MMAO ([Al]/[Ti] = 1000) as an activator (Fig. 2(a)). The reaction was quenched by the addition of methanol/HCl(aq), which precipitated the polyethylene (PE), and the product was then dried in vacuo at 80 °C for 2 h. The activity (16.3 kg of PE/mol of Ti•h) estimated for these reaction conditions is more than 10 times higher than that reported by Mason et al. (1.1 kg of PE/mol of Ti•h, ethylene = 2 atm, [Al]/Ti = 1000,

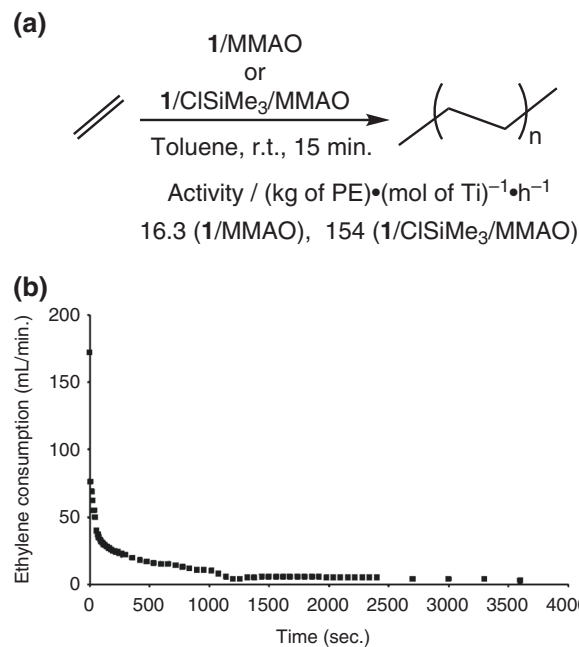


Fig. 2 (a) Ethylene polymerization with the 1/MMAO and 1/CiSiMe₃/MMAO catalyst systems. Conditions: [Ti] 20 μ mol, MMAO (6.5 wt% in toluene, 9 mL, 20 mmol), [Al]/[Ti] = 1000, ethylene = 1 atm. (b) Time-dependent ethylene flow rate for the 1/CiSiMe₃/MMAO catalyst system at room temperature under 1 atm of ethylene monitored by a mass flow meter

25 °C, solv. = toluene) [14], which may be due to the difference in the activator; however, the activity is still low. It has been reported that a dipyrroliide-ligated zirconium amido complex polymerized ethylene when the complex was pretreated with CiSiMe₃ [17]. Thus, **1** was pretreated with CiSiMe₃ at 70 °C, and its activity increased up to 154 kg of PE/mol of Ti•h. Although a higher activity was

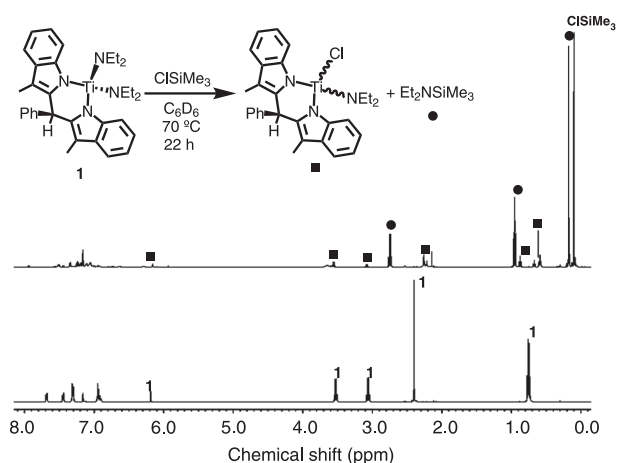


Fig. 3 ^1H NMR (500 MHz) spectra measured at room temperature of (top) the reaction mixture (C_6D_6 , 70°C , 22 h) of **1** and ClSiMe_3 and (bottom) a C_6D_6 solution of **1**

reported for complex **B** ($\text{Si} = \text{Si}^t\text{BuMe}_2$, 709 kg of PE/mol of $\text{Ti}\cdot\text{h}$, ethylene = 4 kg/cm^2 , cocat. = MMAO, $[\text{Al}]/[\text{Ti}] = 1000$, 60°C , 1 h, solv. = heptane) [6], this value is higher than those of **C** (20 kg of PE/mol of $\text{Ti}\cdot\text{h}$, ethylene = 1 atm, cocat. = MMAO, $[\text{Al}]/[\text{Ti}] = 1000$, 40°C , 0.5 h, solv. = toluene) [7] and **D** (7 kg of PE/mol of $\text{Ti}\cdot\text{h}$, ethylene = 1 atm, cocat. = MAO, $[\text{Al}]/[\text{Ti}] = 500$, 20°C , 15 min., solv. = pentane) [8] and is comparable with those of **E** (197 of PE/mol of $\text{Ti}\cdot\text{h}$, ethylene = 1.6 atm, cocat. = MAO, $[\text{Al}]/[\text{Ti}] = 1340$, 60°C , 0.5 h, solv. = toluene) [9] and **F** (101 kg of PE/mol of $\text{Ti}\cdot\text{h}$, ethylene = 1 atm, cocat. = MAO, $[\text{Al}]/[\text{Ti}] = 800$, room temperature, 0.5 h, solv. = toluene) [10]. We have discussed why the pretreatment of **1** with ClSiMe_3 improved the activity (vide infra).

The ethylene flow rate was monitored by a flow meter for to 60 min with the $\text{1/ClSiMe}_3/\text{MMAO}$ catalyst system (Fig. 2(b)). The rate was immediately reduced to 10% in 10 min, and it further slowly decreased to 3 mL/min at 60 min. This result indicates that rapid ethylene polymerization started soon after the injection of catalyst solution, and the major active species was deactivated in a short time.

To identify the species generated by the pretreatment of **1** with ClSiMe_3 , a 1:2 mixture of **1** and ClSiMe_3 in C_6D_6 was heated at 70°C for 22 h, giving rise to a deep brown solution. The ^1H NMR spectrum of the solution (Fig. 3, top) indicated the disappearance of **1** (Fig. 3, bottom), and the resonances assignable to the methyl groups of $\text{Et}_2\text{N-SiMe}_3$ (0.17 ppm) and ClSiMe_3 (0.10 ppm) in a 1:1 ratio were observed, indicating that one of the two diethylamido (NEt_2) ligands is replaced by a chlorido ligand to form the amido chlorido species. The ^1H NMR signals of the NEt_2 ligand in this species were found at 3.56 and 3.08 ppm (NCH_2CH_3 , each quartet, $^3J_{\text{H-H}} = \text{each } 7\text{ Hz}$) and at 0.87 and 0.67 ppm (NCH_2CH_3 , each triplet, $^3J_{\text{H-H}} = \text{each } 7\text{ Hz}$). Two sets of signals identified as the NEt_2 ligand were

observed because two diastereomers of the generated amido chlorido species can be formed. The partial chlorination reactions of amido ligands with ClSiMe_3 are known for the titanium [18] and tantalum [19] complexes. We added excess (10 eq.) ClSiMe_3 and heated the mixture at 100°C in toluene- d_8 , but no further reaction processes were observed. These results suggest the following conclusions: i) ClSiMe_3 serves as a chlorination reagent in the $\text{1/ClSiMe}_3/\text{MMAO}$ catalyst system, and it leaves one of the amido ligands attached to the titanium center, and ii) the substitution of the chlorido ligand by the alkyl ligand by MMAO is faster than that of the amido ligand, which improves the ethylene polymerization activity.

The structures of the resultant polyethylenes were examined by ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy (JEOL JNM-ECA500), SEC (Waters 150C, 1,2-dichlorobenzene as the eluent at a flow rate of 1 mL/min vs polystyrene standard), and DSC (TA instruments Q2000 at a rate of $10^\circ\text{C}/\text{min}$). According to the NMR studies ($\text{C}_2\text{D}_2\text{Cl}_4$, 130°C), all the polyethylenes were linear and had no significant terminal vinyl groups, suggesting that polymer chain transfer to an aluminum center is the dominant termination process, and no β -hydrogen elimination occurs in the initial stage of polymerization; however, it is also possible that the relatively low contents of the vinyl groups relative to the polymer chains make them invisible by NMR spectroscopy. The melting points (T_m) were almost identical for all samples ($131\text{--}134^\circ\text{C}$). The PEs obtained in this work were all monomodal by SEC, and the molecular weight distribution of polyethylene synthesized by the $\text{1/ClSiMe}_3/\text{MMAO}$ catalyst system ($M_w/M_n = 5.8$) was narrower than that prepared using the 1/MMAO system ($M_w/M_n = 13$). Partial chlorination would induce the generation of a relatively uniform cationic active species, while the M_w/M_n value is still broad, probably due to the remaining amido ligand.

Ethylene polymerization with the $\text{1/ClSiMe}_3/\text{MMAO}$ catalyst system in the presence of 1-octene provided an ethylene/1-octene copolymer (Fig. 4(a)). The activity (90 kg of copolymer/mol of $\text{Ti}\cdot\text{h}$) is slightly lower than that of ethylene polymerization (154 kg of PE/mol of $\text{Ti}\cdot\text{h}$). The produced copolymer displayed a lower melting point (123°C) than that of PE ($131\text{--}134^\circ\text{C}$), while the M_n (1.2×10^5) and M_w/M_n (5.7, monomodal molecular weight distribution) values are almost identical ($M_n = 1.1 \times 10^5$ and $M_w/M_n = 5.9$ for PE). The incorporation of 0.4 mol% of 1-octene in the linear high-density PE was determined by ^{13}C NMR in $\text{C}_2\text{D}_2\text{Cl}_4$ at 130°C (Fig. 4(b)), indicating that the catalyst system reacts with ethylene faster than it react with 1-octene. This result is in contrast with that of ethylene/1-octene copolymerization by complex **A** ($\text{R} = ^i\text{Pr}$, $\text{X} = \text{Cl}$) activated by MMAO (36.6–43.2 mol%) [20].

This work demonstrated the catalytic activities of **1** for ethylene polymerization and for ethylene/1-octene

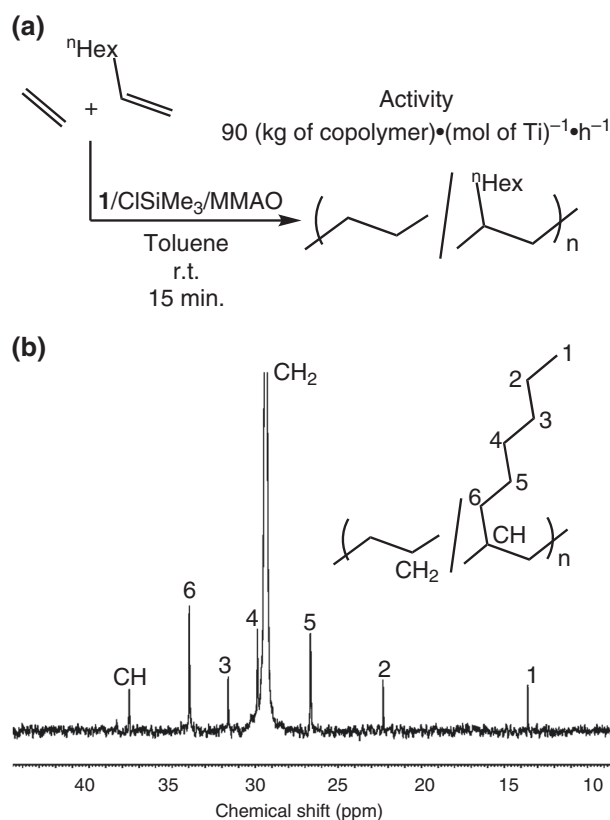


Fig. 4 (a) Ethylene/1-octene copolymerization with the **1**/C*i*SiMe₃/MMAO catalyst system. Conditions: [Ti] 20 μmol, MMAO (6.5 wt% in toluene, 9 mL, 20 mmol), [Al]/[Ti] = 1000, ethylene = 1 atm, 1-octene (5 mL). (b) ¹³C{¹H} NMR (126 MHz) spectrum of the ethylene/1-octene copolymer in C₂D₂Cl₄ at 130 °C

copolymerization. We found that the **1**/MMAO catalyst system shows low activity for ethylene polymerization as preliminary reported by Mason [14], but pretreatment of **1** with C*i*SiMe₃, followed by activation with MMAO, improved the activity. The **1**/C*i*SiMe₃/MMAO catalyst system also works for the copolymerization of ethylene and 1-octene. The ¹H NMR study revealed that C*i*SiMe₃ replaces only one of the two amido ligands in **1** with a chlorido ligand, and the other amido ligand remains on the titanium center. Thus, we are now exploring other chlorination reagents to generate the dichlorido complex. If this complex can be prepared, the obtained species is expected to have higher activity in the polymerization.

Acknowledgements This work was financially supported by the Foundation for Japanese Chemical Research, Hatakeyama Culture Foundation, Aomori Support Center for Industrial Promotion, and Hirosaki University Grant for Exploratory Research by Young Scientists and Newly-appointed Scientists. The authors thank Tosoh-Finechem Co., Ltd. for donating the MMAO. T.T. appreciates the Grant-in-Aid for Young Scientists (B) (No. 15K17866 and No.

17K17742) from JSPS, Nagaoka University of Technology Presidential Research Grant, The Foundation for the Promotion of Ion Engineering, LIXIL JS Foundation, and The Ogasawara Foundation for the Promotion of Science & Engineering.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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