

Synthesis, characterization, and ethylene polymerizations of various N–O chelated mono Cp* titanium complexes

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Abstract

Various mono Cp* type titanium mononuclear complexes (**1–5**) and dinuclear complexes (**6** and **7**) containing non-Cp type chelate ligand, picolinate group, which has multi-binding sites of N and O atoms were synthesized and fully characterized by ¹H and ¹³C NMR spectroscopy, mass spectroscopy, elemental analysis, and X-ray diffraction study. The **1** and **2**/MMAO catalytic systems for ethylene polymerization exhibited a moderate activity and gave the polyethylenes with broad molecular weight distributions.

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1. Introduction

The discovery of homogeneous single-site catalysts for olefin polymerization has brought a revolution in polymer synthesis since the homogeneous catalysts-based polymers can possess excellent physical properties or stereo-regularities that are difficult or impossible to be achieved by other known polymerization methods [1]. For example, metallocene-based polyethylene (PE) shows excellent properties such as high clarity and high impact strength, stemmed from narrow molecular weight distribution (MWD) and a lack of branching [2,3]. But, these factors, essential for the excellent physical properties, are also responsible for the poor processibility of PE, hampering bulk production of the polymer. Thus, the enhancement of the processibility of metallocene-based PE without losing its excellent properties has become an important research subject in recent years with a particular focus on modulating MWD [4–6] and introducing branches [7].

The incidental observation of catalytic systems that gave PE with broad MWD is uncommon [8]. But the control of MWD of PE has been approached by using a series of reactors under different polymerization conditions [4], employing different catalytic systems in one pot [5] and designing metallocene precatalytic systems that can produce multi-catalytic species during the polymerization process [6]. The concept embodied in the design of the foregoing metallocene precatalytic systems includes Lewis acid–base interaction in dialkylamino substituted *ansa*-metallocene [6a], the stepwise dissociation of chelate ligand in half-metallocene catalyst [6b] and *in situ* generation of different isomers for non-Cp type catalyst [6c]. In recent, we reported the synthesis and ethylene polymerization behaviors of Cp*Ti(2-pyridinecarboxylato)₂Cl containing N–O bidentate ligands. The catalytic system gave polyethylenes with multi-modal MWD due to the stepwise dissociation of 2-pyridinecarboxylate group and the interaction of Lewis acid groups of methylaluminoxane (MAO) and lewis base groups in non-Cp type ligand, 2-pyridinecarboxylate group [9].

In this report, we report the synthesis, characterizations and ethylene polymerization behaviors of various mono Cp-type titanium mononuclear and dinuclear complexes containing 2-pyridinecarboxylate group.

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2. Results and discussion

2.1. Synthesis and characterizations

Complexes **1** and **2**, synthesized via HCl elimination reaction with high yields as outlined in Fig. 1, are composed by one pentamethyl cyclopentadienyl ring (Cp*), two 2-pyridinecarboxylate groups, one chloride group, and one Ti metal. Picolinic acid served as a source of 2-pyridinecarboxylate ligand as well as a base to trap HCl by-product, leading to the use of 1:4 molar ratio of Cp*TiCl₃:picolinic acid. The red solids **1** and **2** are soluble in THF and methylene chloride (MC), partially soluble in toluene and insoluble in diethyl ether and hydrocarbon solvents. In addition, they are stable in the air for several days as solid forms. Various attempts, such as a variation of molar ratio of Cp*TiCl₃ and picolinic acid, the change of reaction solvent, the use of Cp*Ti(OMe)₃ as a titanium source, and the reaction of Cp*TiCl₃ and lithium 2-pyridinecarboxylate which is produced from the reaction of picolinic acid and *n*-BuLi, did not afford mononuclear half-titanocene-type complex containing one 2-pyridinecarboxylate group.

The composition of **1** [9] established by single crystal X-ray diffraction study is consistent with other characterization results. The molecular structure of **1** is displayed in Fig. 2 and the selected interatomic distances and angles are given as part of the figure caption. Both 2-pyridinecarboxylate ligands in **1** behave as bidentate chelates with N and O donor centers, forming a distorted octahedral coordination sphere around Ti along with the centroid of Cp* and a chloride atom. Two oxygen donors of the 2-pyridinecarboxylate, O1 and O3, are trans each other, forming cis-configuration to the Cp* ring while two nitrogen donors of the 2-pyridinecarboxylate, N1 and N2, are cis each other and thus N1 and N2 are trans and cis to the Cp* ring, respectively. In addition, two 2-pyridinecarboxylate groups are structurally inequivalent, leading to the generation of eight kinds of peaks corresponding to pyridine group with one proton integral in the ¹H NMR spectrum. The angles of N1–Ti–E (E = O1, O3, N2 and Cl1) are relatively acute with a range of 73–80°, indicating the extent of the distortion of the coordination sphere.

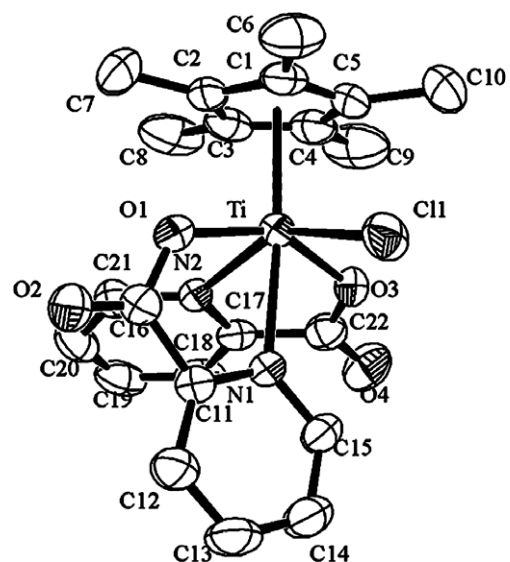


Fig. 2. ORTEP drawing of the compound **1**, showing 50% probability thermal ellipsoids and atom labeling. Hydrogen atoms and the solvate CH₂Cl₂ were omitted for clarity. Selected bond lengths (Å) and angles (°): Ti(1)–O(1) 1.992(2), Ti(1)–O(3) 1.997(3), Ti(1)–Cp centroid 2.122, Ti(1)–N(1) 2.306(3), Ti(1)–N(2) 2.231(3), Ti(1)–Cl(1) 2.3771(13), O(1)–Ti(1)–N(1) 73.21(10), O(3)–Ti(1)–N(1) 79.75(10), N(2)–Ti(1)–N(1) 74.05(11), N(1)–Ti(1)–Cl(1) 75.77(8).

Sometimes, olefin polymerization behaviors of half-titanocene-based catalysts were affected by the variation of leaving groups such as chloride group. So, complexes **3**, **4** and **5** containing methoxy or 2-pyridinecarboxylate groups as the leaving group were synthesized via MeOH elimination reaction in toluene as outlined in Fig. 3. Although **3** has two 2-pyridinecarboxylate bidentate chelating groups per one titanium metal center, **3** was obtained by the reaction of 1:1 molar ratio of Cp*Ti(OMe)₃:picolinic acid because the mixture of **3** and **4** was generated by the reaction of 1:2 molar ratio and then the purification of the mixture was very difficult. The orange solid **3** is soluble in THF and MC and insoluble in toluene, diethyl ether, and hydrocarbon solvents. In addition, it is stable in the air for several days as a solid form. The molecular structure of **3** established by single crystal X-ray diffraction study is shown in Fig. 4. The overall molecular structure of **3** is very similar with that of **1**. The selected interatomic distances and angles are given as part of the figure caption. And the angle of Ti–O5–C23 is 147.96° bending to the opposite side of Cp* group, indicating the steric repulsion between Cp* and OMe groups.

Complexes **4** and **5** were obtained by the reaction of 1:3 molar ratio of Cp*Ti(OMe)₃:picolinic acid with high yield as outlined in Fig. 3. The reddish orange solid **4** and the scarlet solid **5** are soluble in THF and MC and insoluble in toluene, diethyl ether and hydrocarbon solvents and are stable in the air for several days as solid forms. The molecular structures of **4** and **5** were analyzed by elemental analysis (EA), mass and NMR spectroscopy. Because suitable single crystals of them were not obtained, X-ray study was not employed. The absence of the peak about the

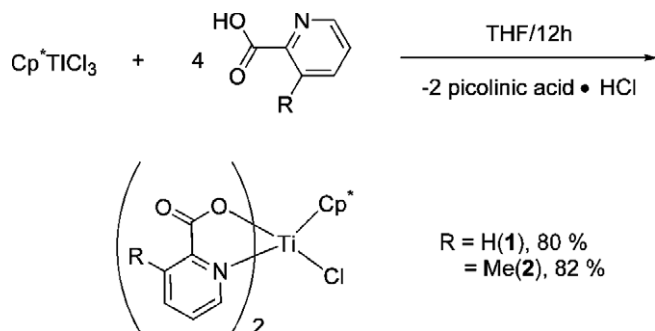


Fig. 1. Synthetic routes for **1** and **2**.

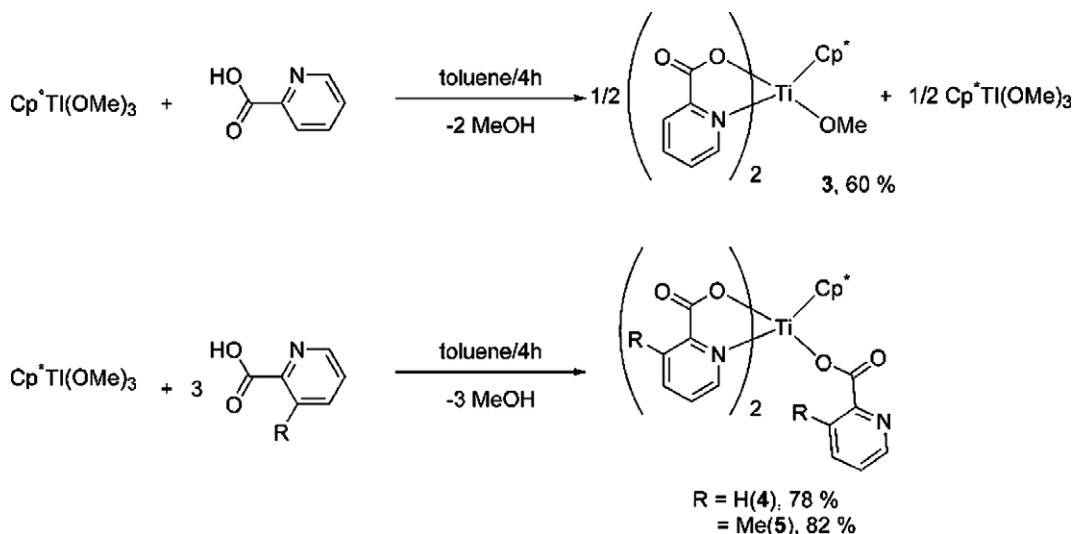


Fig. 3. Synthetic routes for 3, 4 and 5.

region of 3.0–4.0 ppm, which is corresponding to methyl protons of methoxide groups, in the observed ^1H NMR spectra of 4 and 5 indicates the absence of OMe group, meaning the complete substitution reaction 2-pyridinecarboxylate groups for OMe groups of $\text{Cp}^*\text{Ti}(\text{OMe})_3$, starting reagent. EA (4: C, 61.21; H, 4.95; N, 7.64. Found: C, 60.84; H, 5.13; N, 7.59% and 5: C, 62.95; H, 5.62; N, 7.10. Found: C, 62.46; H, 5.81; N, 6.99%) and EI mass spectral data of 4 and 5 agree with the molecular composition

of titanium complexes containing one Cp^* group and three 2-pyridinecarboxylate groups. The 2-pyridinecarboxylate ligand has two possible binding modes; (type I) mono anionic N–O bidentate chelating mode and (type II) mono anionic monodentate mode through an oxygen atom (Fig. 5). To make the octahedral structure around Ti with Cp^* ring, two bidentate type I and a monodentate type II among three 2-pyridinecarboxylate groups have to coordinate to Ti. Octahedral complexes 4 and 5 have six possible geometric isomers as the spatial relationship between Cp^* group and type II group: two isomers that Cp^* and type II group are trans-configuration (Fig. 6a and b) and other four isomers that Cp^* and type II group are cis-configuration (Fig. 6c–f). The (a) and (b) in Fig. 6 have two type I groups, which are chemically equivalent, and one type II group. Otherwise, (c)–(f) in Fig. 6 have two type I group, which are chemically inequivalent, and one type I group. The observed ^1H NMR spectrum (Fig. 7) of 4 showed four pyridine peaks having one proton integral and four pyridines peaks having two proton integrals (Fig. 7b), corresponding to the molecular structures of (a) and (b) in Fig. 6. But, we could not disclose which isomer of (a) and (b) was present.

Compound 5 was analyzed similarly, leading us to deduce that 4 and 5 has octahedral structure around Ti along with one Cp^* group, two type I groups, and one type II group. And Cp^* group and one type II group are located

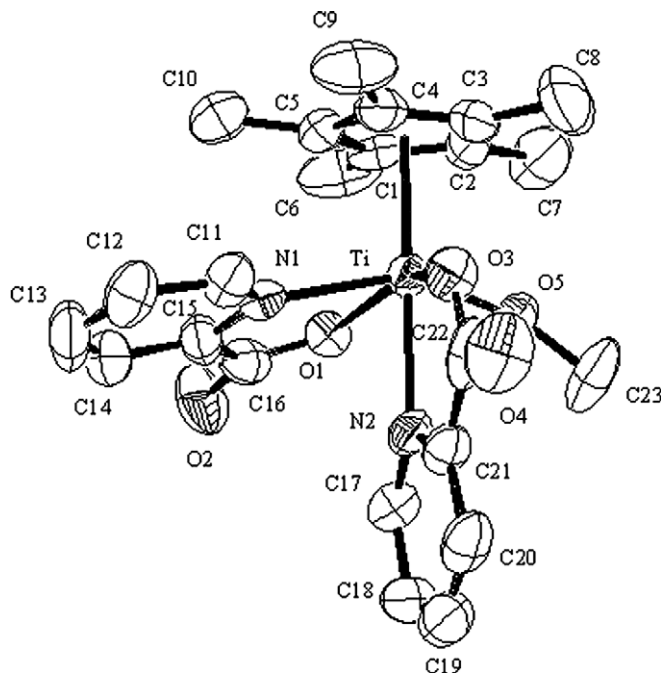


Fig. 4. ORTEP drawing of the compound 3, showing 50% probability thermal ellipsoids and atom labeling. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Ti(1)–O(1) 2.000(6), Ti(1)–O(3) 2.014(6), Ti(1)–Cp centroid 2.147, Ti(1)–N(1) 2.281(7), Ti(1)–N(2) 2.329(8), Ti(1)–O(5) 1.826(6), O(1)–Ti(1)–N(2) 79.2(3), O(3)–Ti(1)–N(2) 72.9(3), N(2)–Ti(1)–N(1) 74.4(2), O(5)–Ti(1)–N(2) 78.6(3).

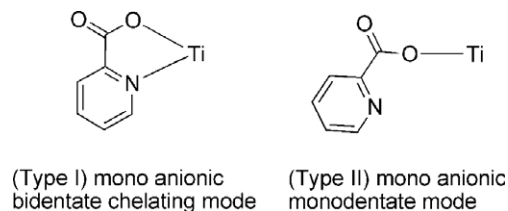


Fig. 5. Two binding modes of between 2-pyridinecarboxylate group and Ti.

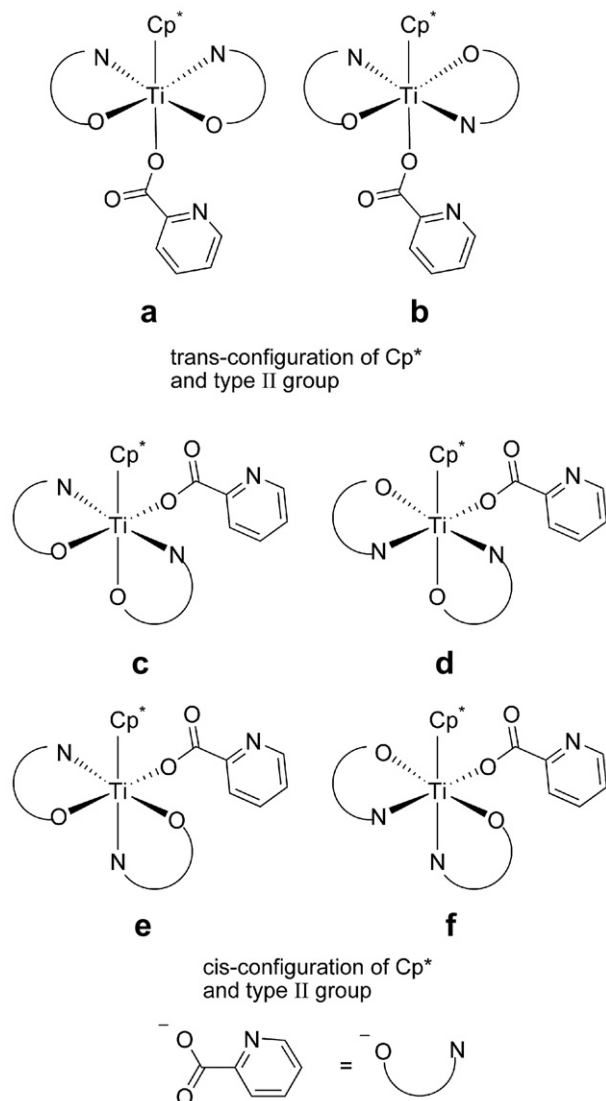


Fig. 6. Possible structural isomers of **4** and **5** as a spatial relation between Cp* and type II 2-pyridinecarboxylate group.

in trans-position each other. The rotation of pyridine group in type II group around Ti–O bond leads to steric hindrance. Consequently, the generation of trans-conformation of Cp* and type II group might be forced by steric repulsion between methyl groups of Cp* and bulky pyridine ring of 2-pyridinecarboxylate group.

Oxo dibridged titanium dinuclear complexes **6** and **7** were synthesized via methanol elimination reaction followed by hydrolysis as outlined in Fig. 8a. The complexes **6** and **7** are soluble in THF, partially soluble in MC and insoluble in toluene, ether and hydrocarbon solvents and are stable in the air for several days. The structural nature of **6** and **7** was characterized by ^1H , ^{13}C NMR, mass spectroscopy and EA. Like the case of the complex **4** and **5**, the absence of the peak about the region of 3.0–4.0 ppm in the observed ^1H NMR spectra of **6** and **7** indicates the absence of OMe group. And four pyridine peaks with one proton integral in the region of 7.0–9.0 ppm mean the presence of one chemical species of 2-pyridinecarboxylate group (Fig. 8b and c). Furthermore, EI mass and EA data (**6**: C, 59.83; H, 5.96; N, 4.36. Found: C, 59.25; H, 6.05; N, 4.32% and **7**: C, 60.91; H, 6.31; N, 4.17. Found: C, 60.28; H, 6.50; N, 4.07%) were consistent with a molecular composition of titanium dinuclear complex containing one Cp* group, one oxygen atom and one 2-pyridinecarboxylate group per Ti metal center. Although we cannot disclose the exact molecular structure, we can deduce that **6** and **7** are oxo dibridged titanium dinuclear complex, which 2-pyridinecarboxylate ligand might be coordinated at Ti center as the bidentate type I system, by analysis of EA, NMR and mass spectroscopy.

2.2. Ethylene polymerization

Compounds **1** and **2** were examined as catalysts for ethylene polymerizations in the presence of MMAO. Compounds **3–7** were not investigated as catalysts for ethylene polymerizations due to their poor solubility.

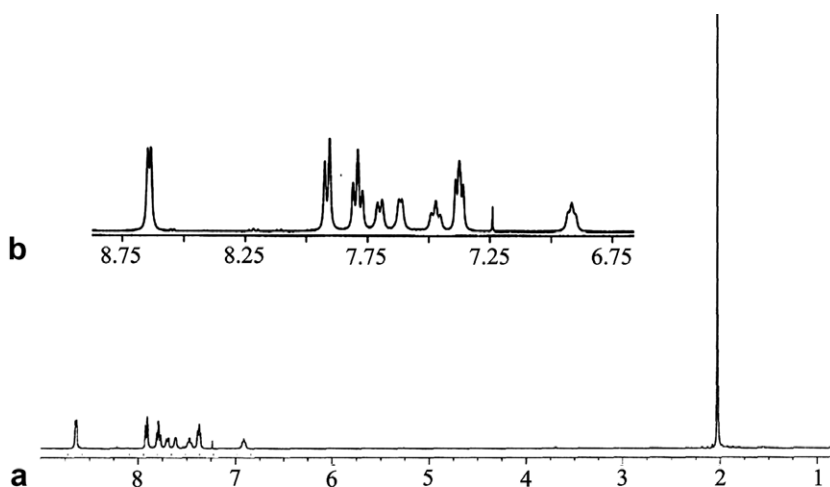


Fig. 7. ^1H NMR spectra of complex **4** at (a) all region and (b) 6.75–8.75 ppm.

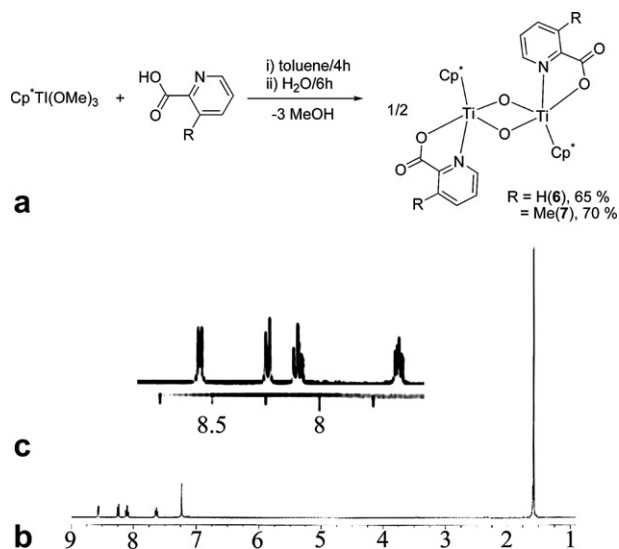


Fig. 8. (a) Synthetic routes for **6** and **7**. ^1H NMR spectra of complex **6** at (b) all region and (c) 7.5–8.75 ppm.

The polymerization results are summarized in Table 1 in terms of polymerization temperature (T_p), catalytic activity (A), molecular weight (M_w), melting temperature (T_m) and PDI of the PEs. The **1** and **2**/MMAO systems show polymerization activity of $10\text{--}10^2$ kg PE/(mol of Ti) \cdot h bar and produce high density polyethylenes with M_w and PDI in the ranges of 15,900–170,700 and 2.60–8.48, respectively. The observed PDI values are very different from 2, the value generally observed for homogeneous single-site catalysts.

As for the origins of the such broad PDIs, the involvement of the three concepts stated in the introduction such

Table 1
Ethylene polymerization results with **1** and **2**/MMAO^a

Run	Catalyst	T_p	Al/Ti	A^c	M_w^d	T_m^e	PDI ^d
1	1	30	2000	Trace	n.d. ^f	n.d.	n.d.
2	1	50	2000	120	88,400	136.5	3.66
3	1	70	2000	96	43,400	133.6	4.51
4	1	90	2000	Trace	15,900	n.d.	5.40
5 ^b	1	30	2000	45	170,700	137.3	5.80
6 ^b	1	50	2000	63	72,900	135.3	3.96
7 ^b	1	70	2000	15	38,500	128.7	7.83
8 ^b	1	90	2000	Trace	43,500	n.d.	8.48
9	2	30	2000	Trace	n.d.	n.d.	n.d.
10	2	50	2000	78	69,300	135.2	3.57
11	2	70	2000	54	21,800	133.5	2.78
12	2	90	2000	Trace	n.d.	n.d.	n.d.
13	2	30	4000	Trace	n.d.	n.d.	n.d.
14	2	50	4000	174	49,900	134.0	2.60
15	2	70	4000	204	20,000	134.1	2.63
16	2	90	4000	Trace	n.d.	n.d.	n.d.
17	Cp^*TiCl_3	50	2000	624	68,800	135.6	1.97

^a Polymerization condition: P (ethylene) 1 bar; Ti 2 μmol ; solvent 50 mL of toluene; T_p 5 min.

^b Ti 5 μmol .

^c A : kg PE/(mol of Ti) \cdot h bar.

^d Determined by GPC.

^e Determined by DSC.

^f n.d. = Not determined.

as Lewis acid–base interaction, *in situ* generation of different isomers and the stepwise dissociation of a chelate ligand might be conceivable. Since the compound **1** and **2** may potentially possess all of these concepts, it is worthy of noting which concepts can be ascribed to the observed MWD of the PEs. As an isolated solid form, the complex **1** appears as one pure form. In solution state, the variable temperature (VT)- ^1H NMR spectra of **1** in toluene- d_8 in

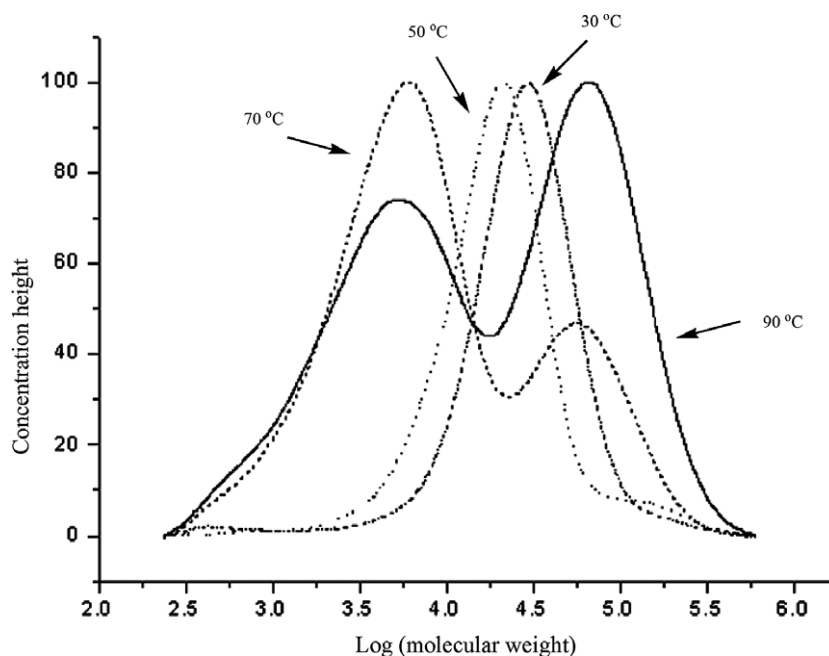


Fig. 9. GPC diagrams of polyethylenes from **1**/MMAO system as variations of polymerization temperatures.

the range of $-20\text{ }^{\circ}\text{C}$ to $90\text{ }^{\circ}\text{C}$ indicate that the complex **1** does not produce any isomer. This observation is quite different from that of Fujita's FI system [6c]. Thus, the contribution of *in situ* generated different isomers to the modulation of MWD can be ruled out in the **1**/MMAO system, leaving Lewis acid–base interaction and the stepwise dissociation of chelate ligand as possible causes for the observed multi-modal behavior.

The GPC diagrams of the PEs as a function of T_p , displayed in Fig. 9, imply that the **1**/MAO catalytic system is capable of modulating the MWD of PEs. The GPC profiles at T_p of 30 and $50\text{ }^{\circ}\text{C}$ show unimodal-like shape with an asymmetric tail in the low molecular weight side and a weak shoulder in the high molecular weight side but as T_p increases to 70 and $90\text{ }^{\circ}\text{C}$ the appearance of an apparent bimodal MWD becomes more evident.

3. Conclusions

Various mono Cp* type titanium mononuclear complexes (**1–5**) and dinuclear complexes (**6** and **7**) containing 2-pyridinecarboxylate ligand were synthesized and structurally characterized. And also, binding modes between 2-pyridinecarboxylate group and Ti center were discussed. The **1** and **2**/MMAO catalytic systems for ethylene polymerization exhibited a moderate activity and produced polyethylenes with multi-modal molecular weight distributions. The modulation of MWD can be explained in terms of the coupled use of Lewis acid–base interaction and the stepwise dissociation of 2-pyridinecarboxylate ligand.

4. Experimental

4.1. General considerations

All manipulations were carried out under the inert atmosphere of nitrogen gas that was deoxygenated with activated Cu catalyst (regenerated by heating to $300\text{ }^{\circ}\text{C}$ under H_2 gas) and dried with Drierite. THF was dried with Na/K alloy with benzophenone. Toluene, *n*-hexane and *n*-pentane were dried with Na/K alloy. Methylene chloride (MC) was distilled from a solution of calcium hydride. CDCl_3 was dried over activated molecular sieves (4 \AA). Modified methylalumoxane (MMAO: 4 A type) was supplied by Akzo Co. All other chemicals were purchased from Aldrich.

4.2. Measurements

^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker Avance 400 at room temperature. The chemical shifts are referenced to the residual peaks of CDCl_3 (7.24 ppm for ^1H NMR and 77.0 ppm for $^{13}\text{C}\{^1\text{H}\}$ NMR). EI and HR mass spectra were obtained on a VG Auto spectrometer. Elemental analyses (EA) were performed by the Environmental Analysis Laboratory at KAIST on an EA1110-FISONS. Thermal properties of PE were investi-

gated on TADSC2910. Molecular weights and molecular weight distributions (polydispersity index, PDI) of polyethylenes (PE) were determined by PLGPC2910.

4.3. Synthesis

4.3.1. $[\text{Cp}^*\text{Ti}(2\text{-Pyridinecarboxylato})_2\text{Cl}]\cdot(\text{CH}_2\text{Cl}_2)$ (**1**) [9]

A reddish solution of 0.29 g (1.0 mmol) pentamethyl cyclopentadienyl titanium trichloride (Cp^*TiCl_3) in 20 ml THF was added to a white slurry of 0.49 g (4.0 mmol) picolinic acid in 20 ml THF at $-78\text{ }^{\circ}\text{C}$. The reaction mixture was allowed to warm to room temperature and stirred for 12 h before the removal of solvent. Dissolution of the resulting residue in MC was followed by filtration. The filtrate was reduced in volume and treated with Et_2O , affording red solid product in 80% yield (0.44 g).

^1H NMR (CDCl_3 , 400 MHz): $\delta = 8.44$ (d, H, C_5NH_4), 8.42 (d, H, C_5NH_4), 8.07 (d, H, C_5NH_4), 7.89 (t, H, C_5NH_4), 7.81 (d, H, C_5NH_4), 7.67 (t, H, C_5NH_4), 7.45 (t, H, C_5NH_4), 7.27 (t, H, C_5NH_4) 5.27 (s, 2H, CH_2Cl_2), 2.03 (s, 15H, $\text{C}_{10}\text{H}_{15}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 400 MHz): $\delta = 168.85$, 166.18 (COO), 150.83, 147.34, 146.57, 145.69, 140.62, 138.77, 128.16, 127.85, 126.02, 124.84 ($(\text{C}_5\text{NH}_4)_2$), 134.45 (C_5Me_5), 53.40 (CH_2Cl_2), 12.98 (C_5H_{15}). MS: $m/z = 462$ (M^+), 427 ($\text{M}^+ - \text{Cl}$), 339 ($\text{M}^+ - \text{C}_5\text{NH}_4\text{COO}$), 327 ($\text{M}^+ - \text{C}_5\text{Me}_5$). Elemental Anal. Calc. for $\text{C}_{10}\text{H}_{15}\text{Ti}(\text{C}_5\text{H}_4\text{NCO}_2)_2\text{Cl}(\text{CH}_2\text{Cl}_2)$: C, 50.43; H, 4.60; N, 5.11. Found: C, 49.70; H, 4.77; N, 5.11%.

4.3.2. $[\text{Cp}^*\text{Ti}(3\text{-Methyl 2-Pyridinecarboxylato})_2\text{Cl}]\cdot(\text{CH}_2\text{Cl}_2)_{0.25}$ (**2**)

An analogous method for compound **1** was used for preparation of compound **2**. 0.55 g (4 mmol) 3-methyl picolinic acid instead of picolinic acid was used. Yield 82% (0.47 g).

^1H NMR (CDCl_3 , 400 MHz): $\delta = 8.38$ (d, H, $\text{C}_5\text{NH}_3\text{CH}_3$), 8.22 (d, H, $\text{C}_5\text{NH}_3\text{CH}_3$), 7.64 (d, H, $\text{C}_5\text{NH}_3\text{CH}_3$), 7.46 (d, H, $\text{C}_5\text{NH}_3\text{CH}_3$), 7.34 (m, H, $\text{C}_5\text{NH}_3\text{CH}_3$), 7.18 (m, H, $\text{C}_5\text{NH}_3\text{CH}_3$), 5.27 (s, 0.5H, CH_2Cl_2), 2.74 (s, 3H, $\text{C}_5\text{NH}_3\text{CH}_3$), 2.59 (s, 3H, $\text{C}_5\text{NH}_3\text{CH}_3$), 1.99 (s, 15H, $\text{C}_{10}\text{H}_{15}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 400 MHz): $\delta = 169.47$, 166.78 (COO), 147.83, 144.53, 144.51, 143.89, 143.61, 141.81, 139.61, 137.90, 127.09, 126.68 ($(\text{C}_5\text{NH}_3\text{CH}_3)_2$), 133.63 (C_5Me_5), 53.40 (CH_2Cl_2), 19.81, 19.42 ($(\text{C}_5\text{NH}_3\text{CH}_3)_2$), 12.88 (C_5H_{15}). MS: $m/z = 490$ (M^+), 455 ($\text{M}^+ - \text{Cl}$), 355 ($\text{M}^+ - \text{C}_5\text{Me}_5$). Elemental Anal. Calc. for $\text{C}_{10}\text{H}_{15}\text{Ti}(\text{C}_5\text{H}_3\text{NCH}_3\text{CO}_2)_2\text{Cl}(\text{CH}_2\text{Cl}_2)_{0.25}$: C, 56.88; H, 5.41; N, 5.47. Found: C, 56.07; H, 5.64; N, 5.51%.

4.3.3. $[\text{Cp}^*\text{Ti}(2\text{-Pyridinecarboxylato})_2\text{OMe}]$ (**3**)

A greenish yellow solution of 0.27 g (1.0 mmol) pentamethyl cyclopentadienyl titanium trimethoxide ($\text{Cp}^*\text{Ti}(\text{OMe})_3$) in 20 ml toluene was added to a white slurry of 0.12 g (1.0 mmol) picolinic acid in 20 ml toluene at $-78\text{ }^{\circ}\text{C}$. The reaction mixture was allowed to warm to room temperature and stirred for 12 h and then precipi-

tated. The supernatant of the reaction mixture was decanted out and then washed by 10 ml diethyl ether two times. The resulting orange solid was dried in vacuum, affording orange solid product in 60% yield (0.14 g).

^1H NMR (CDCl_3 , 400 MHz): $\delta = 8.34$ (d, H, C_5NH_4), 8.29 (d, H, C_5NH_4), 8.06 (d, H, C_5NH_4), 7.95 (d, H, C_5NH_4), 7.82 (t, H, C_5NH_4), 7.69 (t, H, C_5NH_4), 7.36 (t, H, C_5NH_4), 7.25 (t, H, C_5NH_4), 3.53 (s, 3H, OCH_3), 1.86 (s, 15H, $\text{C}_{10}\text{H}_{15}$). ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3 , 400 MHz): $\delta = 169.04$, 167.87 (COO), 150.16, 148.33, 145.98, 144.52, 139.64, 138.60, 127.11, 126.94, 125.41, 124.97 ($(\text{C}_5\text{NH}_4)_2$), 128.95 (C_5Me_5), 65.16 (OCH_3), 11.87 (C_5H_{15}). MS: $m/z = 458$ (M^+), 427 ($\text{M}^+ - \text{OCH}_3$), 323 ($\text{M}^+ - \text{C}_5\text{Me}_5$). Elemental Anal. Calc. for $\text{C}_{10}\text{H}_{15}\text{Ti}(\text{C}_5\text{H}_4\text{NCO}_2)_2\text{OCH}_3$: C, 60.27; H, 5.72; N, 6.11. Found: C, 59.75; H, 5.98; N, 6.16%.

4.3.4. [$\text{Cp}^*\text{Ti}(2\text{-Pyridinecarboxylato})_2\text{OOC}(\text{pyridine})$] (4)

A greenish yellow solution of 0.27 g (1.0 mmol) $\text{Cp}^*\text{Ti}(\text{OMe})_3$ in 20 ml toluene was added to a white slurry of 0.36 g (3.0 mmol) picolinic acid in 20 ml toluene at -78°C . The reaction mixture was allowed to warm to room temperature and stirred for 12 h and then precipitated. The supernatant of the reaction mixture was decanted out and then washed by 10 ml diethyl ether two times. The resulting red solid was dried in vacuum, affording red solid product in 78% yield (0.43 g).

^1H NMR (CDCl_3 , 400 MHz): $\delta = 8.64$ (d, 2H, C_5NH_4), 7.92 (d, 2H, C_5NH_4), 7.80 (t, 2H, C_5NH_4), 7.70 (d, H, C_5NH_4), 7.62 (d, H, C_5NH_4), 7.49 (t, H, C_5NH_4), 7.39 (t, 2H, C_5NH_4), 6.93 (t, H, C_5NH_4), 2.02 (s, 15H, $\text{C}_{10}\text{H}_{15}$). ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3 , 400 MHz): $\delta = 168.74$, 167.45 (COO), 151.41, 148.96, 148.85, 143.99, 139.09, 138.56, 127.27, 126.39, 124.96, 124.37 ($(\text{C}_5\text{NH}_4)_2$), 133.89 (C_5Me_5), 12.49 (C_5H_{15}). MS: $m/z = 549$ (M^+), 427 ($\text{M}^+ - \text{C}_5\text{NH}_4\text{COO}$), 414 ($\text{M}^+ - \text{C}_5\text{Me}_5$). Elemental Anal. Calc. for $\text{C}_{10}\text{H}_{15}\text{Ti}(\text{C}_5\text{H}_4\text{NCO}_2)_2\text{OOC}\text{C}_5\text{H}_4\text{N}$: C, 61.21; H, 4.95; N, 7.64. Found: C, 60.84; H, 5.13; N, 7.59%.

4.3.5. [$\text{Cp}^*\text{Ti}(3\text{-Methyl 2-pyridinecarboxylato})_2\text{OOC}(3\text{-methylpyridine})$] (5)

An analogous method for compound 4 was used for preparation of compound 5. 0.41 g (3 mmol) of 3-methyl picolinic acid instead of picolinic acid was used. Yield 82% (0.48 g).

^1H NMR (CDCl_3 , 400 MHz): $\delta = 8.43$ (d, 2H, $\text{C}_5\text{NH}_3\text{CH}_3$), 7.81 (d, H, $\text{C}_5\text{NH}_3\text{CH}_3$), 7.49 (d, 2H, $\text{C}_5\text{NH}_3\text{CH}_3$), 7.32 (d, H, $\text{C}_5\text{NH}_3\text{CH}_3$), 7.22 (t, 2H, $\text{C}_5\text{NH}_3\text{CH}_3$), 6.96 (t, H, $\text{C}_5\text{NH}_3\text{CH}_3$), 2.54 (s, 3H, $\text{C}_5\text{NH}_3\text{CH}_3$), 2.43 (s, 6H, $\text{C}_5\text{NH}_3\text{CH}_3$), 1.96 (s, 15H, $\text{C}_{10}\text{H}_{15}$). ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3 , 400 MHz): $\delta = 169.50$, 168.41 (COO), 150.61, 146.35, 145.86, 142.77, 141.77, 141.56, 140.94, 137.10, 135.36, 126.16, 124.97 ($\text{C}_5\text{NH}_3\text{CH}_3$), 132.93 (C_5Me_5), 15.53 ($\text{C}_5\text{NH}_3\text{CH}_3$), 12.31 ($\text{C}_5(\text{CH}_3)_5$). MS: $m/z = 591$ (M^+), 456 ($\text{M}^+ - \text{C}_5\text{NH}_3\text{CH}_3\text{COO}$), 455 ($\text{M}^+ - \text{C}_5\text{Me}_5$). Elemental Anal. Calc. for $\text{C}_{10}\text{H}_{15}\text{Ti}(\text{C}_5\text{H}_3\text{CH}_3\text{NCO}_2)_2$ -

$\text{OOC}\text{C}_5\text{H}_3\text{CH}_3\text{N}$: C, 62.95; H, 5.62; N, 7.10. Found: C, 62.46; H, 5.81; N, 6.99%.

4.3.6. [$\text{Cp}^*\text{Ti}(2\text{-Pyridinecarboxylato})_2\text{O}$] (6)

A greenish yellow solution of 0.27 g (1.0 mmol) $\text{Cp}^*\text{Ti}(\text{OMe})_3$ in 20 ml toluene was added to a white slurry of 0.12 g (1.0 mmol) picolinic acid in 20 ml toluene at -78°C . The reaction mixture was allowed to warm to room temperature and stirred for 5 h. An excess of H_2O was added to the reaction mixture and stirred for 12 h and then precipitated. The supernatant of the reaction mixture was decanted out and then washed by 10 ml diethyl ether two times. The resulting yellow solid was dried in vacuum, affording the solid product in 65% yield (0.21 g).

^1H NMR (CDCl_3 , 400 MHz): $\delta = 8.57$ (d, H, C_5NH_4), 8.25 (d, H, C_5NH_4), 8.12 (t, H, C_5NH_4), 7.65 (t, H, C_5NH_4), 1.58 (s, 15H, $\text{C}_{10}\text{H}_{15}$). ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3 , 400 MHz): $\delta = 167.18$ (COO), 151.73, 148.63, 140.90, 126.60, 124.43 (C_5NH_4), 124.94 (C_5Me_5), 11.51 ($\text{C}_5(\text{CH}_3)_5$). MS: $m/z = 642$ (M^+), 507 ($\text{M}^+ - \text{C}_5\text{Me}_5$), 519 ($\text{M}^+ - \text{C}_5\text{NH}_4\text{COO}$). Elemental Anal. Calc. for $(\text{C}_{10}\text{H}_{15}\text{Ti}(\text{C}_5\text{H}_4\text{NCO}_2)\text{O})_2$: C, 59.83; H, 5.96; N, 4.36. Found: C, 59.25; H, 6.05; N, 4.32%.

4.3.7. [$\text{Cp}^*\text{Ti}(3\text{-Methyl 2-pyridinecarboxylato})_2\text{O}$] (7)

An analogous method for compound 6 was used for preparation of compound 7. 0.13 g (1.0 mmol) of 3-methyl picolinic acid instead of picolinic acid was used. Yield 70% (0.23 g).

^1H NMR (CDCl_3 , 400 MHz): $\delta = 8.47$ (d, H, $\text{C}_5\text{NH}_3\text{CH}_3$), 7.86 (d, H, $\text{C}_5\text{NH}_3\text{CH}_3$), 7.49 (m, H, $\text{C}_5\text{NH}_3\text{CH}_3$), 2.90 (s, 3H, $\text{C}_5\text{NH}_3\text{CH}_3$), 1.58 (s, 15H, $\text{C}_{10}\text{H}_{15}$). ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3 , 400 MHz): $\delta = 167.76$ (COO), 148.79, 146.63, 143.84, 137.87, 125.64 ($\text{C}_5\text{NH}_3\text{CH}_3$), 124.54 (C_5Me_5), 19.76 ($\text{C}_5\text{NH}_3\text{CH}_3$), 11.49 ($\text{C}_5(\text{CH}_3)_5$). MS: $m/z = 670$ (M^+), 535 ($\text{M}^+ - \text{C}_5\text{Me}_5$), 534 ($\text{M}^+ - \text{C}_5\text{NH}_3\text{CH}_3\text{COO}$). Elemental Anal. Calc. for $(\text{C}_{10}\text{H}_{15}\text{Ti}(\text{C}_5\text{H}_3\text{CH}_3\text{NCO}_2)\text{O})_2$: C, 60.91; H, 6.31; N, 4.17. Found: C, 60.28; H, 6.50; N, 4.07%.

4.4. X-ray structure determination

Crystal suitable for single crystal X-ray diffraction study grown from MC/hexane recrystallization for 3 was mounted on glass capillaries. A set of independent reflections was measured on a Bruker AXS SMART CCD-equipped diffractometer with graphite-monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 293 K. The hemisphere of reflection data were collected as ω scan frames with a width of $0.3^\circ/\text{frame}$ and exposure time of 10 s/frame. Cell parameters were determined and refined by SMART program [10]. Data reduction was performed using SAINT software [11], which corrects for Lorentz polarization effects. Empirical absorption correction was applied with SADABS program [12]. Structures were solved and all non-hydrogen atoms were refined by full-matrix least-square techniques with anisotropic

Table 2
Crystal data and structure refinement of complex **3**

	3
Formula	C ₄₆ H ₅₂ N ₄ O ₁₀ Ti ₂
<i>M_r</i> (g mol ⁻¹)	916.72
Crystal system	Orthorhombic
Space group	<i>Pbca</i>
<i>a</i> (Å)	19.604(10)
<i>b</i> (Å)	17.575(11)
<i>c</i> (Å)	25.850(16)
α (°)	90
β (°)	90
γ (°)	90
<i>V</i> (Å ⁻³)	8906(9)
<i>Z</i>	8
ρ_{calcd} (Mg m ⁻³)	1.367
μ (mm ⁻¹)	0.421
<i>F</i> (000)	3840
Crystal size (mm)	0.60 × 0.58 × 0.65
Reflections collected, unique	51,456, 10,381
<i>R</i> _{int}	0.2907
Data/restraints/parameters	10,381/0/571
GOF on <i>F</i> ²	1.013
<i>R</i> ₁ , ωR ₂	0.1248, 0.2635
Largest difference in peak/hole (e Å ⁻³)	0.606, -0.846

parameters by SHELXTL program [13]. Hydrogen atoms except non-coordinated water hydrogen atoms were calculated at idealized positions and refined riding on the corresponding carbon atoms with isotropic thermal parameters. The crystallographic data for compound **3** are listed in Table 2.

4.5. Ethylene polymerization procedures

Toluene, the polymerization solvent, was distilled from sodium-potassium alloy under nitrogen atmosphere just before use. Ethylene polymerizations were carried out in a 250 mL Schlenk flask equipped with a magnetic stirrer, a continuous supply of neat gaseous ethylene at 1 bar and a thermocouple to measure the reaction temperature that was regulated by an external circulation bath. In all polymerization experiments, the reactor was charged with 100 mL of toluene and purged by ethylene. And then, a solution of MAO was added and then a solution of catalyst in toluene was added. After 5 min, polymerizations were terminated by removing ethylene gas from the reaction mixture and quenching with a small volume of acidified MeOH (10 vol.% HCl). The precipitated polymers were collected by filtration, washed with methanol and dried in a vacuum oven at 70 °C for 12 h.

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Appendix A. Supplementary material

CCDC 255802 contains the supplementary crystallographic data for **3**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2006.12.007](https://doi.org/10.1016/j.jorganchem.2006.12.007).

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