

# Synthesis and Polymerization Behavior of Cp\*Ti(2-pyridinecarboxylato)<sub>2</sub>Cl: A New Cp/non-Cp Hybrid Catalyst for Polyethylene with Multimodal Molecular Weight Distribution

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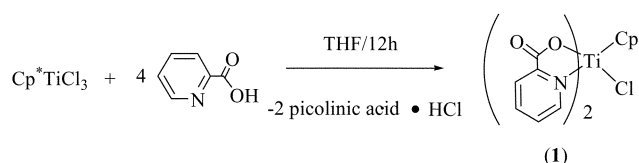
Received February 1, 2005

**Key Words :** 2-Pyridinecarboxylate, Titanium, Catalysts, Polyethylene, Multimodal

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. For example, metallocene-based polyethylene (PE) shows excellent properties such as high clarity and high impact strength, aroused from narrow molecular weight distribution (MWD) and a lack of branching.<sup>1,2</sup> 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<sup>3-5</sup> and introducing branches.<sup>6</sup>

The incidental observation of catalytic systems that gave PE with broad MWD is uncommon.<sup>7</sup> But the control of MWD of PE has been approached by using a series of reactors under different polymerization conditions,<sup>3</sup> employing different catalytic systems in one pot<sup>4</sup> and designing metallocene precatalytic systems that can produce multi catalytic species during the polymerization process.<sup>5</sup> The concept embodied in the design of the foregoing metallocene precatalytic systems includes Lewis acid-base interaction in dialkylamino substituted *ansa*-metallocene,<sup>5a</sup> *in situ* generation of different isomers for non-Cp type catalyst<sup>5c</sup> and the stepwise dissociation of chelate ligand in half-metallocene catalyst.<sup>5b</sup> To date, the attempt to modulate MWD of PE based on the coupled use of those concepts has not been reported. Thus, we have developed a new Cp/non-Cp hybrid catalytic system that produces PE with multimodal MWD by employing 2-pyridinecarboxylate, a potential chelate ligand<sup>8</sup> with multi Lewis base centers of N and O atoms, as a non-Cp ligand.

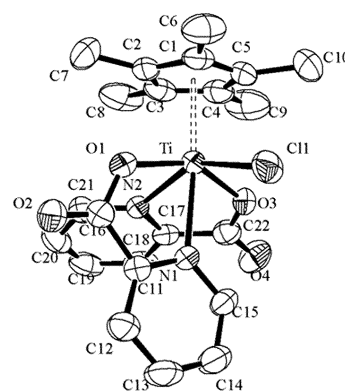
The complex **1** was synthesized via HCl elimination reaction in high yield (80%) as outlined in Scheme 1 and fully characterized.<sup>9</sup> The molecular structure of **1** is displayed in Figure 1 and the selected interatomic distances and angles are given as part of the figure caption. Both 2-pyridinecarboxylate ligands in **1** behave as bidentate chelates with N and O donor centers. The compound **1** was examined as a



**Scheme 1.** Reaction route for the compound **1**.

catalyst for ethylene polymerization in the presence of MMAO (3A type from TOSOH AKZO Co.) (Table 1). The 1/MMAO system shows polymerization activity of 10-10<sup>2</sup> KgPE/(mol of Ti)-h-bar and produces high density polyethylenes. The observed PDI values are very different from around 2 generally observed for single site catalysts.

The GPC diagrams of the PEs as a function of T<sub>p</sub>, displayed in Figure 2. The GPC profiles at T<sub>p</sub> of 30 and 50 °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. As T<sub>p</sub> increases to 70 and 90 °C the appearance of an apparent bimodal MWD becomes more evident. The analysis of GPC profiles by deconvolution based on the Gaussian distribution indicates the possible involvement of at least three unimodal curves since the GPC profiles at all T<sub>p</sub>s are best fitted with three kinds of

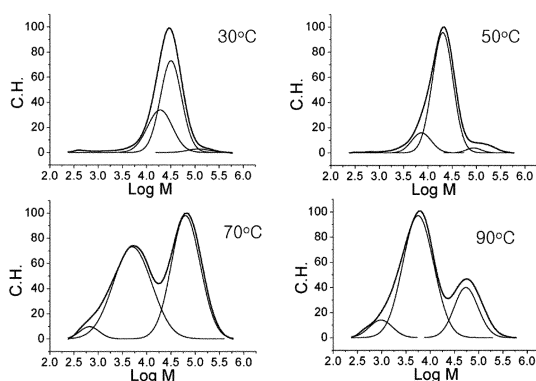


**Figure 1.** ORTEP drawing of the compound **1**, showing 50% probability thermal ellipsoids and atom labeling. Hydrogen atoms and the solvate CH<sub>2</sub>Cl<sub>2</sub> were omitted for clarity.; Selected bond lengths (Å) and angles (°): Ti(1)-O(1) 1.992(2), Ti(1)-O(3) 1.997(3), Ti(1)-Cp centroid 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).

**Table 1.** Ethylene polymerizations with **1**/MMAO

Run	Tp	Al/Ti	A <sup>c</sup>	Mw	Tm	PDI
1 <sup>a</sup>	30	2000	Trace	—	—	—
2 <sup>a</sup>	50	2000	120	88,440	136.49	3.66
3 <sup>a</sup>	70	2000	96	43,420	133.56	4.51
4 <sup>a</sup>	90	2000	Trace	15,900	—	5.40
5 <sup>b</sup>	30	2000	45	170,700	137.28	5.80
6 <sup>b</sup>	50	2000	63	72,930	135.32	3.96
7 <sup>b</sup>	70	2000	15	38,510	128.68	7.83
8 <sup>b</sup>	90	2000	trace	43,520	—	8.48

<sup>a</sup>Polymerization condition: P(ethylene) 1 bar; Ti 2  $\mu$ mol; solvent 50 mL of toluene; t<sub>p</sub> 5 min; <sup>b</sup>Ti 5  $\mu$ mol; <sup>c</sup>A KgPE/(mol of Ti)-h-bar



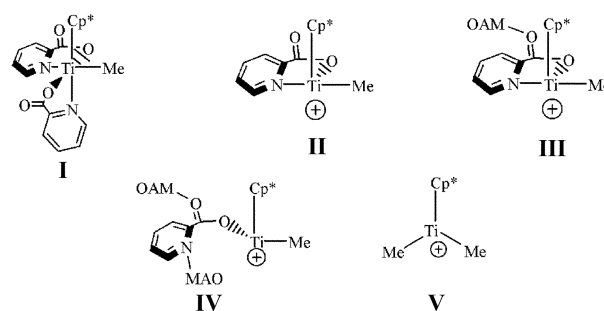
**Figure 2.** GPC diagrams of polyethylenes produced with the complex **1**/MMAO at various temperature (runs 5-8 in Table 1); C.H. in Y axis = Concentration Height, Log M in X axis = Log (Molecular Weight); — : observed, ··· : deconvoluted.

distributions.

As stated in the introduction, three concepts such as Lewis acid-base interaction, *in situ* generation of different isomers and the stepwise dissociation of a chelate ligand have been utilized in modulating the MWD. Since the compound **1** may potentially possess all of these concepts, it is worthy of noting which concepts can be ascribed to the observed MWD of the **1**/MMAO system. As an isolated solid form, the complex **1** appears as one pure form. In solution state, the variable temperature(VT)-<sup>1</sup>H-NMR spectra of **1** in toluene-d<sub>8</sub> in the range of -20 °C ~ 90 °C indicate that the complex **1** does not produce any isomers. Thus, the contribution of *in situ* generated different isomers<sup>5c</sup> 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 reaction of the precursor **1** with MMAO could result in the formation of species such as **I**, **II**, **III**, **IV** and **V** shown in Figure 3. Certainly, the species **III** and **IV** include the concepts of Lewis acid-base interaction and the stepwise dissociation of the chelate ligand. Among those, all species except **I** have vacant sites for incoming monomers, are likely to show different thermal stabilities and therefore can serve as active centers for ethylene polymerization, leading to the temperature dependent modulation of MWD of PEs.

The **1**/MMAO catalytic system produces PEs with multi-



**Figure 3.** Possible species from the reaction of the complex **1** and MMAO.

modal MWD. 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.

**Acknowledgement.** The authors gratefully acknowledge financial supports from the KOSEF (R02-2002-000-00057-0), CMDS and the BK 21 Project.

**Supplementary Material Available.** Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC 249165). These data can be obtained free of charge via [www.ccdc.ac.uk/data\\_request/cif](http://www.ccdc.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

## References

- For a review of polyethylene polymerization see Alt, H. G.; Köppl, A. *Chem. Rev.* **2000**, *100*, 1205.
- Kulshrestha, A. K.; Tarapatra, S. In *Handbook of Polyolefins*; Vasile, C., Ed; Marcel Dekker: New York, 2000; pp 1-70.
- Scheirs, J.; Böhm, L. L.; Boot, J. C.; Leevers, P. S. *Trends Polym. Sci.* **1996**, *4*, 408.
- (a) Ahn, T. O.; Hong, S. C.; Kim, J. H.; Lee, D. *J. Appl. Polym. Sci.* **1998**, *67*, 2213; (b) Kim, Y.; Park, S.; Han, Y.; Do, Y. *Bull. Korean Chem. Soc.* **2004**, *25*, 1648.
- (a) Müller, C.; Lilge, D.; Kristen, M. O.; Jutzi, P. *Angew. Chem. Int. Ed.* **2000**, *39*, 789; (b) Kim, Y.; Han, Y.; Lee, M. H.; Yoon, S. W.; Choi, K. H.; Song, B. G.; Do, Y. *Macromol. Rapid Commun.* **2001**, *22*, 573; (c) Tohi, Y.; Makio, H.; Matsui, S.; Onda, M.; Fujita, T. *Macromolecules* **2003**, *36*, 523.
- Przybyla, C.; Tesche, B.; Fink, G. *Macromol. Rapid Commun.* **1999**, *20*, 328.
- Murtuza, S.; Casagrande, Jr., O. L.; Jordan, R. F. *Organometallics* **2002**, *21*, 1882.
- Kim, S. I.; Woo, D.-J.; Lee, M.-H.; Woo, G.-J.; Kang, D.-K.; Cha, K.-W. *Bull. Korean Chem. Soc.* **2003**, *24*, 1517.
- Compound **1**: 80% yield <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 8.44 (d, H, C<sub>5</sub>NH<sub>4</sub>), 8.42 (d, H, C<sub>5</sub>NH<sub>4</sub>), 8.07 (d, H, C<sub>5</sub>NH<sub>4</sub>), 7.89 (t, H, C<sub>5</sub>NH<sub>4</sub>), 7.81 (d, H, C<sub>5</sub>NH<sub>4</sub>), 7.67 (t, H, C<sub>5</sub>NH<sub>4</sub>), 7.45 (t, H, C<sub>5</sub>NH<sub>4</sub>), 7.27 (t, H, C<sub>5</sub>NH<sub>4</sub>), 5.27 (s, 2H, CH<sub>2</sub>Cl<sub>2</sub>), 2.03 (s, 15H, C<sub>10</sub>H<sub>15</sub>). <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 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 ((C<sub>5</sub>NH<sub>4</sub>)<sub>2</sub>), 134.45 (C<sub>5</sub>Me<sub>5</sub>), 53.40 (CH<sub>2</sub>Cl<sub>2</sub>), 12.98 (C<sub>5</sub>H<sub>15</sub>). Elemental Analysis, C<sub>10</sub>H<sub>15</sub>Ti(C<sub>5</sub>H<sub>4</sub>NCO<sub>2</sub>)<sub>2</sub>Cl(CH<sub>2</sub>Cl<sub>2</sub>): Calcd. C 50.43, H 4.60, N 5.11; Found C 49.70, H 4.77, N 5.11. MS: m/z = 462 (M<sup>+</sup>), 427 (M<sup>+</sup>-Cl), 339 (M<sup>+</sup>-C<sub>5</sub>NH<sub>4</sub>COO), 327 (M<sup>+</sup>-C<sub>5</sub>Me<sub>5</sub>). X-ray crystallographic data: Crystal system = Triclinic, space group = P-1, a = 9.322(3) Å, b = 12.819(5) Å, c = 20.631(7) Å, alpha = 89.932(7) deg, beta = 89.897(6) deg, gamma = 86.080(7) deg, R1 = 0.0539.