

## High-molecular-weight Polyethylene Prepared with Early Transition Metal Catalysts

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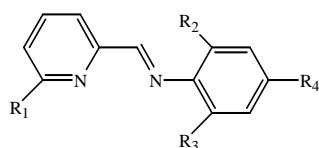
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**Abstract:** Early transition metal catalysts  $[N,N]MCl_n$ , in which  $[N,N]$  is N-(2,6-diisopropylphenyl)pyridine-2-carboxaldimine ( $C_{18}H_{22}N_2$ , NN-1), N-(2,6-diisopropylphenyl)-6-methylpyridine-2-carboxaldimine ( $C_{19}H_{24}N_2$ , NN-2), N-(2,4,6-trimethylphenyl)pyridine-2-carboxaldimine ( $C_{15}H_{16}N_2$ , NN-3), M is Ti, Zr and V, and  $n$  is 3 or 4, *e.g.*  $[NN-1]TiCl_4$  **1a**,  $[NN-1]ZrCl_4$  **1b**,  $[NN-1]VCl_3$  **1c**,  $[NN-2]TiCl_4$  **2a**,  $[NN-2]ZrCl_4$  **2b**,  $[NN-2]VCl_3$  **2c**,  $[NN-3]TiCl_4$  **3a** have been investigated to catalyze ethylene polymerization in the presence of methylaluminoxane (MAO). It was noteworthy that polyethylene characteristic of high molecular weight and wide or bimodal molecular weight distribution was formed with moderate to high activities.

**Keywords:** Early transition metal, catalyst, ethylene, polymerization.

In the rapidly advancing and technologically important field of olefin polymerization catalysts, tremendous attentions were paid to homogeneous single-site transition metallic complexes with fine-tuning electronic and geometric structure of coordinated ligands<sup>1-2</sup>. Carefully tuning of ligands of transition metal catalysts can vary composition of the product from oligomers to polymer. For example, as to the cationic Ni (II)  $\alpha$ -diimine catalysts, bearing bulky aryl *ortho* substituents of  $\alpha$ -diimine ligands, which efficiently retard the rate of chain transfer relative to chain propagation, results in forming the polymer<sup>3a</sup>. Instead, lacking bulky aryl *ortho* substituents gives rise to oligomerization catalysts<sup>3b</sup>. We have reported that nickel complexes bearing the N-(2-pyridinylmethylene)phenylamine ligands ( $[N, N]$ , **Scheme 1**) served as high active catalysts for ethylene oligomerization in the presence of organoaluminum compounds<sup>4</sup>. Recently we found that variation of metal centers from nickel to early transition metals (IVB or VB) with the same ligands generated ethylene polymerization catalysts to produce polyethylene with high molecular weight and wide or bimodal molecular weight distribution.

**Scheme 1** Structure of N-(2-pyridinylmethylene)-phenylamine ( $[N, N]$ )



NN-1:  $R_1=H, R_2=R_3=CH(CH_3)_2, R_4=H$   
 NN-2:  $R_1=CH_3, R_2=R_3=CH(CH_3)_2, R_4=H$   
 NN-3:  $R_1=H, R_2=R_3=R_4=CH_3$

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Treatment of the dichloromethane solution of  $\text{TiCl}_4$ ,  $\text{ZrCl}_4$  or  $\text{VCl}_3$  with ligands  $[\text{N},\text{N}]^4$  (molar ratio of metal to ligand is 1:1) in Schlenk tube at room temperature for several hours, respectively, followed by filtration, washing with ether and drying under vacuum, gave early transition metal compounds with yield of 70-90% (**1a**:  $[\text{NN-1}]\text{TiCl}_4$ ; **1b**:  $[\text{NN-1}]\text{ZrCl}_4$ ; **1c**:  $[\text{NN-1}]\text{VCl}_3$ ; **2a**:  $[\text{NN-2}]\text{TiCl}_4$ ; **2b**:  $[\text{NN-2}]\text{ZrCl}_4$ ; **2c**:  $[\text{NN-2}]\text{VCl}_3$ ; **3a**:  $[\text{NN-3}]\text{TiCl}_4$ )<sup>5</sup>.

The results of catalytic ethylene polymerization tests with activation of methylaluminoxane (MAO) are collected in **Table 1**. It is noteworthy that high-molecular-weight polyethylene with wide or bimodal distribution for titanium and zirconium precursors and relatively narrow distribution for vanadium ones are produced, in contrast to ethylene oligomers which were formed with late transition metal systems<sup>3</sup>. The activities of the early transition catalysts are between moderate to high, and lower than those of nickel ones<sup>3</sup>. The obtained polyethylene has high melting points (133-137°C), suggesting its high density and high crystallization. Its <sup>13</sup>C-NMR spectra showed rare methyl branches in the backbone.

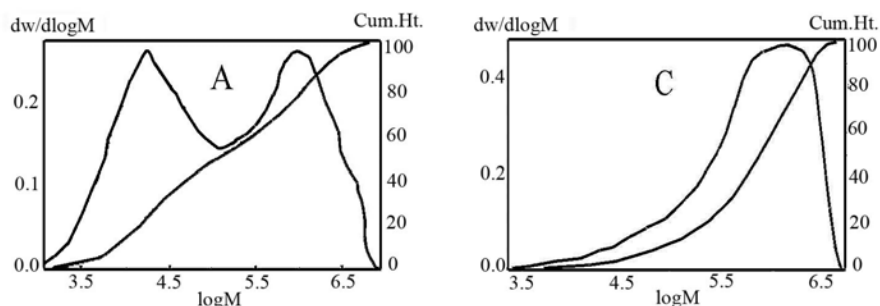
The activities and molecular weight of polyethylene were not very sensitive to the amount of MAO in a certain scales (entries 1-3, 8-9), however, the large amount of MAO resulted in a dramatic fall-off in molecular weight and bimodal distribution of polyethylene (entries 4), see **Figure 1** (A). When the Al/M molar ration was *ca.* 200, the activity of **1a** was the highest, and this ratio was much lower than that of homogeneous metallocene catalysts<sup>1b</sup>.

Activities are dependent upon the aryl and pyridine substitution pattern. *Ortho* bulky substituents on the aryl ring are in favor of the activities for titanium precursors, *e.g.* **1a** (*o*-isopropyl) > **3a** (*o*-methyl) (entries 2, 6), while methyl group *ortho* to N atom on pyridine ring leads to a dramatic reduce in activity, **1a**>**2a** or **1c**>**2c** (entries 2, 5 or 12, 14). This phenomena was similar to that of nickel catalysts<sup>4</sup>, but completely different

**Table 1** Results of ethylene polymerization with the  $[\text{N}, \text{N}]\text{MCl}_n/\text{MAO}$  catalytic system<sup>a</sup>

Entry	Catalyst	Al/M <sup>b</sup>	Activity gPE/molM·h	M <sub>w</sub> (×10 <sup>3</sup> )	M <sub>w</sub> /M <sub>n</sub>	T <sub>m</sub> (°C) <sup>d</sup>
1	<b>1a</b>	100	1.4×10 <sup>5</sup>	1188	17.6	137
2	<b>1a</b>	200	1.6×10 <sup>5</sup>	1210	20.5	135
3	<b>1a</b>	500	1.5×10 <sup>5</sup>	1214	12.4	136
4	<b>1a</b>	1000	7.6×10 <sup>4</sup>	635	26.8 <sup>b</sup>	135
5	<b>2a</b>	200	3.2×10 <sup>3</sup>			
6	<b>3a</b>	200	2.9×10 <sup>4</sup>			
7	<b>1b</b>	500	-			
8	<b>2b</b>	200	1.7×10 <sup>4</sup>	878	44.2	136
9	<b>2b</b>	1000	1.5×10 <sup>4</sup>			
10	<b>VCl<sub>3</sub></b>	200	1.1×10 <sup>3</sup>	1828	3.0	
11	<b>VCl<sub>3</sub> + NN-1</b>	200	4.3×10 <sup>3</sup>	1688	6.7	133
12	<b>1c</b>	500	8.6×10 <sup>4</sup>	1050	7.0	134
13 <sup>c</sup>	<b>1c</b>	500	1.0×10 <sup>5</sup>	1448	6.7	136
14	<b>2c</b>	300	3.0×10 <sup>4</sup>	888	3.1	

a. M = Ti, Zr or V, n = 3 or 4; Ethylene polymerizations run at 0.1 MPa pressure otherwise indicated; concentration of the complexes 1.2×10<sup>-5</sup>mol for Ti, 2.0 × 10<sup>-5</sup>mol for Zr or V; Polymerization temperature at 30°C; Polymerization time 0.5 hr; Toluene 50 mL. b. Bimodal. c. Pressure of ethylene 0.8 Mpa. d. tested *via* DSC.

**Figure 1** GPC curve of polyethylene produced with **1a**/MAO system (A) and **1c**/MAO (C)

from that of zirconium ones (entries 7-9), in which the catalyst **1b** was almost inactive, and **2b** showed moderate activity.

The  $\text{VCl}_3/\text{MAO}$  system displayed quite low activity, which was lower than that of the *in-situ* ( $\text{VCl}_3 + \text{NN-1}$ )/MAO system, and considerable lower than that of the formed **1c**/MAO system (entries 10-12). It was suggested that the interaction between metal centers and ligands played a very important role in formation of the active sites. Molecular weight of polyethylene obtained from  $\text{VCl}_3$ ,  $\text{VCl}_3 + \text{NN-1}$ , and  $[\text{NN-1}]\text{VCl}_3$  decreased orderly (entries 10-12). The typical GPC curve of polyethylene formed by **1c**/MAO catalytic system (entries 12) was showed in **Figure 1** (C). The dependence of the activity and molecular weight of polyethylene on the ethylene pressure was significant, *e.g.*, both the activity and molecular weight were promoted, while the polydispersity was not varied (entries 12, 13).

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### References and Notes

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- J. Yi, X. Huang, W. Zhang, X. Hong, Z. Jing, *J. Natural Gas Chem.*, **2003**, *12* (1), 98.
- Data of elemental analysis **1a**: Calcd. (%) C 48.40, H 4.87, N 6.14; Found (%) C 48.31, H 5.01, N 5.98. **2a**: Calcd. (%) C 48.24, H 5.58, N 5.96; Found (%) C 48.51, H 5.36, N 5.65. **3a**: Calcd. (%) C 43.51, H 3.90, N 5.46; Found (%) C 43.38, H 3.73, N 5.22. **1b**: Calcd. (%) C 43.28, H 4.45, N 5.61; Found (%) C 43.67, H 4.28, N 5.33. **2b**: Calcd. (%) C 44.44, H 4.72, N 5.46; Found (%) C 44.64, H 4.96, N 5.22. **1c**: Calcd. (%) C 51.02, H 5.24, N 6.61; Found (%) C 51.35, H 5.38, N 6.80. **2c**: Calcd. (%) C 52.13, H 5.54, N 6.40; Found (%) C 52.28, H 5.68, N 6.23.

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