

Synthesis of late transition nickel(II) coordination polymer and their catalysis for olefinic polymerization

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Abstract. It was illustrated in this paper the successful synthesization of one α -diimine ligand and one new polycondensate ligand. The structure of the ligand was characterized by ^1H NMR spectrum, and the structure of the polycondensate ligand was characterized by Thermogravimetric Analysis (TGA) and Element Analysis. Then these two ligands reacted with $(\text{DME})\text{NiBr}_2$ for the purpose of preparing α -diimine nickel complex and nickel coordination polymer characterized by Element Analysis and X-ray Photoelectron Spectroscopy (XPS). Then these two catalysts were adopted to facilitate ethylene polymerization and to compare the difference between them. It was found that the activities from nickel coordination polymer/MAO reached $10^6(\text{g/molNi}\cdot\text{h})$ and the molecule weights were about 10^5 .

1.Introduction

The area of ethylene polymerization with late metal catalysts was rejuvenated when Brookhart and his group reported a family of new cationic Pd(II) and Ni(II) α -diimine catalysts for the polymerization of ethylene, the late metal catalysts have high activities on ethylene polymerization¹, however, they have low stability. On the other side, metal coordination polymer has been studied these years²⁻⁴ and it was found that the effects of activity on the metal coordination were recognized in the following points. The separation of the catalytic active centers overcomes the disadvantages of inactivation and with the protection of polymer chain, the catalysts became more stable⁵. In this paper, two kinds of catalysts were used to polymerize ethylene. The influence of the ratio of Al/Ni, temperature, pressure, time, the dosage of catalyst, solvent and the structure of catalyst on the activities and molecular weights were studied. As for the result, the α -diimine nickel complex generated the oligomer, while the Metal Coordination Polymer produced the polyethylene. The activity was around $10^5\text{g PE}/(\text{molNi}\cdot\text{h})$, the molecular weight of PE was about 10^5 . Among these conditions, the ratio of Al/Ni, pressure and solvent affect the polymerization greatly.

2.Materials

All compounds sensitive to air and moisture were handled under an atmosphere of dried and purified argon using standard Schlenk techniques. Dichloromethane and diethyl were distilled under an argon atmosphere from sodium/benzophenone. The nickel complex $[\text{ArN}=\text{C}(\text{CH}_3)-\text{C}(\text{CH}_3)=\text{NAr}]\text{NiBr}_2$ ($\text{Ar} = \text{C}_6\text{H}_5$) and nickel coordination polymer $[-\text{N}=\text{C}(\text{CH}_3)-\text{C}(\text{CH}_3)=\text{NAr}-]_n[\text{NiBr}_2]_m$ ($\text{Ar} = \text{C}_6\text{H}_5$, $m < n$) were synthesized. MAO (10 wt. % in toluene, containing ca. 30% AlMe_3) was purchased from



ALBEMARLE CORPORATION and can be used to conduct the experiment directly. Ethylene monomer (99.9%) was supplied by Shanghai petrochemical company and used after dehydration by 4Å molecular sieve.

3.Preparation of α -diimine Catalysts and Nickel Coordination Polymer

In a clean and dry 250 mL tri-mouth flask, diacetyl (5 mmol) and phenylamine (10 mmol) in ethanol (70 mL) reacted about 4 hours to synthesize the ligand **L1** [$\text{ArN}=\text{C}(\text{CH}_3)-\text{C}(\text{CH}_3)=\text{NAr}$ ($\text{Ar} = \text{C}_6\text{H}_5$)]. The production process of polycondensate ligand **L2** [$-\text{N}=\text{C}(\text{CH}_3)-\text{C}(\text{CH}_3)=\text{NAr}-$] $_n$ ($\text{Ar} = \text{C}_6\text{H}_5$) was modeled on the method adopted above while p-phenylenediamine (5 mmol) took the place of phenylamine (10 mmol). Separation and purification of the production were achieved during the ligand synthesis, as the Figure 1 illustrates. Yields: 0.65g, 55% for **L1**; 0.23g, 29% for **L2**. Then in a clean dry 100 mL Schlenk flask, the nickel complex **C1** and nickel coordination polymer **C2** were synthesized by reacting the ligands with $\text{DME}(\text{NiBr}_2)$ under argon atmosphere. Separation and purification of the production were achieved. Yields: 78% for **C1**; 79% for **C2**.

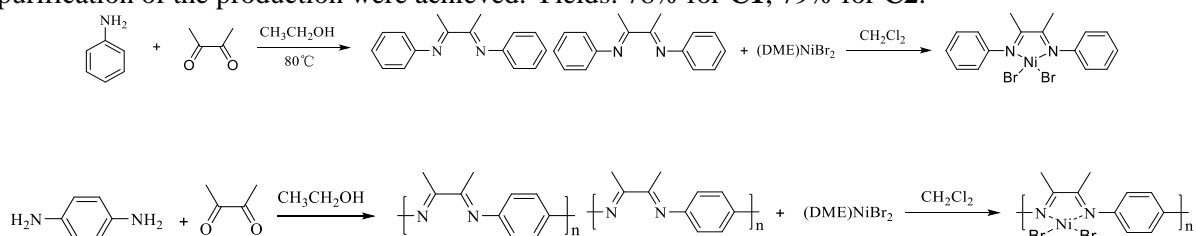


Figure 1. synthesis of nickel complex and nickel coordination polymer

4.Characterization

Nuclear magnetic resonance (NMR) analysis of α -diimine ligand was performed on a Varian Unity 400 MHz spectrometer at 298K using CDCl_3 as solvent. ^1H NMR spectrum referred to solvent peaks. And Element Analysis of nickel complex was performed on Vario EL cube. Element Analysis of polycondensate ligand was performed on Vario EL cube. Matrix-Assisted Laser Desorption/Ionization Time of Flight Mass Spectrometry of nickel coordination polymer was performed on AB Sciex 4800 plus. In addition, polycondensate ligand was characterized by Thermogravimetric Analysis (TGA) and nickel coordination polymer was characterized by X-ray Photoelectron Spectroscopy (XPS).

5.Results and Discussion

The ^1H -NMR of α -diimine ligand **L1**

^1H -NMR(400 MHz, CDCl_3 , 298K), δ :2.149(s, 6 H, CH_3), 6.79(d, $J=7.2$ Hz, 4 H, Ar), 7.11(t, $J=14.8$ Hz, 2 H, Ar), 7.37(t, $J=15.6$ Hz, 4 H, Ar), as the Figure 2 illustrates.

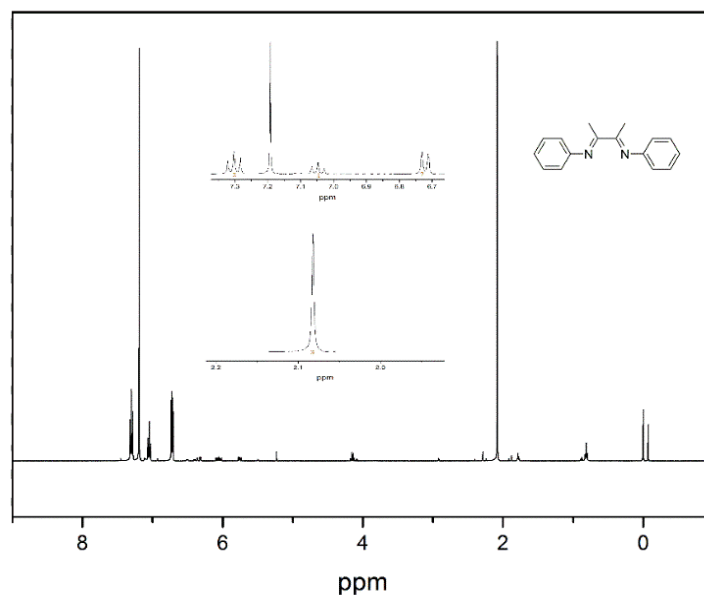


Figure 2. The ^1H NMR spectrum of ligand **L1**

The Element Analysis of nickel complex **C1** and polycondensate ligand **L2**

Calcd for $\text{C}_{16}\text{H}_{16}\text{N}_2\text{Br}_2\text{Ni}$ (**C1**): C, 42.25; H, 3.55; N, 6.16. Found: C, 42.18; H, 3.51; N, 6.12.

Calcd for $(\text{C}_{10}\text{H}_{10}\text{N}_2)_n$ (**L2**): C, 75.92; H, 6.37; N, 17.71. Found: C, 71.90; H, 6.39; N, 16.86.

The Thermogravimetric Analysis of polycondensate ligand **L2**

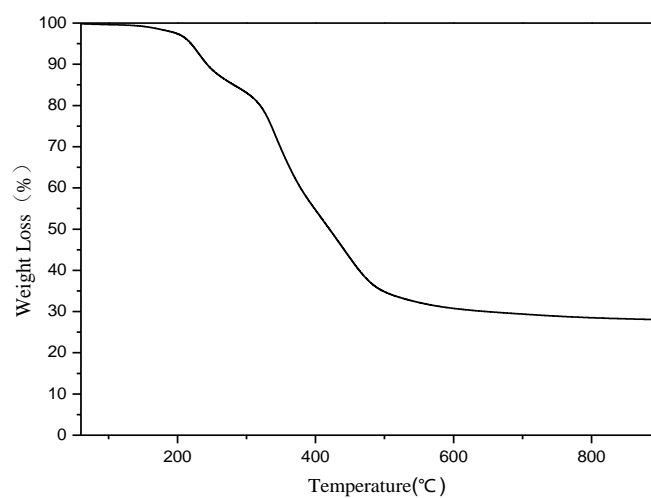


Figure 3. The TGA of ligand **L2**

The polycondensate ligand **L2** has a good heat-resistance. Its TD5 was 220°C, and when the temperature got 900°C, the Char-yield was 28%, as the Figure 3 illustrates.

The XPS of nickel coordination polymer **C2**

Table 1. The block of X-ray photoelectron spectroscopy

Name	Start BE(eV)	Peak BE(eV)	End BE(eV)	Atomic%	FWHM(eV)
C1s	296.73	284.84	279.83	78.43	1.83
N1s	410.73	399.69	392.83	14.03	1.30
Ni2p	890.73	855.43	844.83	7.54	2.14

From Table 1, the peak position of Ni to be tested was 855.4 eV. According to the table of the Ni element, this Ni element valence was +2 price, and the binding energy of NiBr₂ was 854.9 eV. There was an deviation according to the result of experiment. It could be considered that Ni had a complexation with the coordination polymer. In addition, the ratio of N and Ni was close to 2:1. So nickel coordination polymer **C2** could verify the correctness of the structure.

Ethylene polymerization with Ni complex **C1** and nickel coordination polymer **C2**

Table 2. Influence of reaction conditions on ethylene polymerization

No.	Al/Ni	<i>T</i> (°C)	10 ⁻⁵ <i>P</i> _{C₂H₄} (Pa)	<i>t</i> (h)	10 ⁻⁵ Activity (g.mol ⁻¹ Ni·h ⁻¹)	10 ⁻⁴ <i>M</i> _η ^c
1 ^b	400	25	10	1	0.39	10.54
2 ^b	600	25	10	1	0.57	13.98
3 ^b	800	25	10	1	1.73	16.39
4 ^b	1000	25	10	1	1.73	15.85
5 ^b	1200	25	10	1	1.79	15.13
6 ^a	800	25	10	1	--	--
7 ^b	800	50	10	1	1.75	19.21
8 ^b	800	70	10	1	1.13	12.43
9 ^b	800	25	5	1	1.03	15.36
10 ^b	800	25	15	1	4.42	19.04
11 ^b	800	25	10	2	1.68	17.23
12 ^b	800	25	10	4	1.67	18.69
13 ^b	800	25	10	8	1.65	20.17

m(Catalyst)=0.001 g, a. C1; b. C2; Co-catalyst: MAO; V(dichloromethane) = 40 mL. c Molecular weights of the polymers were determined by viscosity average molecular weight in decalin at 135°C. $[\eta] = \frac{\sqrt{2(\eta_{sp}-\ln\eta_r)}}{c}$; $[\eta] = K [M_\eta]^\alpha$ ($K = 6.77 \times 10^{-2}$, $\alpha = 0.67$)

A series of polymerization experiments in different polymerization conditions were showed in Table 2. Comparing from No.1 to No.5, the catalytic activity improved as Al/Ni increases. It was because that as the number of active centers grew, the impact probability would be increased to improve the activity. Comparing No.3 with No.6, it was found that using **C1** produced oligomer as the main product, while **C2** produced polyethylene as the main product. Comparing No.1, No.7 with No.8, it could be seen that the catalytic activity increased firstly, and then decreased with the temperature growing higher. As it was shown in the table 2, the catalytic activity was significantly affected by ethylene pressure. Besides, as the polymerization time prolonged, the catalytic activity kept stable as well. Under most conditions, the catalytic activity was about 1.7×10^6 g.mol⁻¹Ni·h⁻¹, and the *M*_η approached 10⁵.

According to the temperature-time figure, three minutes before the polymerization, if **C1** was adopted, the temperature of autoclave experienced obvious change, reaching approximately at 70°C in a quick period. When it came to **C2**, the change of temperature was not obvious. Because of the high temperature, **C1** lost its activity and the temperature dropped immediately. While **C2** kept active and the temperature remained the same. It reflects that **C2** has a relatively stable structure which is mild to the polymerization process.

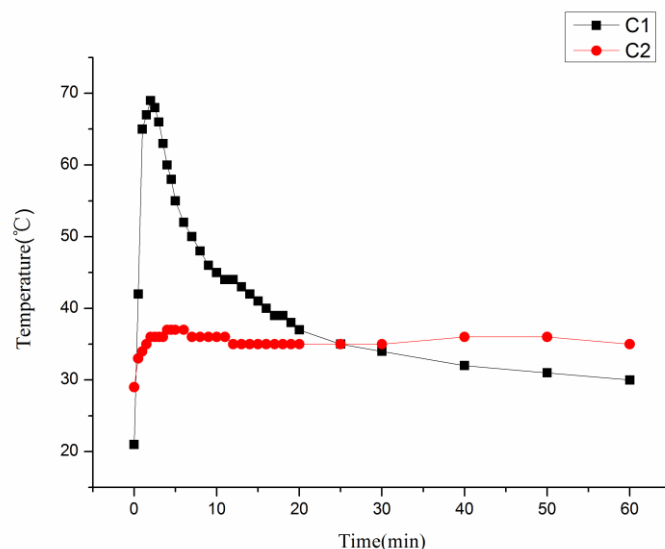


Figure 4 The temperature-time rate curve of ethylene polymerization

6. Summary

One nickel complex **C1** $[\text{ArN}=\text{C}(\text{CH}_3)-\text{C}(\text{CH}_3)=\text{NAr}]\text{NiBr}_2$ ($\text{Ar} = \text{C}_6\text{H}_5$) and one nickel coordination polymer **C2** $[-\text{N}=\text{C}(\text{CH}_3)-\text{C}(\text{CH}_3)=\text{NAr}-]_n[\text{NiBr}_2]_m$ ($\text{Ar}=\text{C}_6\text{H}_5$, $m < n$) were synthesized. Then they were used to facilitate polymerization. The effects of polymerization conditions, such as ethylene pressure, temperature and time on ethylene polymerization were investigated. The results showed that the polymerization which used **C1** produced oligomer while **C2** produced polyethylene, whose molecule weight reached 10^5 . Also, the catalytic activity could reach 10^6 g PE/(molNi·h). A series of experiments showed that **C2** had a satisfactory heat resistance and stable structure.

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