

# Ethylene Homo- and Copolymerization by Single Component Phosphinophenolate Neutral Nickel Catalysts

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**Abstract** A series of phosphinophenolate neutral nickel catalysts bearing pyridine as spectator ligands ( $(2\text{-P(R}_1\text{)(R}_2\text{)}\text{-C}_6\text{H}_3\text{(R)O)Ni(Me)(Py)}$ ) (**3a**,  $\text{R} = \text{H}$ ,  $\text{R}_1 = \text{R}_2 = \text{Ph}$ ; **3b**,  $\text{R} = t\text{-Bu}$ ,  $\text{R}_1 = \text{R}_2 = \text{Ph}$ ; **3c**,  $\text{R} = \text{R}_1 = \text{R}_2 = \text{Ph}$ ; **3d**,  $\text{R} = \text{anthr}$ ,  $\text{R}_1 = \text{R}_2 = \text{Ph}$ ; **3e**,  $\text{R} = \text{R}_1 = t\text{-Bu}$ ,  $\text{R}_2 = \text{Ph}$ ) have been synthesized and characterized by  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR. As a kind of single component catalysts, other than **3a** they all showed a higher catalytic activity to ethylene polymerization reaction, and a high catalytic activity up to  $4460 \text{ kg PE}/(\text{mol}(\text{Ni}) \cdot \text{h})$  was achieved by introducing proper steric effect groups at ortho position of its phenoxy group (**3c** ~ **3d**). Molecular mass of the polymer can be adjusted by varying the substituents as the ortho-position of phenoxy group, and using catalysts **3c** ~ **3d** with aryl substituents in ethylene polymerization reaction could produced higher molecular mass polymer. Catalyst **3e** with a *tert*-butyl group at its phosphorous atom showed similar activity as that of catalyst **3b** and was more readily initiated, producing polymers of lower molecular masses under the same conditions. Moreover, these catalysts were tolerant towards polar groups and able to catalyze copolymerization of ethylene with norbornene or its polar derivative 5-norbornene-2-yl acetate.

**Keywords** neutral nickel catalyst, ethylene polymerization, polar group tolerance, single component catalyst

CLC number: O613.5

Document code: A

Article ID: 1000-0518(2012)12-1381-08

DOI: 10.3724/SP.J.1095.2012.20490

Inspired by the work of Ziegler and Wilke, Keim developed shell higher olefin process (SHOP) catalysts for the production of higher  $\alpha$ -olefins through ethylene oligomerization, which constitutes one of the most important applications of homogeneous catalysis. In 1978, Keim and his coworkers reported the first well-known SHOP catalyst with the general formula  $(\text{P}, \text{O})\text{NiPh}(\text{PPh}_3)^{[1]}$ . These catalysts are tolerant towards polar groups, even can be used in polar solvents like alcohol, while their works had not received further attention during the following two decades due to incapability of producing high molecular mass polyethylene. In 1995, Brookhart *et al.* found that a series of  $\alpha$ -diimine nickel and palladium catalysts was highly active towards ethylene polymerization under the activation of methylaluminoxane (MAO) or organoborates, affording high molecular mass branched polyethylene<sup>[2]</sup>. Remarkably, the  $\alpha$ -diimine palladium catalysts are active towards the copolymerization of ethylene with methyl acrylate<sup>[3-4]</sup>, producing the branched copolymer with the polar groups positioned at the end of the branches *via* the chain walking process. In 2000, Grubbs and his coworkers reported a family of highly active neutral nickel catalysts for ethylene polymerization<sup>[5-6]</sup>. The high molecular mass polyethylene with some short branches was produced, and the molecular mass and branch content of the polymer can be tuned by manipulation of the catalyst structure. Importantly, these catalysts are

Received: 2012-10-29, Revised: 2012-11-06

Supported by the National Natural Science Foundation of China (21234006)

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tolerant towards polar additives, and are able to copolymerize ethylene with norbornene or its polar derivatives. The reports of Brookhart and Grubbs represents an important milestone in the research field of olefin polymerization catalysts, which overthrows the previous point of view that late transition metal catalysts are only capable of catalyzing oligomerization reactions. Since then, their design concepts have been applying to other researches, greatly improved the development of new catalytic systems and novel polymer materials.

As a family of ligands used in SHOP catalysts, phosphinophenolate compounds began to be applied in olefin polymerization reactions. Some researches were conducted by Heinicke<sup>[7-10]</sup>, most of which were reported as *in situ* catalysts, rare examples of well defined phosphinophenolate neutral nickel catalysts were only active for ethylene oligomerization<sup>[11-12]</sup>. The researches on substituent effects were limited to some alkyl groups, such as methyl and *tert*-butyl groups, and the spectator ligands were almost alkyl or aryl phosphines. The insufficient researches on phosphinophenolate nickel catalysts for ethylene polymerization were strange concerning the tremendous success of SHOP catalysts. In this contribution, we designed a series of phosphinophenolate ligands with different substituents at the ortho-position of the phenoxy or at the phosphorous atom, and pyridine stabilized neutral nickel complexes (P, O) NiMe (Py) were obtained by reacting them with Ni (Py)<sub>2</sub> Me<sub>2</sub>. Without the help of phosphine scavenger or cocatalyst, these nickel complexes are efficient catalysts for ethylene polymerization, and the molecular mass of the resultant polymer can be tuned by varying the substituents, and preliminary experiments also showed that these catalysts are tolerant towards polar groups.

## 1 Experimentals

### 1.1 Instruments and Reagents

All work involving air- and/or moisture-sensitive compounds were carried out in a M-Braun glovebox or under an argon atmosphere by using standard Schlenk technique. Anhydrous toluene was purified by solvent purification system purchased from M-Braun. The NMR spectra of the phosphinophenolate ligands and the organo-nickel complexes were recorded on a Bruker 400 MHz spectrometer at room temperature in CDCl<sub>3</sub> or C<sub>6</sub>D<sub>6</sub> solvents, and at 120 °C in *o*-dichlorobenzene solvent for the polymers respectively. Differential scanning calorimetry (DSC) measurements were performed on a Perkin-Elmer Pyris-1 differential scanning calorimeter at a heating rate of 10 °C/min. The mass-average molecular mass ( $M_w$ ) and the polydispersity index (PDI) values of polymer samples were determined *via* high-temperature gel permeation chromatography (GPC) using a PL-GPC 220 gel permeation chromatographer with 1,2,4-trichlorobenzene as mobile phase at a flow rate of 1.0 mL/min.

### 1.2 Synthesis of catalysts 3a ~ 3e

**1.2.1 Synthesis of the Ligands** Ligands **2a** ~ **2d** were synthesized according to literature procedures<sup>[13]</sup>.

**6-(*t*-Bu)-2-(*t*-Bu)(Ph)P-C<sub>6</sub>H<sub>3</sub>OH (2e)**: 20 mmol of diphenylphosphinous chloride (PPh<sub>2</sub>Cl) was dissolved in ethyl ether, to which 11 mL of <sup>t</sup>BuMgCl (2 mol/L) was added. The mixture was allowed to react for 4 h at room temperature. MgCl<sub>2</sub> was removed by filtration, and the filtrate was concentrated to give a colorless liquid (*A*) which was directly used for the next step. 3.74 g 3,4-dihydro-2*H*-pyran protected 2-*tert*-butyl-phenol (16.0 mmol) was reacted with 1.05 equiv of *n*-BuLi for 4 h to yield a yellow suspension (*B*). The *A* was dissolved in 20 mL ethyl ether and was slowly transferred to *B* under 0 °C. The color of the resultant mixture gradually became lighter during 10 h reaction. Then 4 mL of concentration 6 mol/L hydrochloric acid was added to the reaction mixture and stand for 8 h. H<sub>2</sub>O and ethyl ether was added, to it and was mixed. The organic layer was washed with saturated NaHCO<sub>3</sub> solution. Purification by column chromatograph afforded 3.80 g colorless liquid, which solidified on standing. Yield: 69.9%. <sup>1</sup>H NMR

(400 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 7.81 (d,  $J = 12.2$  Hz, 1H), 7.58 ~ 7.55 (m, 2H), 7.32 ~ 7.30 (m, 5H), 6.84 (t,  $J = 7.7$  Hz, 1H), 1.41 (s, 9H), 1.20 (d,  $J = 13.8$  Hz, 9H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 159.7 (d,  $J = 21.0$  Hz), 136.0, 134.8, 133.7, 133.6, 132.5, 128.8, 128.4, 128.2 (d,  $J = 7.1$  Hz), 119.5, 119.2, 34.9 (d,  $J = 2.0$  Hz), 31.4 (d,  $J = 7.1$  Hz), 29.5, 28.5 (d,  $J = 13.6$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ),  $\delta$ : -20.97.

**1.2.2 Synthesis of  $\text{NiMe}_2\text{Py}_2$**  According to the literature procedure<sup>[14]</sup>, 1.6 g (3.6 mmol)  $\text{NiPy}_4\text{Cl}_2$  was suspended in 40 mL ethyl ether and cooled to  $-60^\circ\text{C}$ . 1 mL pyridine was added before 4.5 mL (1.6 mol/L, 7.2 mmol) MeLi was injected to the system. The reaction was maintained at this temperature for 20 min, and allowed to warm to room temperature. After the color of the reaction mixture turned to dark green, most of the solvent was removed under vacuum. The residue was extracted with 40 mL toluene under inert atmosphere and filtrated to give dark red filtrate. After concentrated to about 10 mL, *n*-hexane was added and recrystallized under  $-30^\circ\text{C}$  to yield the target compound as golden yellow lamellar crystals in 60% yield.

**1.2.3 Synthesis of the Complexes** General procedure for the synthesis of the phosphinophenolate neutral nickel catalysts is as following: the phosphinophenolate ligands were mixed with 1.5 equiv of  $\text{NiPy}_2\text{Me}_2$ , and toluene was added to initiate the reaction. After stirring for 5 h at room temperature, the reaction mixture was filtrated to remove the nickel black generated by excess nickel source. Some toluene was added to help filtration, other than complex **3d** bearing bulky anthryl substituent, added THF. The filtrate was concentrated and *n*-hexane was added to the residue, the yellow brown solid was precipitated which was pure according to NMR spectroscopy.

(2-PPh<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>O) Ni (Me) (Py) (**3a**): Complex **3a** without any substituent at the ortho position of its phenoxy group is a kind of dark brown solid and has a yield of 87%.  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ),  $\delta$ : 7.91 ~ 7.82 (m, 5H), 7.21-7.00 (m, 12H), 6.51 (m, 2H), 0.33 (br, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{C}_6\text{D}_6$ ),  $\delta$ : 177.4, 133.4, 130.0, 128.7 (d,  $J = 10.0$  Hz), 13.53.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 30.66. Anal. calcd. for  $\text{C}_{24}\text{H}_{22}\text{NNiOP}$ : C 67.02, H 5.16, N 3.26. Found: C 66.98, H 5.18, N 3.20.

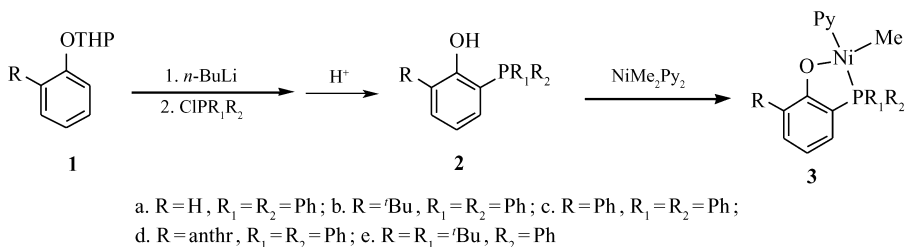
(6-*t*-Bu-2-PPh<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>O) Ni (Me) (Py) (**3b**): Complex **3b** with *tert*-butyl group at the ortho position of its phenoxy moiety is a kind of yellowish brown solid and has a yield of 93%.  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ),  $\delta$ : 7.91 (ddd,  $J = 10.8, 7.6, 1.9$  Hz, 4H), 7.38 (dd,  $J = 7.2, 0.7$  Hz, 1H), 7.18 ~ 7.05 (m, 12H), 6.60 (td,  $J = 7.4, 2.1$  Hz, 1H), 1.58 (s, 9H, *t*-Bu), -0.32 (d,  $J = 4.9$  Hz, 3H, Ni-CH<sub>3</sub>).  $^{13}\text{C}$  NMR (101 MHz,  $\text{C}_6\text{D}_6$ ),  $\delta$ : 175.8 (d,  $J = 20.6$  Hz), 138.8 (d,  $J = 8.8$  Hz), 133.9, 133.7 (d,  $J = 10.6$  Hz), 133.4, 130.4, 130.1 (d,  $J = 2.2$  Hz), 129.9 (d,  $J = 1.0$  Hz), 129.3, 128.7 (d,  $J = 10.2$  Hz), 119.9 (d,  $J = 51.3$  Hz), 114.2 (d,  $J = 7.7$  Hz), 35.3, 29.8, -13.21 (d,  $J = 36.7$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 31.55. Anal. calcd. for  $\text{C}_{28}\text{H}_{30}\text{NNiOP}$ : C 69.17, H 6.22, N 2.88. Found: C 69.12, H 6.18, N 2.92.

(6-Ph-2-PPh<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>O) Ni (Me) (Py) (**3c**): Complex **3c** with phenyl group at the ortho position of its phenoxy moiety is a kind of dark brown solid and has a yield of 90%.  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ),  $\delta$ : 7.92 (m, 8H), 7.51 (m, 3H), 7.24 ~ 7.08 (m, 9H), 6.60 (m, 3H), -0.33 (br, 3H, Ni-CH<sub>3</sub>).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 174.32 (d,  $J = 19.7$  Hz), 133.7, 133.0, 131.9, 130.2, 129.9, 128.9, 127.7, 126.6, 126.2, 125.6, 121.6, 121.1, 114.9, -13.34 (d,  $J = 37.1$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 30.98. Anal. calcd. for  $\text{C}_{30}\text{H}_{26}\text{NNiOP}$ : C 71.18, H 5.18, N 2.77. Found: C 71.10, H 5.20, N 2.79.

(6-C<sub>14</sub>H<sub>9</sub>-2-PPh<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>O) Ni (Me) (Py) (**3d**): Complex **3d** with anthryl group at the ortho position of its phenoxy moiety is a kind of yellowish brown solid and has a yield of 94%.  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ),  $\delta$ : 8.30 (s, 1H), 8.27 (d,  $J = 3.2$  Hz, 2H), 8.04 ~ 7.97 (m, 6H), 7.88 (d,  $J = 8.4$  Hz, 2H), 7.42 (d,  $J = 7.5$  Hz, 2H), 7.38 ~ 7.36 (m, 1H), 7.25 ~ 7.20 (m, 2H), 7.13 ~ 7.10 (m, 7H), 6.72 (td,  $J = 7.4, 1.8$  Hz, 1H), 6.44 (t,  $J = 7.4$  Hz, 1H), 6.02 (dd,  $J = 13.1, 7.1$  Hz, 2H), -0.42 (d,  $J = 4.8$  Hz, 3H, Ni-CH<sub>3</sub>).

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 30.35. Anal. calcd. for  $\text{C}_{38}\text{H}_{30}\text{NNiOP}$ : C 75.28, H 4.99, N 2.31. Found: C 75.21, H 4.93, N 2.40.

[6- $t$ -Bu-2-( $t$ -Bu)(Ph)P- $\text{C}_6\text{H}_3\text{O}$ ]Ni(Me)(Py)(**3e**): Complex **3e** is a kind of yellowish brown solid and has a yield of 91%.  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ),  $\delta$ : 7.96 (br, 2H), 7.36 (m, 2H), 7.15 ~ 7.08 (m, 7H), 6.57 (m, 2H), 1.54 ~ 1.50 (m, 18H), -0.49 (br, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{C}_6\text{D}_6$ ),  $\delta$ : 175.83 (d,  $J$  = 18.6 Hz), 138.47 (d,  $J$  = 8.1 Hz), 133.58 (d,  $J$  = 8.5 Hz), 132.65 (d,  $J$  = 40.4 Hz), 130.88, 129.46, 128.5, 119.05 (d,  $J$  = 47.0 Hz), 113.12 (d,  $J$  = 6.9 Hz), 35.11, 34.52 (d,  $J$  = 25.5 Hz), 29.67, 28.64 (d,  $J$  = 3.8 Hz), -14.35 (d,  $J$  = 35.0 Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 47.75. Anal. calcd. for  $\text{C}_{36}\text{H}_{38}\text{NNiO}_3\text{P}$ : C 69.48, H 6.15, N 2.25. Found: C 69.44, H 6.10, N 2.20.



Scheme 1 Synthesis of phosphinophenolate ligands and neutral nickel catalysts

### 1.3 Ethylene Homo- and Copolymerization

A 200 mL autoclave was heated under vacuum up to 140  $^{\circ}\text{C}$  in period of 5 h and filled with nitrogen to keep a positive pressure at desired reaction temperature. The reactor was filled with toluene under vacuum, and then the stirring motor was engaged to facilitate heat transfer. For ethylene homopolymerization, a toluene solution of the catalyst was injected to the reactor, and ethylene was fed continuously, which was manually adjusted to maintain a desired constant pressure. For the copolymerization of ethylene with norbornene or their polar derivatives, the toluene was pre-saturated with ethylene before catalyst solution and the comonomer was added. Temperature control was conducted by internal cooling water coils. After the prescribed reaction time, the stirring motor was stopped, the reactor was vented. The solid polymer was obtained by filtration after precipitation from ethanol, washed with ethanol and acetone, dried at 60  $^{\circ}\text{C}$  under vacuum to constant mass.

## 2 Results and Discussion

As we all know, the substituents at the ortho position of phenoxy group of the salicylaldiminato neutral nickel catalysts are of great importance for catalyzing ethylene polymerization and the molecular mass of the resultant polymer. Bulky groups in this position are beneficial for high catalytic activity and high molecular mass of the polymer, while the analogue without substituent is inactive towards ethylene polymerization as single component catalyst. What are the relationships, as for phosphinophenolate neutral nickel catalysts, between the catalytic performance and the substituents in the C3 position? To answer this question is very important to the development of novel efficient olefin polymerization catalysts. Therefore, we designed phosphinophenolate neutral nickel catalysts with H (**3a**), *tert*-butyl (**3b**), phenyl (**3c**) and anthryl (**3d**) groups at the ortho position of the phenoxy moiety of the ligands, and explored their catalytic behaviors towards ethylene polymerization. Reaction conditions and representative results were summarized in Table 1. As a single component catalyst, catalyst **3a** showed only a lower activity, which was improved from 40 kg PE/(mol(Ni)·h) to 170 kg PE/(mol(Ni)·h) as the reaction temperature was elevated from 70  $^{\circ}\text{C}$  to 90  $^{\circ}\text{C}$  (Table 1, entries 1 ~ 2). This indicates that catalyst **3a** is efficiently initiated in the more harsh conditions, although it is stabilized by liable pyridine spectator ligand. By introducing a *tert*-butyl group into the C3 position of the ligand, catalyst **3b** showed higher activity of up to 2510 kg PE/(mol(Ni)·h) (Table 1, entry 4). Catalyst **3c**

bearing phenyl group in the C3 position exhibited an activity of 4460 kg PE/(mol(Ni)·h) (Table 1, entry 6) under optimal conditions, which was almost 20 times higher than that of catalyst **3a**. Further increasing steric hindrance( anthryl) to form catalyst **3d** did not lead to higher catalytic activity( Table 1, entries 8 ~ 11). This indicates that the steric hindrance of phenyl group can enough inhibit dissociation of pyridine ligand. In general, minor differences of catalytic activity would be observed when the ortho-phenoxy substituent is *tert*-butyl, phenyl or anthryl group respectively, which all presented a striking difference relative to salicylaldiminato neutral nickel catalysts.

**Table 1** Ethylene polymerization data using phosphinophenolate neutral nickel catalysts <sup>a</sup>

Entry	<i>n</i> (Cat)/μmol	Temperature/℃	<i>p</i> /MPa	Time/min	Yield/g	Activity <sup>b</sup>	<i>M</i> <sub>w</sub> <sup>c</sup> /(kg·mol <sup>-1</sup> )	PDI <sup>c</sup>	<i>t</i> <sub>m</sub> <sup>d</sup> /℃
1	<b>3a</b> (24)	70	30	20	0.32	40.0	5.30	2.0	128
2	<b>3a</b> (32)	87	30	20	1.83	170	4.60	2.2	127
3	<b>3b</b> (30)	70	30	15	9.7	1 300	4.60	3.3	126
4	<b>3b</b> (30)	80	10	20	24.9	2 510	6.30	2.3	128
5	<b>3c</b> (27)	70	30	20	0.51	56.0	11.0	2.3	132
6	<b>3c</b> (31)	80	30	20	45.4	4 460	7.90	2.3	129
7	<b>3c</b> (30)	90	10	20	10.7	1070	9.00	2.2	130
8	<b>3d</b> (23)	70	16	20	26.2	3 450	6.80	2.7	127
9	<b>3d</b> (11)	70	16	20	4.05	1 120	9.40	2.1	131
10	<b>3d</b> (29)	58	16	20	0.72	75.0	13.60	2.2	130
11	<b>3d</b> (13)	70	30	20	5.26	12.0	8.70	2.1	131
12	<b>3e</b> (29)	60	30	20	12.62	1 320	2.20	2.4	121
13	<b>3e</b> (28)	86	30	20	35.03	3 820	2.20	2.5	120
14	<b>3e</b> (29)	86	10	20	25.13	2 640	3.00	2.7	121
15	<b>3e</b> (30)	25	25	60	—	—	—	—	—
16	<b>3e</b> (31)	40	25	60	4.1	132	7.90	2.2	129
17	<b>3e</b> (27)	40	10	60	0.79	29.0	8.40	2.2	128
18	<b>3e</b> (29)	40	10	20	0.41	43.0	8.40	2.1	129

*a.* Polymerization conditions; 100 mL toluene, no cocatalyst was used; *b.* catalytic activity in the unit of kg PE/(mol(Ni)·h); *c.* mass-average molecular mass determined by high temperature GPC using polystyrene standard; *d.* melting temperature determined by DSC.

With respect to the polymer molecular mass, the differences among phosphinophenolate neutral nickel catalysts are not so obvious as the case of salicylaldiminato catalysts, while some clues can be obtained by carefully examining the catalytic results. Low molecular mass (< 10 kg/mol) polyethylenes were obtained using the catalyst without substituent(**3a**) or with alkyl substituent(**3b**) in the ortho position of phenoxy group (Table 1, entries 1 ~ 4), while higher molecular mass polymers were produced by catalyst **3c** and **3d** bearing aryl substituent in the C3 position. The relatively high *T<sub>m</sub>* value (> 120 ℃) of the low molecular mass PE indicated its substantially linear structure, which was confirmed by the <sup>13</sup>C NMR spectrum of the representative polymer sample( Fig. 1).

Previous studies on SHOP catalysts showed that substituents at the phosphorous atom would greatly influence the catalytic performance. The catalysts with alkyl groups, *e.g.* cyclohexyl groups, at the phosphorous atom can improve the molecular mass of

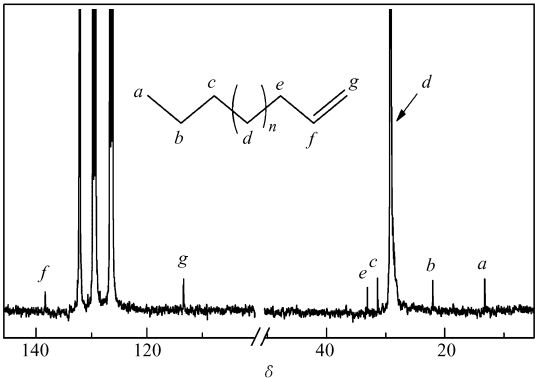


Fig. 1 <sup>13</sup>C NMR spectrum of the PE produced by catalyst **3e**(Table 1, entry 16)

the resultant polymer. Thus, we also did some researches on this subject, which showed that phenyl groups at the phosphorous atom could lead to some unique catalytic properties of the catalyst. So, we applied to substitute an *tert*-butyl group one of the phenyl groups at the phosphorous atom designed and synthesized catalyst **3e**, which enhance the molecular mass of the polymer. However, using catalyst **3e** to catalyze ethylene polymerization under temperatures higher than 60 °C, the molecular mass of the resultant polymer is lower than 3.0 kg/mol (Table 1, entries 12 ~ 14). Noticeably, catalyst **3e** was more readily initiated, compared with catalysts **3a** ~ **3d** with diphenylphosphino moieties. Under 40 °C, catalyst **3e** showed moderate activity (Table 1, entries 16 ~ 18), while the bulky catalyst **3d** bearing diphenylphosphino moiety was not active under such conditions. Since lower temperature would inhibit the  $\beta$ -H elimination reaction and the rate of chain transfer to monomers to some extent, the molecular mass of the resultant polymer was promoted from 3.0 kg/mol to 8.0 kg/mol.

We investigate the catalytic ability of catalyst **3c** and **3e** to the copolymerization of ethylene with other monomers. The representative results for the copolymerization of ethylene with norbornene (NB) and its derivative (NB<sub>OCOMe</sub>) were summarized in Table 2. The results indicate that the introduction of norborne as comonomer accelerates the polymerization reaction. For example, the activity of catalyst **3c** increased with the addition of norbornene (Table 2, entries 4 ~ 5). Catalyst **3e** was even able to copolymerize ethylene with norbornene under 40 °C, while the homopolymerization of ethylene could not proceed under the same conditions, this means that the addition of norbornene promoted the formation of catalytic active sites. The molar incorporations of norbornene comonomer were similar, ca. 10% (Fig. 2) for the two catalysts (Table 2, entries 1, 5). As catalyst **3c** could produce the E/NB copolymer with  $M_w$  of about 13.4 kg/mol it was a better catalyst for enhancing the molecular mass of the resultant copolymer. It is noteworthy that the introduction of norbornene which was considered to inhibit  $\beta$ -H elimination reactions did not significantly increase the molecular mass of the copolymer, indicating that the major chain transfer did not originate from  $\beta$ -H elimination. Since no cocatalysts like aluminium compounds were used in the copolymerization, we reckoned that chain transfer to monomers was the main chain transfer pattern.

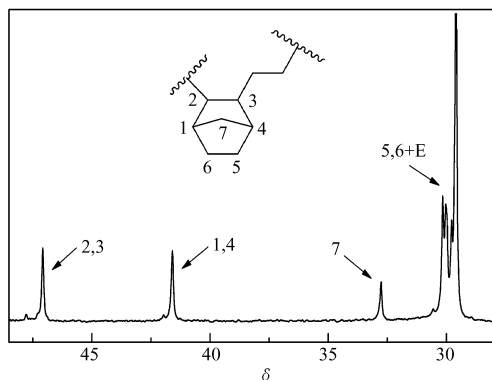


Fig. 2 Representative  $^{13}\text{C}$  NMR spectrum of the E/NB copolymer (Table 2, entry 1)

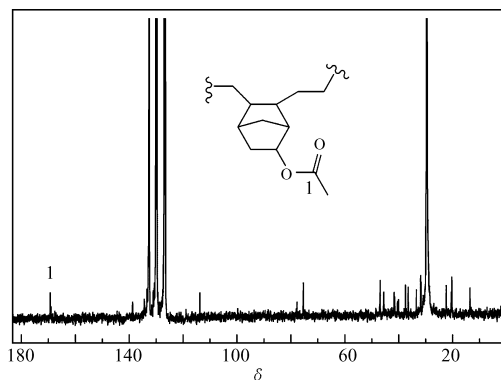


Fig. 3  $^{13}\text{C}$  NMR spectrum of the E/NB<sub>OCOMe</sub> copolymer (Table 2, entry 7)

The data listed in Table 2 also indicate that catalysts **3c** and **3e** were tolerant towards polar groups, and still exhibited moderate activity in the presence of 1000 equiv of polar comonomer NB<sub>OCOMe</sub>. Obvious resonances attributed to carbonyl groups can be observed from the  $^{13}\text{C}$  NMR spectrum of the copolymer (Fig. 3). Due to the monomer was low polar, it was difficult to calculate the accurate molar incorporation values, which were finally obtained from  $^1\text{H}$  NMR to be 1% ~ 3%.

Table 2 Ethylene/NB and ethylene/NB<sub>OCOMe</sub> copolymerization data using catalysts 3c and 3e<sup>a</sup>

Entry	<i>n</i> (Cat. )/ μmol	Comonomer (equiv)	Temperature/°C	<i>p</i> /MPa	Yield/g	Activity <sup>b</sup>	Incorp. <sup>c</sup> /mol%	<i>M</i> <sub>w</sub> <sup>d</sup> / ( kg·mol <sup>-1</sup> )	PDI <sup>d</sup>
1	3c(29)	NB(1 000)	40	21	2. 25	78. 0	12. 7	13. 4	2. 2
2	3c(29)	NB <sub>OCOMe</sub> (1 000)	85	10	0. 35	12. 0	3. 0	11. 2	2. 1
3	3e(30)	NB(1 000)	40	25	13. 51	455	n. d.	7. 60	2. 1
4	3e(29)	NB(1 000)	40	10	1. 82	62. 0	n. d.	8. 10	1. 9
5	3e(30)	NB(2 000)	40	10	4. 05	135	13. 3	8. 60	1. 9
6	3e(30)	NB <sub>OCOMe</sub> (1 000)	90	10	0. 29	10. 0	2. 0	3. 60	2. 1
7	3e(31)	NB <sub>OCOMe</sub> (500)	40	10	5. 92	194	1. 0	8. 30	2. 1

*a.* Polymerization conditions: 100 mL of toluene, polymerization for 1 h; *b.* activity in the unit of kg/( mol ( Ni ) · h ); *c.* NB molar incorporations calculated by <sup>13</sup>C NMR, NB<sub>OCOMe</sub> molar incorporations calculated by <sup>1</sup>H NMR; *d.* mass-average molecular mass and PDI determined by GPC using polystyrene standard.

3 Conclusions

By modifying the substituents at the ortho position of phenoxy group and at the phosphorous atom of the phosphinophenolate ligands, we have designed and synthesized catalysts **3a** ~ **3e**, and investigated the influence of these variances on the catalytic activity and on the molecular mass of the resultant polymer. Moreover, the activities of these catalysts to copolymerization reaction were also studied. As single component catalysts, the complex without substituent at the C3 position(**3a**) exhibited only low activity towards ethylene polymerization. Introducing *tert*-butyl (**3b**) or phenyl group (**3c**) to this position, the catalytic activity was greatly improved, while no obvious difference was observed by further increasing the steric hindrance. Catalysts bearing aryl substituents at the ortho position of phenoxy (**3c** and **3d**) produced higher molecular mass polymer, and the steric effects of the substituents did not obviously effect on the polymer molecular mass not like the salicylaldiminato neutral nickel catalysts. Replacing one of the phenyl groups at the phosphorous atom with a *tert*-butyl group(catalyst **3e**) only had a little influence on the catalytic activity, while led to more readily initiated catalyst producing lower molecular mass polymer. Phosphinophenolate neutral nickel catalysts are able to copolymerize ethylene with norbornene and its polar derivative NB<sub>OCOMe</sub> to give functionalized polyolefin, showing the great tolerance of phosphinophenolate neutral nickel catalysts towards polar functionalities.

参 考 文 献

[1] Keim W, Kowaldt F H, Goddard R, *et al.* Novel Coordination of ( Benzoylmethylene ) Triphenylphosphorane in a Nickel Oligomerization Catalyst[J]. *Angew Chem Int Ed*, 1978, **17**(6) :466-467.

[2] Johnson L K, Killian C M, Brookhart M. New Pd( II )-Based and Ni( II )-Based Catalysts for Polymerization of Ethylene and α-Olefins[J]. *J Am Chem Soc*, 1995, **117**(23) :6414-6415.

[3] Johnson L K, Mecking S, Brookhart M. Copolymerization of Ethylene and Propylene with Functionalized Vinyl Monomers by Palladium( II ) Catalysts[J]. *J Am Chem Soc*, 1996, **118**(1) :267-268.

[4] Mecking S, Johnson L K, Wang L, *et al.* Mechanistic Studies of the Palladium-Catalyzed Copolymerization of Ethylene and α-Olefins with Methyl Acrylate[J]. *J Am Chem Soc*, 1998, **120**(5) :888-899.

[5] Wang C M, Friedrich S, Younkin T R, *et al.* Neutral Nickel( II )-Based Catalysts for Ethylene Polymerization[J]. *Organometallics*, 1998, **17**(15) :3149-3151.

[6] Younkin T R, Conner E F, Henderson J I, *et al.* Neutral, Single-Component Nickel( II ) Polyolefin Catalysts that Tolerate Heteroatoms[J]. *Science*, 2000, **287**(5452) :460-462.

[7] Heinicke J, Köhler M, Peulecke N, *et al.* The Impact of P Substituents on the Oligomerization of Ethylene with Nickel 2-Di-phenyl and 2-Dicyclohexylphosphinophenolate Phosphine Catalysts[J]. *J Catal*, 2004, **225**(1) :16-23.

[8] Heinicke J, Koesling M, Brüll R, *et al.* Nickel Chelate Complexes of 2-Alkylphenyl-phosphanylphenolates: Synthesis, Structural Investigation and Use in Ethylene Polymerization[J]. *Eur J Inorg Chem*, 2000, (2) :299-305.

[9] Guo C Y, Peulecke N, Basvani K R, *et al.* 2-Phosphinophenolate Nickel Catalysts: Formation of Ethylene Copolymers with Isolated Sec-Alkyl, Aryl, and Functionally Substituted Alkyl Groups[J]. *Macromolecules*, 2010, **43**(3) :1416-1424.

- [10] Guo C Y, Peulecke N, Kindermann M K, *et al.* Copolymerization of Ethylene with Linear  $\alpha$ -Olefins by 2-Phosphinophenolate Nickel Catalysts[J]. *J Polym Sci Part A: Polym Chem*, 2009, **47**(1):258-266.
- [11] Heinicke J, He M Z, Dal A, *et al.* Methyl(2-Phosphanylphenolato) P, O ) Nickel( II ) Complexes: Synthesis, Structure, and Activity as Ethene Oligomerization Catalysts[J]. *Eur J Inorg Chem*, 2000, (3):431-440.
- [12] Heinicke J, Peulecke N, Kindermann M K, *et al.* A Novel Access to Phenylnickel Phosphinophenolate Trimethylphosphine Complexes as Single Component Oligo- or Polymerization Catalysts[J]. *Z Anorg Allg Chem*, 2005, **631**(1):67-73.
- [13] He L P. Investigation of Novel Titanium and Chromium Nonmetallocene Polymerization Catalysts[D]. Changchun: Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 2009.
- [14] Cámpora J, Conejo M D, Mereiter K, *et al.* Synthesis of Dialkyl, Diaryl and Metallacyclic Complexes of Ni and Pd Containing Pyridine,  $\alpha$ -Diimines and Other Nitrogen Ligands Crystal Structures of the Complexes *Cis*-NiR<sub>2</sub>Py<sub>2</sub> (R = Benzyl, Mesityl) [J]. *J Organomet Chem*, 2003, **683**(1):220-239.

## 单组分酚膦中性镍催化乙烯均聚与共聚反应

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**摘 要** 以酚膦化合物为双齿配体, 合成与表征了一系列单组分中性镍烯炔聚合催化剂。研究表明, 酚膦配体结构显著影响中性镍的催化性能, 酚氧邻位无取代基的(2-PPh<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>O) Ni(Me)(Py) (**3a**) 活性较低, 向酚氧邻位引入叔丁基或苯基等位阻基团可大幅度提高(2-PPh<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>(R)O) Ni(Me)(Py) (**3b**~**3d**) 的催化效率, 最高催化活性可达  $4.46 \times 10^6$  g PE/(mol(Ni)·h)。同时, 聚乙烯的分子量也可以通过取代基效应进行适度调控, 使用酚氧邻位带有苯基或蒽基的催化剂(**3c**~**3d**) 可获得较高分子量的聚乙烯。用供电子叔丁基替代二苯膦的一个苯环可提高催化活性中心镍原子的电子云密度, 使辅助配体吡啶更容易离去, 从而可在较低温度下引发乙烯聚合反应。此外, 这类酚膦中性镍催化剂对极性基团具有较强的耐受性, 可催化乙烯与极性 5-降冰片烯-2-乙酸酯的共聚反应。

**关键词** 中性镍催化剂, 乙烯聚合, 极性基团耐受性, 单组分催化剂