Ethylene Polymerization by (α-Diimine)Nickel(II) Complexes Bearing Different Substituents on *para*-Position of Imines Activated with MMAO

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ABSTRACT: A series of (α-diimine)nickel(II) complexes [ArN $=$ C(Nap)C $=$ NAr]NiBr$_2$ (Nap $=$ 1,8-naphthdiyl, Ar $=$ 2,6-Me$_2$C$_6$H$_3$, **3a**; Ar $=$ 2,4,6-Me$_3$C$_6$H$_2$ **3b**; Ar $=$ 2,6-Me$_2$-4-*t*BuC$_6$H$_2$, **3c**; Ar $=$ 2,6-Me$_2$-4-BrC$_6$H$_2$, **3d**; Ar $=$ 2,6-Me$_2$-4-ClC$_6$H$_2$, **3e**; Ar $=$ 2,6-*i*Pr$_2$C$_6$H$_3$, **3f**; Ar $=$ 2,4,6-*i*Pr$_3$C$_6$H$_2$, **3g**; Ar $=$ 2,6-iPr-4-BrC$_6$H$_2$, **3h**) have been synthesized, characterized, and investigated as precatalysts for ethylene polymerization in the presence of modified methylaluminoxane (MMAO). The substituents of α-diimine ligands and their positions located significantly influence catalyst activity and polymer property. It is found that the catalytic activities of the nickel complex/MMAO systems and the microstructure of the polymer obtained are dominated by not only hindering effect of *ortho*-position substituents but also electronical effect of *para*-position substituents. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 700–707, 2008

Key words: Ziegler-Natta polymerization; catalyst; polyolefins

INTRODUCTION

Although early transition metal catalyst currently dominates the industrial process of olefin polymerization, there has been a trend toward the development of the catalysts containing late transition metal elements because of the potential to yield polymers with different microstructures and more tolerant of functionalized monomers.[1–32] An important advance in late transition metal catalyst for olefin polymerization was described by Brookhart and coworkers, who showed that Ni(II) and Pd(II) complexes incorporating bulky α-diimine ligands are capable of polymerizing ethylene to high molecular weight branched polyethylenes.[5–9]

As well known, two factors can affect catalyst activity and the behavior of olefin polymerization. One is steric hindrance, and the other is electronic effect of ligands. The effect of the steric hindrance of *ortho*-position substituent on the catalytic activity of (α-diimine)nickel(II) complexes and the property of resultant polymers has been studied in detail by Brookhart and coworkers.[9] However, there are only a few studies on the correlation between the catalytic activities of the (α-diimine)nickel(II) complexes and the electronic effects of ligands.[31–34]

We are interested in the effect of electronic effect of ligands on the behavior of olefin polymerization. Previously, we have reported that incorporating different substituents into *ortho*- or *para*-position of the two imine groups of pyridinebisimine ligands could change the activity of iron or cobalt catalyst and the property of the polyethylene obtained.[35,36] Here, we wish to report the synthesis and characterization of a series of (α-diimine)nickel(II) complexes, in which the *para*-positions on the imine groups were replaced by substituents with different electronical effects (see Scheme 1). We also demonstrate that not only the hindering effect but also electronic effect significantly influences the behavior of the (α-diimine)nickel(II) complexes towards ethylene polymerization.

EXPERIMENTAL

General procedures and materials

All manipulations of water and/or moisture sensitive compounds were performed by means of standard high vacuum Schlenk and cannula techniques under a N$_2$ atmosphere. Toluene was refluxed and distilled from sodium/benzophenone under dry nitrogen. Modified methylaluminoxane (MMAO) (7% aluminum in heptane solution) was purchased from Akzo
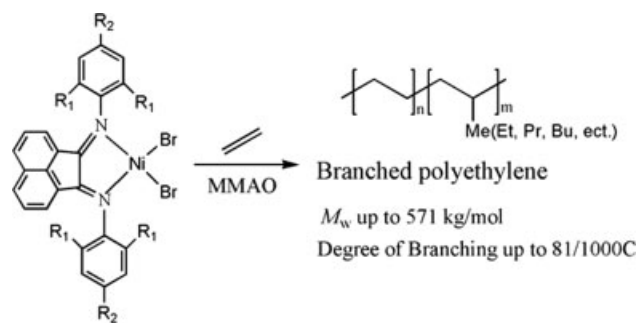
Scheme 1

Nobel Chemical. All other chemicals for ligand synthesis were purchased from Aldrich Chemical or Acros Organics and used without further purification. The α-diimine complexes **3a-h** were prepared according to the procedure reported by Brookhart.[5]

The NMR data of the polymers obtained were obtained on a Varian Unity-400 MHz spectrometer at 110°C with o-$C_6D_4Cl_2$ as a solvent. The NMR data of the ligands used were obtained on a Bruker 300 MHz spectrometer at ambient temperature, $CDCl_3$ as a solvent. Mass spectra were obtained using Electron Impact Mass Spectroscopy (EI-MS). Single-crystal X-ray diffraction data were collected by Siemens P4 X-ray crystallography. The data of Elemental analyses were obtained using Carlo Erba 1106 and ST02 apparatus. The FTIR spectra of the ligands and complexes used were recorded on a Bio-Rad FTS-135 spectrophotometer. The DSC measurements were performed on a Perkin–Elmer Pyris 1 Differential Scanning Calorimeter at a heating/cooling rate of 10°C/min. The molecular weights and the molecular weight distributions of the polymer samples were determined at 150°C with a PL-GPC 220 type high temperature chromatograph equipped with three PLgel 10 μm Mixed-B LS type columns. 1,2,4-Trichlorobenzene (TCB) was employed as the solvent at a flow rate of 1.0 mL/min. The calibration was made by polystyrene standard EasiCal PS-1 (PL).

Synthesis of aniline derivatives

2,6-Dimethyl-4-tert-butylaniline (1c)

A mixture of fuming HNO_3 (16 g, 0.25 mol), CH_3COOH (10 g), Ac_2O (10 g) was dropped into a solution of 5-$tert$-butyl-m-xylene (26 g, 0.16 mol) and Ac_2O (30 g) at 0°C within 2 h. The precipitate was filtered and recrystallized in methanol, and then dried to afford 2,6-dimethyl-4-$tert$-butyl nitrobenzene as yellow crystals 28 g (84%). ^{1}H-NMR ($CDCl_3$): δ7.13 (s, 2H, Ar—H), 2.34 (s, 6H, ArMe), 1.33 (s, 9H, Ar—tBu).

A 500-mL Schlenk flask containing 200 mL of degassed ethanol was charged with above product (10.4 g, 0.05 mol), 5% Pd/C (12 g), and 150 mL $NH_2NH_2·H_2O$. The reaction mixture was refluxed

for 18 h. After the reaction mixture was cooled to room temperature, the Pd-C catalyst was filtrated and the solvent was removed. The residual was washed with 20% aqueous NaOH, extracted with diethyl ether (100 mL), and dried over Na_2SO_4. The diethyl ether was vaporized to give **1c** as a colorless liquid (8.11 g, 91.6%). ^{1}H-NMR ($CDCl_3$): δ7.06 (s, 2H, Ar—H), 3.50 (s, 2H, H_2N—), 2.28 (s, 6H, ArMe), 1.37 (s, 9H, Ar—tBu). Anal. Calc. for $C_{12}H_{19}N$: C, 81.30; H, 10.80; N, 7.90. Found: C, 81.39; H, 10.76; N, 7.87.

2,6-Dimethyl-4-bromoaniline (1d)

Br_2 (15 g, 0.094 mol) was dropped into the mixture of 2,6-dimethylaniline (12 g, 0.102 mol) and iron powder (0.056 g, 1 mmol) within 2 h. The precipitate was separated by filtration, recrystallized in ethanol. The white solid was washed with 20% aqueous NaOH, extracted with diethyl ether (100 mL), and dried over Na_2SO_4. The solvent was removed to give **1d** as a white powder (12.2 g, 61%). ^{1}H-NMR ($CDCl_3$): δ7.09 (s, 2H, Ar—H), 3.60 (s, 2H, H_2N—), 2.15 (s, 6H, ArMe). Anal. Calc. for $C_8H_{10}BrN$: C, 48.02; H, 5.04; N, 7.00. Found: C, 48.14; H, 4.99; N, 7.03.

2,4,6-Triisopropylaniline (1g)

Analogous to the synthesis of compound **1c**, compound **1g** as a colorless liquid was obtained in 67% yield. ^{1}H-NMR ($CDCl_3$): δ6.99 (s, 2H, Ar—H), 3.60 (s, 2H, H_2N—), 2.95 (m, 3H, CHMe_2), 1.36 (d, 18H, CHMe_2). Anal. Calc. for $C_{15}H_{25}N$: C, 82.13; H, 11.49; N, 6.39. Found: C, 82.03; H, 11.52; N, 6.42.

4-Bromo-2,6-diisopropylaniline (1h)

Analogous to the synthesis of compound **1d**, compound **1h** as a colorless powder was obtained in 41% yield. ^{1}H-NMR ($CDCl_3$): δ 7.14 (s, 2H, Ar—H), 3.52 (s, 2H, NH_2), 2.91 (m, 2H, CHMe_2), 1.27 (d, 12H, CH—CH_3). Anal. Calc. for $C_{12}H_{18}BrN$: C, 56.26; H, 7.08; N, 5.47. Found: C, 56.20; H, 7.04; N, 5.44.

Synthesis of ligands

[N,N-2,6-Dimethyl-benzene-2,3-(1,8-naphthyl)-1,4-diazabutadiene] (2a)

A solution of acenaphthenequinone (0.73 g, 4 mmol), **1a** (1.09 g, 9 mmol), and p-toluenesulfonic acid (0.02 g) in toluene (100 mL) was refluxed for 3 days, with azeotropic removal of water using a Dean-Stark trap. Upon cooling to room temperature, the product was precipitated from ethanol. After filtration, the solid was washed with cold ethanol and dried in a vacuum oven (50°C) over night. The ligand **2a** as a yellow–orange powder was obtained in 82% yield. The

other ligands **2b–h** were prepared by the same procedure with similar yields. ^{1}H-NMR (CDCl$_3$): δ7.90 (d, 2H, Nap—*H*), 7.40 (t, 2H, Nap—*H*), 7.08 (m, 6H, Ar—*H*), 6.70 (d, 2H, Nap—*H*), 2.17 (s, 12H, Ar—*Me*). Anal. Calc. for C$_{28}$H$_{24}$N$_2$: C, 86.56; H, 6.23; N, 7.21. Found: C, 86.78; H, 6.19; N, 7.18.

[N,N-2,4,6-Trimethyl-benzene-2, 3-(1,8-naphthyl)-1,4-diazabutadiene] (2b)

Yield: 84%. ^{1}H-NMR (CDCl$_3$): δ7.89 (d, 2H, Nap—*H*), 7.40 (t, 2H, Nap—*H*), 6.98 (s, 4H, Ar—*H*), 6.69 (d, 2H, Nap—*H*), 2.18 (m, 18H, Ar—*Me*). Anal. Calc. for C$_{30}$H$_{28}$N$_2$: C, 86.50; H, 6.78; N, 6.73. Found: C, 86.64; H, 6.76; N, 6.69.

[(N,N-2,6-Dimethyl-4-butyl-benzene)-2, 3-(1,8-naphthyl)-1,4-diazabutadiene] (2c)

Yield: 78%. ^{1}HNMR (CDCl$_3$): δ7.88 (d, 2H, Nap—*H*), 7.38 (t, 2H, Nap—*H*), 7.15 (s, 4H, Ar—*H*), 6.67 (d, 2H, Nap—*H*), 2.15 (s, 12H, Ar—*Me*), 1.40 (s, 18H, C—*Me*$_3$). Anal. Calc. for C$_{36}$H$_{40}$N$_2$: C, 86.35; H, 8.05; N, 5.59. Found: C, 86.21; H, 8.02; N, 5.55.

[(N,N-2,6-Dimethyl-4-bromobenzene)-2, 3-(1,8-naphthyl)-1,4-diazabutadiene] (2d)

Yield: 63%. ^{1}HNMR (CDCl$_3$): δ7.96 (d, 2H, Nap—*H*), 7.46 (t, 2H, Nap—*H*), 7.33 (s, 4H, Ar—*H*), 6.84 (d, 2H, Nap—*H*), 2.11 (s, 12H, Ar—*Me*). Anal. Calc. for C$_{28}$H$_{22}$Br$_2$N$_2$: C, 61.56; H, 4.06; N, 5.13. Found: C, 61.41; H, 4.10; N, 5.09.

[(N,N-2,6-Dimethyl-4-Cl-benzene)-2, 3-(1,8-naphthyl)-1,4-diazabutadiene] (2e)

Yield: 51%. ^{1}HNMR (CDCl$_3$): δ8.01 (d, 2H, Nap—*H*), 7.54 (t, 2H, Nap—*H*), 7.35 (s, 4H, Ar—*H*), 6.89 (d, 2H, Nap—*H*), 2.15 (s, 12H, Ar—*Me*). Anal. Calc. for C$_{28}$H$_{22}$Cl$_2$N$_2$: C, 73.53; H, 4.85; N, 6.12. Found: C, 73.41; H, 4.89; N, 6.09.

[(N,N-2,6-Diisopropyl-benzene)-2, 3-(1,8-naphthyl)-1,4-diazabutadiene] (2f)

Yield: 85%. ^{1}HNMR (CDCl$_3$): δ7.87 (d, 2H, Nap—*H*), 7.38 (t, 2H, Nap—*H*), 7.26 (m, 6H, Ar—*H*), 6.63 (d, 2H, Nap—*H*), 3.03 (m, 4H, C*H*Me$_2$), 1.20 (m, 24H, CH*Me*$_2$). Anal. Calc. for C$_{36}$H$_{40}$N$_2$: C, 86.35; H, 8.05; N, 5.59. Found: C, 86.19; H, 8.07; N, 5.62.

[(N,N-2,4,6-Triisopropylbenzene)-2, 3-(1,8-naphthyl)-1,4-diazabutadiene] (2g)

Yield: 84%. ^{1}HNMR (CDCl$_3$): δ7.85 (d, 2H, Nap—*H*), 7.35 (t, 2H, Nap—*H*), 7.10 (s, 4H, Ar—*H*), 6.56 (d, 2H, Nap—*H*), 3.01 (m, 6H, C*H*Me$_2$), 1.21 (m, 36H,

CH*Me*$_2$). Anal. Calc. for C$_{42}$H$_{52}$N$_2$: C, 86.25; H, 8.96; N, 4.79. Found: C, 86.33; H, 8.92; N, 4.75.

[(N,N-2,6-Diisopropyl-4-bromobenzene)-2, 3-(1,8-naphthyl)-1,4-diazabutadiene] (2h)

Yield: 54%. ^{1}HNMR (CDCl$_3$): δ7.93 (d, 2H, Nap—*H*), 7.44 (t, 2H, Nap—*H*), 7.39 (s, 4H, Ar—*H*), 6.78 (d, 2H, Nap—*H*), 2.96 (m, 4H, C*H*Me$_2$), 1.11 (d, 24H, CH*Me*$_2$). Anal. Calc. for C$_{36}$H$_{38}$Br$_2$N$_2$: C, 65.66; H, 5.82; N, 4.25. Found: C, 65.41; H, 5.77; N, 4.22.

Synthesis of α-diimine complexes (3a–h)

[(N,N-2,6-Dimethylbenzene)-2,3-(1,8-naphthyl)-1, 4-diazabutadiene] dibromonickel (3a)

(DME)NiBr$_2$ (111 mg, 0.36 mmol) and **2a** (0.16 g, 0.4 mmol) was combined in a Schlenk flask under an argon atmosphere. CH$_2$Cl$_2$ (20 mL) was added, and the reaction mixture stirred at room temperature for 18 h. The supernatant liquid was removed, and the product washed with 2 × 10 mL of Et$_2$O and dried *in vacuo*. The product was isolated as a red–brown powder in 75% yield. EI-MS (70 ev): *m/z* = 604 [M$^+$]. Anal. Calcd for C$_{28}$H$_{24}$Br$_2$NiN$_2$: C, 55.40; H, 3.99; N, 4.62. Found: C, 55.32; H, 3.96; N, 4.60. The other complexes **3b–h** were prepared via the same procedure.

[(N,N-2,4,6-Trimethylbenzene)-2,3-(1,8-naphthyl)-1, 4-diazabutadiene] dibromonickel (3b)

Yield: 87.5%. EI-MS (70 ev): *m/z* = 632 [M$^+$]. Anal. Calcd for C$_{30}$H$_{28}$Br$_2$NiN$_2$: C, 56.74; H, 4.44; N, 4.41. Found: C, 56.51; H, 4.40; N, 4.43.

[(N,N-2,6-Dimethyl-4-Butyl-benzene)-2,3-(1, 8-naphthyl)-1,4-diazabutadiene] dibromonickel (3c)

Yield: 70.1%. EI-MS (70 ev): *m/z* = 716 [M$^+$]. Anal. Calcd for C$_{36}$H$_{40}$Br$_2$NiN$_2$: C, 60.12; H, 5.61; N, 3.89. Found: C, 60.17; H, 5.65; N, 3.87.

[(N,N-2,6-Dimethyl-4-bromobenzene)-2,3-(1, 8-naphthyl)-1,4-diazabutadiene] dibromonickel (3d)

Yield: 62.7%. EI-MS (70 ev): *m/z* = 760 [M$^+$]. Anal. Calcd for C$_{28}$H$_{22}$Br$_4$NiN$_2$: C, 43.97; H, 2.90; N, 3.66. Found: C, 43.71; H, 2.87; N, 3.69.

[(N,N-2,6-Dimethyl-4-Cl-benzene)-2,3-(1,8-naphthyl)-1,4-diazabutadiene] dibromonickel (3e)

Yield: 58.9%. EI-MS (70 ev): *m/z* = 672 [M$^+$]. Anal. Calcd for C$_{28}$H$_{22}$Br$_2$Cl$_2$NiN$_2$: C, 49.76; H, 3.28; N, 4.14. Found: C, 49.68; H, 3.27; N, 4.17.

a: R_1=Me, R_2=H
b: R_1=R_2=Me
c: R_1=Me, R_2=t-Bu
d: R_1=Me, R_2=Br
e: R_1=Me, R_2=Cl
f: R_1=iPr, R_2=H
g: R_1=R_2=iPr
h: R_1=iPr, R_2=Br

Scheme 2

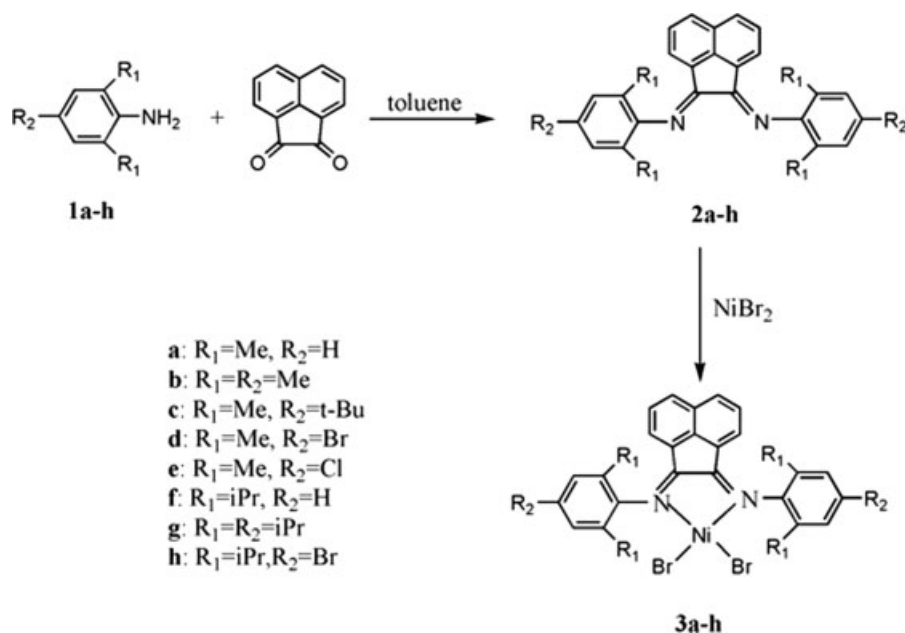[(N,N-2,6-Diisopropyl-benzene)-2,3-(1,8-naphthyl)-1,4-diazabutadiene] dibromonickel (3f)

Yield: 70.7%. EI-MS (70 ev): $m/z = 716$ [M$^+$]. Anal. Calcd for $C_{36}H_{40}Br_2NiN_2$: C, 60.12; H, 5.61; N, 3.89. Found: C, 60.28; H, 5.58; N, 3.91.

[(N,N-2,4,6-Triisopropyl-benzene)-2,3-(1,8-naphthyl)-1,4-diazabutadiene] dibromonickel (3g)

Yield: 84%. EI-MS (70 ev): $m/z = 800$ [M$^+$]. Anal. Calcd for $C_{42}H_{52}Br_2NiN_2$: C, 62.79; H, 6.52; N, 3.49. Found: C, 62.33; H, 6.49; N, 3.47.

[(N,N-2,6-Diisopropyl-4-bromobenzene)-2,3-(1,8-naphthyl)-1,4-diazabutadiene] dibromonickel (3h)

Yield: 86.5%. EI-MS (70 ev): $m/z = 872$ [M$^+$]. Anal. Calcd for $C_{36}H_{38}Br_4NiN_2$: C, 49.30; H, 4.37; N, 3.19. Found: C, 50.12; H, 4.34; N, 3.16.

Polymerization procedure

The polymerization was carried out in a 200-mL Schlenk flask equipped with a magnetic stirrer. The flask was repeatedly evacuated and refilled with nitrogen and finally filled with ethylene gas (ambient pressure) from an Schlenk line. MMAO and toluene were added via a gastight syringe. The catalyst was dissolved in toluene under a dry nitrogen atmosphere. The solution was transferred into the Schlenk flask to initiate the polymerization. After 10 min at given temperature, all the polymerization experiments were stopped by a large excess of methanol containing a small amount of hydrochloric acid. The coagu-

lated polymer was washed with methanol, filtered, and dried under vacuum.

High pressure polymerization experiments were carried out in a mechanically stirred 200 mL stainless steel reactor, equipped with an electric heating mantle controlled by a thermocouple dipping into the reaction mixture. The reactor was baked under nitrogen flow for 24 h at 150°C and subsequently cooled to the temperature of polymerization. The reagents were transferred via a gastight syringe to the evacuated reactor. Ethylene was introduced into the reactor, and the reactor pressure was maintained at 10 atm throughout the polymerization run by continuously feeding the ethylene gas. After proceeding for 10 min, the polymerization was stopped by turning the ethylene off and relieving the pressure. The reaction mixture was poured into a solution of HCl/ethanol (10 vol %) to precipitate the polymer. The polymer was isolated by filtration, washed with ethanol, and dried under vacuum.

RESULTS AND DISCUSSION

Synthesis and characterization of nickel complexes

A general synthetic route for these nickel(II) complexes is shown in Scheme 2. Ligands **2a–h** were prepared in high yields by the condensation reaction of two equivalents of appropriate aniline derivates **1a–h** with one equivalent of acenaphthenequinone. (α-Diimine)nickel(II) complexes **3a–h** were synthesized in good yields by treating (DME)NiBr$_2$ with corresponding Schiff-base ligands **2a–h** in dichloromethane (CH$_2$Cl$_2$) at room temperature. All the nickel complexes **3a–h** are red–brown powders.
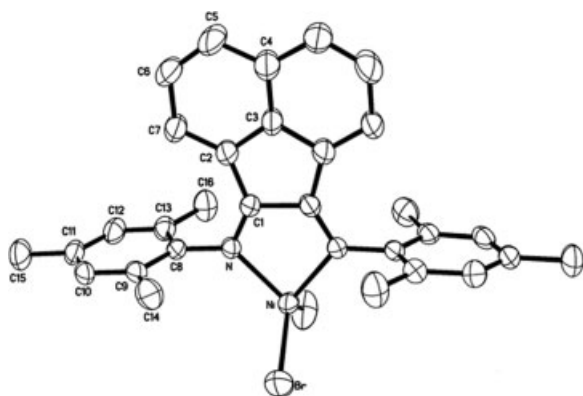
Figure 1 Molecular structure of the nickel complex **3b**. Thermal ellipsoids at the 30% level are shown. Hydrogen atoms are omitted for clarity. Ni-N, 2.027 (3); Ni-Br(1), 2.3205 (5); C(1)-N, 1.268 (4); C(8)-N, 1.452 (4); N-NiN, 82.34 (15); N-Ni-Br(1), 115.96 (8); C(1)-N-Ni, 111.4 (2); C(8)-N-Ni, 129.7 (2); C(2)-C(1)-N, 135.2 (3).

Crystals **3b** and **3d**, grown from a CH_2Cl_2 solution layered by pentane, were subjected to single-crystal X-ray diffraction study. The molecular structures of nickel complexes **3b** and **3d** are shown in Figures 1 and 2, respectively. The data collection and refinement data of the analysis are summarized in Table I. In both cases, the nickel complexes display C_{2v} molecular symmetry. In both structures, the aryl rings of the α-diimine lie nearly perpendicular to the plane formed by the nickel and coordinated nitrogen atoms. However, some differences between the two molecules are still observed. The bond length of Ni—N (2.026(3) Å) in complex **3d**, bearing more electron-withdrawing ligand, is slightly shorter compared with that (2.027(3) Å) in complex **3b**, while the bond length of Ni—Br (2.3229(5) Å) in complex **3b** is slightly longer compared with that (2.3205(6) Å) in complex **3d**. In addition, the bond angle of N—Ni—N (82.34(15)°) in complex **3b** is somewhat smaller than that (83.19(15)°) in complex **3d**, while the bond angle of N—Ni—Br(1) (115.96(8)°) in complex **3b** is larger compared with that (113.32(8)°) in complex **3d**.

Ethylene polymerization with the nickel complexes 3a–h

On treatment with modified methylaluminoxane (MMAO), all nickel complexes **3a–h** are highly active towards ethylene polymerization. To evaluate the effect of ligand structure on the performance of the nickel precatalysts, we first polymerize ethylene with precatalysts **3a–h** under the atmospheric pressure (1 atm ethylene pressure) at 0 and 30°C. The typical results are summarized in Table II. The data listed in Table II show that catalyst activities and the molecular weights of the polyethylenes obtained decrease with the increase of polymerization temperature, which indicates that there is an increase in the rate of chain transfer at high temperature although further complications with catalyst degradation may also affect molecular weight. In addition, the branching numbers of the polyethylenes obtained increase dramatically, while the melting temperatures (T_m) decrease with the increase of the reaction temperature. For example, the branching numbers of the PEs obtained with precatalyst **3d** increase from 7 per thousand carbons at 0°C (Entry 4 in Table II) to 19 per thousand carbons at 30°C (Entry 12 in Table II).

Interestingly, the variation of the *para*-substituents of α-diimine ligands has a pronounced effect not only on catalyst activity, but also on the molecular weight and branching degree of the resulting polymers. The replacement of the *para*-aryl proton (**3a**) with an electron-donating methyl group (**3b**) causes the decrease of both catalyst activity and the weight-average molecular weight ($\overline{M}_w$) of the polymers obtained (catalyst activity from 3610 to 3300 kg PE/mol$_{Ni}$·h, $\overline{M}_w$ from 386 to 337 kg/mol, 0°C). However, *t*-Bu (**3c**) and electron-withdrawing groups Br (**3d**) and Cl (**3e**) on the *para*-position of the imines increase catalyst activity to 3930, 4110 and 4320 kg PE/mol$_{Ni}$·h, respectively, and $\overline{M}_w$ to 424, 482, and 520 kg/mol, respectively. It is noteworthy that the branching degree of the polymers obtained shows the contrary trend. When an electron-withdrawing substituent is introduced into the *para*-position of the imines in the ligands, the branching degree of the polyethylenes decreases dramatically. For example, when **3d** (Br) is compared with **3a** (H), the branching degree of the polymer decreases from 13 to 7 per thousand carbons.

Precatalysts **3a–e** hold the same substituents on the *ortho*-positions of the imines in the ligands, therefore, the rate of chain transfer for these systems should be
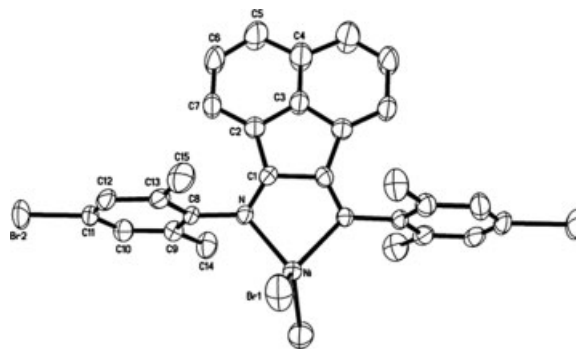
Figure 2 Molecular structure of the nickel complex **3d**. Thermal ellipsoids at the 30% level are shown. Hydrogen atoms are omitted for clarity. Ni-N, 2.026 (3); Ni-Br(1), 2.3229 (6); C(1)-N, 1.275 (4); C(8)-N, 1.434 (4); N-Ni-N, 83.19 (15); N-Ni-Br(1), 113.32 (8); C(1)-N-Ni, 110.7 (2); C(8)-N-Ni, 129.4 (2); C(2)-C(1)-N, 134.6 (3).

TABLE I
The Crystal Data and Structure Refinements of the Complex 3b and 3d

	3b	3d
Empirical formula	$C_{30}H_{28}Br_2N_2Ni$	$C_{28}H_{22}Br_4N_2Ni$
Formula mass	635.07	764.83
Crystal size [mm^3]	$0.31 \times 0.15 \times 0.09$	$0.26 \times 0.18 \times 0.08$
Crystal system	Orthorhombic	Orthorhombic
Space group	Pcca	Pcca
a [Å]	16.7234 (6)	17.2425 (6)
b [Å]	11.3686 (4)	11.2747 (4)
c [Å]	17.7476 (6)	17.6689 (6)
α°	90	90
β°	90	90
γ°	90	90
V [Å^3]	3374.2 (2)	3434.9 (2)
Z	4	4
Density (calcd.) [Mg cm^{-3}]	1.250	1.479
Absorption coefficient [mm^{-1}]	2.960	5.234
$F(000)$	1280	1488
θ range for data collection$^\circ$	2.30 to 26.03	2.36 to 26.02
Reflection collected	17857	18085
Data/restrains/parameters	3304/0/163	3364/0/162
Independent reflections	3304	3364
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0567$, w$R_2 = 0.1655$	$R_1 = 0.0450$, w$R_2 = 0.1323$
R indices (all data)	$R_1 = 0.0680$, w$R_2 = 0.1773$	$R_1 = 0.0567$, w$R_2 = 0.1426$
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Goodness-of-fit on F^2	1.008	1.004
Max. and min. transmission	0.7765 and 0.4605	0.6795 and 0.3431
Largest peak/hole in final diff map (e Å^{-3})	1.642 and –0.927	1.499 and –0.461

the same. The exclusive difference among these precatalysts is the substituents on the *para*-positions of the imines. The Cl substituted catalyst **3e** is more active than the methyl group system **3b** (4110 kg PE/mol$_{Ni}$·h versus 3300 kg PE/mol$_{Ni}$·h). There are two sides which might explain the difference of the catalyst activities and the polymer mass. One is the bulk of the substituents, and the other is the electronic effect of the substituents. The fairly similar sizes of Cl and CH$_3$ groups suggest the electron-withdrawing nature of the Cl group, which results in a more electrophilic nickel center and may increase catalytic activity.

TABLE II
The Results of Polymerization with the Nickel Complexes Under 1 atm of Ethylene[a]

Entry	Preatalyst	Yield (g)	Temp. (°C)	Activity (kg PE/mol$_{Ni}$·h·atm)	T_m[b] (°C)	$\overline{M}_w$[c] (kg/mol)	$\overline{M}_w/\overline{M}_n$[c]	Branches[d] (per 1000C)
1	**3a**	1.20	0	3610	120.7	386	2.90	13
2	**3b**	1.10	0	3300	120.2	337	2.52	15
3	**3c**	1.31	0	3930	121.8	424	3.01	12
4	**3d**	1.37	0	4110	124.7	482	3.14	7
5	**3e**	1.44	0	4320	125.5	520	3.52	5
6	**3f**	1.42	0	4260	80.6	591	2.50	53
7	**3g**	1.33	0	3990	78.7	503	2.21	55
8	**3h**	1.51	0	4530	82.9	633	2.49	50
9	**3a**	0.61	30	1820	89.2	43.8	2.11	30
10	**3b**	0.46	30	1370	86.3	41.8	2.10	37
11	**3c**	0.64	30	1920	95.7	56.4	2.54	28
12	**3d**	0.76	30	2290	120.2	83.5	2.83	19
13	**3e**	0.80	30	2400	122.9	89.7	2.99	15
14	**3f**	0.75	30	2250	–	235	1.79	79
15	**3g**	0.62	30	1860	–	196	1.66	81
16	**3h**	0.96	30	2880	–	283	1.93	73

[a] Polymerization condition: 2 μmol precatalyst, Al/Ni = 1200 (molar ratio), polymerization reaction under 10 atm for 10 min.
[b] Melting temperature determined by DSC (heating rate: 10°C/min).
[c] Weight-average molecular weight and polydispersity index determined by GPC.
[d] Degree of branching determined by ^{1}H NMR.

TABLE III
The Results of Polymerization with the Nickel Complexes Under 10 atm of Ethylene[a]

Entry	Preatalyst	Yield (g)	Activity (kg PE/mol$_{Ni}$·h·atm)	T_m[b] (°C)	$\overline{M}_w$[c] (kg/mol)	$\overline{M}_w/\overline{M}_n$[c]	Branches[d] (per 1000C)
1	3a	3.32	996	123.9	116	1.94	9
2	3b	3.08	924	123.4	204	1.63	10
3	3c	3.67	1101	124.6	261	2.17	7
4	3d	3.71	1113	132.3	282	2.54	2
5	3e	4.10	1230	133.7	304	2.63	1
6	3f	3.85	1155	89.3	394	1.86	31
7	3g	3.27	981	86.5	354	1.81	37
8	3h	4.29	1287	98.2	571	2.28	23

[a] Polymerization condition: 2 μmol precatalyst, Al/Ni = 1200 (molar ratio), polymerization reaction at 30°C under 10 atm for 10 min.
[b] Melting temperature determined by DSC (heating rate: 10°C/min).
[c] Weight-average molecular weight and polydispersity index determined by GPC.
[d] Degree of branching determined by ^{1}H NMR.

When isopropyl substituent was introduced into the *ortho* positions of the imines in the ligands, the molecular weight and branching degree of the polymer obtained increased dramatically. For example, if 3d is compared with 3h, the $\overline{M}_w$ of the polyethylene obtained at 0°C increases from 482 to 633 kg PE/mol$_{Ni}$·h, and the branching degree of the polymers increases from 7 to 50 per thousand carbons. These observations are in accord with the results reported by Brookhart and coworkers.[9] The *para*-position substituents of the imines in the ligands show similar effect on the performance of the isopropyl substituented precatalysts. For example, the replacement of the *para*-aryl proton (3f) with an electron-donating isopropyl group (3g) causes the decrease of catalyst activity and $\overline{M}_w$ of the polyethylene obtained at 0°C (catalyst activity from 4260 to 3990 kg PE/mol$_{Ni}$·h, and $\overline{M}_w$ from 591 to 503 kg/mol). However, an electron-withdrawing Br (3h) on the *para*-position of imines increases the catalyst activity to 4530 kg PE/mol$_{Ni}$·h and $\overline{M}_w$ to 633 kg/mol. The branching degree of the polymers obtained was also found to decrease in the order 3g (*i*Pr) > 3f (H) > 3h (Br) although the trend is not very clear.

A series of polymerization experiments under 10 atm of ethylene at 30°C, were also conducted. The typical results are summarized in Table III. Compared with Table II, the data in Table III show that the polyethylenes obtained under high pressure are characterized with more linear and less branches due to an increased rate of trapping and insertion relative to the rate of chain isomerization, which is independent of ethylene concentration.[9] For example, precatalyst 3d produces the polyethylene exhibiting 19 branches per thousand carbons at 1 atm, which drops to 2 branches per thousand carbons at 30°C under 10 atm. Similarly, precatalyst 3h yields polyethylene containing 73 branches per thousand carbons at 30°C under 1 atm of ethylene, 23 branches

per thousand carbons under pressures of 10 atm. In addition, the molecular weight of the resultant polymer enhances about twofold with the increase of ethylene pressure for individual precatalysts.

To gain insights into the thermal properties of these branched polyethylenes, we have characterized the polymers by differential scanning calorimetry (DSC). As we known, the linear polymers (<5 branches per thousand carbons) exhibited melt transitions (T_ms) between 125 and 135°C. The linear polyethylene produced at high pressure with precatalyst 3e displays a branching number of only 1 per thousand carbons and a T_m of 133.7°C. As the branching numbers increases, the T_m shifts to lower temperature and occurs over a much broader temperature range. Therefore, the branched polyethylenes produced by precatalysts 3a–c at 30°C and 10 atm of ethylene pressure exhibit T_ms of ~120–125°C. The polymers obtained with the complexes 3f–h/MMAO catalytic systems displays low crystallinity. As shown in Figure 3, the polymer obtained with precatalyst 3h display slightly lower T_m, much lower crystalline temperature (T_c), and much smaller melting enthalpy as well as crystallization heat than the polyethylenes obtained with precatalyst 3d.

CONCLUSIONS

The synthesis and characterization of a series of (α-diimine)nickel(II) precatalysts for ethylene polymerization have been introduced. For these precatalysts, not only the steric bulk but also the electronic effect of the substituents on the *para*-positions of the imines in the ligands plays important roles in the catalyst activities and the properties of the resulting polyethylenes. The electron-withdrawing group on the *para*-position of the imines in the ligands can increase the electrophilic character of the center
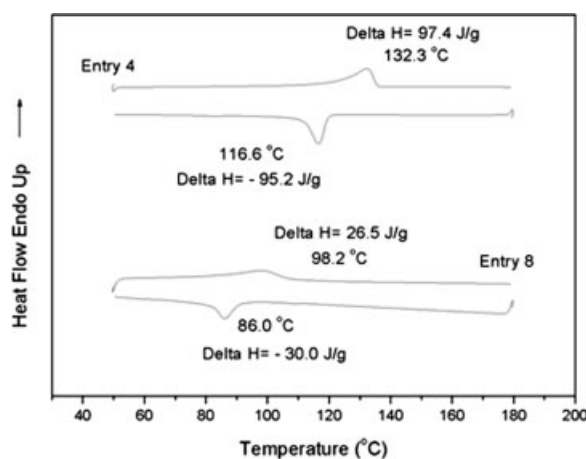
Figure 3 DSC profiles of the polyethylenes obtained (Table III) with complex **3d** and **3h**/MMAO systems at 30°C, 10 atm ethylene pressure.

nickel atom, which favors the chain propagation. The acceleration of chain propagation results in the increase of catalyst activity. Contrarily, electron-donating group weakens the electrophilic character of the center nickel atom, which decreases the rate of chain propagation relative to chain transfer, leading to the decrease in the molecular weight of the polyethylenes obtained. Increase in the polymerization temperature results in increased branching and decreased molecular weights for **3a–h**. Increases in ethylene pressure lead to dramatic reductions in the extent of branching in the polymer. The physical properties of the polyethylenes produced by these catalyst systems vary widely depending on the extent of branching and molecular weight. The structural variations of α-diimine ligands coupled with the conditions of polymerization, such as temperature and ethylene pressure can be used to control branching and molecular weight.

SUPPLEMENTARY MATERIAL

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC nos. 285488 and 285489 for the nickel complexes **3b** and **3d**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://ccdc.cam.ac.uk).

References

1. Ittel, S. D.; Johnson, L. K.; Brookhart, M. Chem Rev 2000, 100, 1169.
2. Boffa, L. S.; Novak, B. M. Chem Rev 2000, 100, 1479.
3. Mecking, S. Ang Chem Int Ed 2001, 40, 534.
4. Rieger, B.; Baugh, L. S.; Kacker, S.; Striegler, S. Late Transition Metal Polymerization Catalysis; Wiley-VCH: Weiheim, 2004.
5. Johnson, L. K.; Christopher, M.; Brookhart, M. J Am Chem Soc 1995, 117, 6414.
6. Johnson, L. K.; Mecking, S.; Brookhart, M. J Am Chem Soc 1996, 118, 267.
7. Killian, C. M.; Tempel, D. J.; Johnson, L K; Brookhart, M. J Am Chem Soc 1996, 118, 11664.
8. Mecking, S.; Johnson, L. K.; Wang, L.; Brookhart, M. J Am Chem Soc 1998, 120, 888.
9. Gates, D. P.; Svejda, S. A.; Onate, E.; Killian, C. M.; Johnson, L. K.; White, P. S.; Brookhart, M. Macromolecules 2000, 33, 2320.
10. Schmid, M.; Eberhardt, R.; Klinga, M.; Leskela, M.; Rieger, B. Organometallics 2001, 20, 2321.
11. Camacho, D. H.; Salo, E. V.; Ziller, J. W.; Guan, Z. B. Angew Chem Int Ed 2004, 43, 1821.
12. Liu, H. R.; Gomes, P. T.; Costa, S. I.; Duarte, M. T.; Branquinho, R.; Fernandes, A. C.; Chien, J. C. W.; Singh, R. P.; Marques, M. M. J Organomet Chem 2005, 690, 1314.
13. Strauch, J. W.; Erker, G.; Kehr, G.; Froehlich, R. Angew Chem Int Ed 2002, 41, 2543.
14. Liu, J. Y.; Li, Y. S.; Liu, J. Y.; Li, Z. S. Macromolecules 2005, 38, 2559.
15. Zheng, Z. J.; Liu, J. Y.; Li, Y. S. J Catal 2005, 234, 101.
16. Hicks, F. A.; Brookhart, M. Organometallics 2001, 20, 3217.
17. Jenkins, J. C.; Brookhart, M. Organometallics 2003, 22, 250.
18. Hu, T.; Tang, L. M.; Li, X. F.; Li, Y. S.; Hu, N. H. Organometallics 2005, 24, 2628.
19. Diamanti, S. J.; Ghosh, P.; Shimizu, F.; Bazan, G. C. Macromolecules 2003, 36, 9731.
20. Hicks, F. A.; Jenkins, J. C.; Brookhart, M. Organometallics 2003, 22, 3533.
21. Li, X. F.; Li, Y. G.; Li, Y. S.; Cheng, Y. X.; Hu, N. H. Organometallics 2005, 24, 2502.
22. Bauers, F. M.; Chowdhry, M. M.; Mecking, S. Macromolecules 2003, 36, 6711.
23. Soula, R.; Novat, C.; Tomov, A.; Spitz, R.; Claverie, J.; Drujon, X.; Malinge, J.; Saudemont, T. Macromolecules 2001, 34, 2022.
24. Soula, R.; Broyer, J. P.; Llauro, M. F.; Tomov, A.; Spitz, R.; Claverie, J.; Drujon, X.; Malinge, J.; Saudemont, T. Macromolecules 2001, 34, 2438.
25. Cooley, N. A.; Green, S. M.; Wass, D. F.; Heslop, K.; Orpen, A. G.; Pringle, P. G. Organometallics 2001, 20, 4769.
26. Kim, Y. H.; Kim, T. H.; Lee, B. Y.; Woodmansee, D.; Bu, X.; Bazan, G. C. Organometallics 2002, 21, 3082.
27. Tanabiki, M.; Tsuchiya, K.; Kumanomido, Y.; Matsubara, K.; Motoyama, Y.; Nagashima, H. Organometallics 2004, 23, 3976.
28. Watanab, M. Macromol Rapid Commun 2005, 26, 34.
29. Carlini, C.; Macinai, A.; Masi, F.; Galletti, A. M. R.; Santi, R.; Sbrana, G.; Sommazzi, A. J Polym Sci Part A: Polym Chem 2004, 42, 2534.
30. He, X. H.; Yao, Y.; Luo, X.; Zhang, J.; Liu, Y.; Zhang, L.; Wu, Q. Organometallics 2003, 22, 4952.
31. Helldörfer, M.; Backhaus, J.; Milius, W.; Alt, H. G. J Mol Catal A Chem 2003, 193, 59.
32. Helldörfer, M.; Milius, W.; Alt, H. G. J Mol Catal A Chem 2003, 197, 1.
33. Zhang, T. Z.; Guo, D. W.; Jie, S. Y.; Sun, W. H.; Li, T.; Yang, X. Z. J Polym Sci Part A: Polym Chem 2004, 42, 4765.
34. Woo, T. K.; Ziegler, T. J Organomet Chem 1999, 591, 204.
35. Liu, J. Y.; Zheng, Y.; Li, Y. G.; Pan, L.; Li, Y. S. J Organomet Chem 2005, 690, 1233.
36. Liu, J. Y.; Zheng, Y.; Hu, N. H.; Li, Y. S. Chin J Chem, to appear.