# Synthesis and Characterization of Tridentate Phenoxy-Imine Ligand [*N,N,O*] Nickel(II) and Palladium(II) Complexes and Their Catalytic Behaviors in Vinyl Polymerization of Norbornene

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**ABSTRACT:** In this study, new complexes LNiCl(**1**), LNiBr(**2**), LNiI(**3**), and LPdCl(**4**) (L = 4,6-di-*tert*-butyl-2-(*N*-(quinolin-8-yl)iminomethyl)phenolato) have been synthesized and characterized. X-ray diffraction studies on Complexes **1** and **4** revealed that N, N, O, and halogen atoms coordinated to metal, with a nearly square planar geometries in all cases. All these complexes are robust and exhibit high activities for the addition polymerization of norbornene (NB) with methylaluminoxane as cocatalyst [up to 47.62 kg PNB(mmol of Ni)$^{-1}$h$^{-1}$] and also lead to various activities and molecular weights of polynorbornenes under different reaction conditions. It is noteworthy that Complexes **1** and **4** show better activity under higher reaction temperature of 80°C. However, Complex **2** showed lower activity, and Complex **3** was found nearly inert toward NB polymerization, probably, because of thermal instability. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 1642–1650, 2009

**Key words:** nickel; palladium; catalyst; norbornene; polymerization

## INTRODUCTION

During the last decades, there have been tremendous advances in the field of olefin polymerization catalysts based on the late transition metals.[1–3] The pioneering studies of Brookhart and coworkers[4–8] reported on the discovery of the α-diimine complexes of Ni and Pd catalysts for the polymerization of ethylene and α-olefins. Subsequently, increasing interest has been focused on the α-diimine catalyst system.[9–22] Also, there has been considerable research on new ligands for nickel and palladium catalysts.[23–36] Among the various families of organic ligands, the complexes possessing phenoxyimine ligands are one of the promising examples that show excellent performance in olefin polymerization over the past 10 years.[37–51] A key attraction of these ligands is their ready availability and amenability to modification via straightforward Schiff-base condensation procedures. Recently, new and highly active group 4 polymerization catalysts based on phenoxyimine ligands have been discovered by the Fujita group,[41–49] which attract considerable interest with regard to their ability to conduct living olefin polymerization. Also, Grubbs and coworkers reported a series of highly active neutral single-component salicylaldimine-based nickel(II) catalysts, which can homopolymerize olefins and copolymerize ethylene with polar monomers.[50,51]

Homopolymer addition of polynorbornenes (PNBs) are of considerable interest because of their unique physical properties, including good mechanical strength and heat resistivity ($T_g > 350°C$), and optical transparency for applications such as deep ultraviolet photoresists, excellent dielectrics in microelectronics applications, and as cover layers for liquid-crystal displays. Deming and Novak[52] introduced the first nickel complexes for the addition polymerization of norbornene (NB) in 1993, and recently some nickel and palladium complexes were

found to be highly active for the polymerization of NB. Of them, most are involved in bidentate ligand-derived complexes.[53–61] A few nickel and palladium complexes based on tridentate ligands were reported for NB polymerization,[62–65] except limited examples related to oligomerization of ethylene.[66–71] For developing new late-metal olefin polymerization catalysis, we designed and synthesized the nickel and palladium complexes based on 4,6-di-*tert*-butyl-2-(*N*-(quinolin-8-yl)iminome thyl)phenol (LH). It was found that the Complexes **1–4** could catalyze the polymerization of NB with high activities up to 47.62 kg PNB(mmol of Ni)$^{-1}$ h$^{-1}$ by varying their reaction conditions. In this article, we report the results in detail.

## EXPERIMENTAL SECTION

### General considerations

All manipulations of air- and/or moisture-sensitive compounds were performed under a nitrogen atmosphere using standard Schlenk techniques. Chlorobenzene, methylene dichloride (DCM), and 1,1,2,2-tetrachloroethane (TCE) were distilled from drying CaH$_2$ under nitrogen. Toluene, diethyl ether, hexane, and tetrahydrofuran (THF) were refluxed with sodium/benzophenone ketyl and were distilled under nitrogen before use. 3,5-Di-*tert*-butyl-2-hydroxybenzaldehyde and 8-aminoquinoline were bought from Alfa Aesar Co. Ltd. (Tianjin, China) NB (bicyclo-[2.2.1]hept-2-ene; Alfa Aesar) was purified by distillation with sodium and used as a solution (0.94 g/mL) in DCM. Methylaluminoxane (MAO, 10% solution in toluene) was bought from Aldrich Chemical and used without further purification.

### Measurements

Elemental analyses were obtained using a Vario MICRO microanalyzer. IR spectra were recorded on a Nicolet AV-360 IR spectrometer. Mass spectra were carried out with a LCQ Deca XP Max spectrometer. TGA data were measured with a TGA/SDTA851 series thermal analysis system instrument. The viscosity–average molar masses ($M_v$) of the PNB were obtained using the Mark–Houwink coefficients[72]: $\alpha = 0.56$, $K = 7.78 \times 10^{-4}$ dL/g. Scanning electron microscopy (SEM) images were obtained on a KYKY-1000B electron microscope. The wide-angle X-ray diffraction (WAXD) curves of the PNB powders were obtained using a Philips X'Pert Diffractometer.

### Synthesis of ligand LH

LH was conveniently synthesized by Schiff base condensation. To a stirred solution of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (0.944 g, 4 mmol) in anhydrous ethanol (35 mL), 8-aminoquinoline (0.576 g, 4 mmol) and a few drops of glacial acetic acid as a catalyst were added under nitrogen atmosphere. The mixture was refluxed and stirred for 12 h, during which time the reaction mixture turned pink. Then, the resultant pink solution was removed by a rotary evaporator to give a pink solid and finally dried in vacuum. Yield: 1.401 g (97%). ESI-MS (m/z): 361.7 (M+H$^+$). Anal. Calcd for C$_{24}$H$_{28}$N$_2$O (360.33): C, 79.96; H, 7.82; N, 7.77. Found: C, 79.77; H, 7.69; N, 7.91. IR (KBr, cm$^{-1}$): 3437, 2954, 1611, 1467, 1367, 1322, 1248, 1204, 1172, 1090, 1050, 984, 884, 829, 791, 574.

### Synthesis of Complex 1

To a stirred solution of LH (0.332 g, 0.92 mmol) in anhydrous ethanol (25 mL), NiCl$_2$·6H$_2$O (0.228 g, 0.96 mmol) was added, and the reaction mixture was stirred at room temperature for 3 h. The resultant dark-red solution was filtered, and the filtrate was concentrated under vacuum to ca. 3 mL. Diethyl ether (30 mL) was added to precipitate Complex **1**. The dark-red precipitate was filtered, washed repeatedly with diethyl ether and dried in vacuum. Yield: 0.317 g (76%). ESI-MS (m/z): 490.5 (M+K$^+$). Anal. Calcd for C$_{24}$H$_{27}$N$_2$ONiCl (453.64): C, 63.55; H, 6.00; N, 6.18. Found: C, 63.37; H, 5.89; N, 6.30. IR (KBr; cm$^{-1}$): 3434, 3133, 2955, 1608, 1515, 1460, 1403, 1240, 1209, 1168, 1087, 1042, 932, 827, 778, 579.

### Synthesis of Complex 2

In a similar manner with **1**, Complex **2** was prepared as a red/brown solid in 75% yield. Anal. Calcd for C$_{24}$H$_{27}$N$_2$ONiBr (497.90): C, 57.87; H, 5.46; N, 5.62. Found: C, 57.51; H, 5.36; N, 5.76; Br, 16.34. IR (KBr; cm$^{-1}$): 3434, 3133, 2954, 1605, 1505, 1458, 1404, 1227, 1155, 1083, 1029, 965, 908, 835, 792, 587.

### Synthesis of Complex 3

In a similar manner with **1**, Complex **3** was prepared as a red/brown solid in 71% yield. Anal. Calcd for C$_{24}$H$_{27}$N$_2$ONiI (544.89): C, 52.88; H, 4.99; N, 5.14. Found: C, 52.86; H, 4.72; N, 5.27. IR (KBr; cm$^{-1}$): 3432, 3149, 2954, 1605, 1505, 1458, 1403, 1227, 1155, 1082, 1031, 967, 908, 835, 794, 579.

### Synthesis of Complex 4

A dark-brown suspension of LH (0.332 g, 0.92 mmol) and palladium dichloride (0.168 g, 0.95 mmol) in anhydrous THF (25 mL) was refluxed for 8 h, giving a red solution. The resultant mixture was filtered, and the filtrate was concentrated under vacuum to ca. 3 mL. Hexane (25 mL) was added to

**TABLE I**
**Crystal Data and Structure Refinement for Complexes 1 and 4**

| | Complex | |
| --- | --- | --- |
| | **1** | **4** |
| Empirical formula | $C_{24}H_{27}N_2ONiCl$ | $C_{24}H_{27}N_2OPdCl$ |
| Formula weight | 453.64 | 501.37 |
| Space group | Orthorhombic | Monoclinic |
| Crystal system | Pbca | P2(1)/c |
| $a$ (Å) | 9.165(3) | 18.895(7) |
| $b$ (Å) | 13.040(5) | 9.216(3) |
| $c$ (Å) | 35.978(16) | 13.695(6) |
| $\alpha$ (°) | 90 | 90 |
| $\beta$ (°) | 90 | 110.178(15) |
| $\gamma$ (°) | 90 | 90 |
| Volume (Å$^3$) | 4300(3) | 2238.3(15) |
| Z | 8 | 2 |
| $D_{calcd}$ (Mg/m$^3$) | 1.402 | 0.274 |
| Absorption coefficient (mm$^{-1}$) | 1.044 | 0.456 |
| F(000) | 1904 | 170 |
| $\theta$ range (°) | 3.12–27.50 | 3.16–27.47 |
| Index ranges | $-11 \leq h \leq 11$ | $-24 \leq h \leq 24$ |
| | $-16 \leq k \leq 16$ | $-11 \leq k \leq 11$ |
| | $-46 \leq l \leq 46$ | $-17 \leq l \leq 17$ |
| Reflections collected/unique | 30496/4837 [$R$(int) = 0.1920] | 21238/5113 [$R$(int) = 0.0677] |
| Data/restraints/parameters | 4837/0/262 | 5113/0/263 |
| Goodness-of-fit on F^2 | 1.065 | 0.880 |
| Final $R$ indices [$I > 2sigma(I)$] | $R_1 = 0.1619$, $wR_2 = 0.2508$ | $R_1 = 0.0450$, $wR_2 = 0.1221$ |
| $R$ indices (all data) | $R_1 = 0.2065$, $wR_2 = 0.2723$ | $R_1 = 0.0668$, $wR_2 = 0.1370$ |
| Largest diff. peak and hole[a] (e/Å$^{-3}$) | 0.719 and $-0.568$ | 0.469 and $-1.057$ |

[a] Largest peak (hole) in difference Fourier map, $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$, $wR_2 = [\Sigma(|F_o|^2 - |F_c|^2)^2/\Sigma(F_o^2)]^{1/2}$.

precipitate the complex. The formed precipitate was filtered and washed with hexane and dried in vacuum. Complex **4** was obtained as a red solid. Yield: 0.189 g (41%). Anal. Calcd for $C_{24}H_{27}N_2OPdCl$ (501.37): C, 57.50; H, 5.43; N, 5.87. Found: C, 57.33; H, 5.27; N, 5.93. IR (KBr; cm$^{-1}$): 3434, 3132, 2957, 1602, 1515, 1456, 1401, 1326, 1242, 1167, 1091, 945, 831, 790, 758, 579.

### Crystal structure determination

Single-crystal X-ray diffraction studies for Complexes **1** and **4** were carried out on a Rigaku R-AXIS RAPID Weissenberg IP diffractometer equipped with a graphite-monochromatized Mo K radiation ($\lambda$ = 0.71073 Å) at 293 K. Unit-cell dimensions were obtained with least-squares refinements. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods with SHELXS-97[73] and refined by full-matrix least-square on $F^2$ with SHELXL-97.[74] All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in calculated positions with the displacement factors of the host carbon atoms. Crystal data and details of data collection and structure refinements are given in Table I. The crystallographic data for Complexes

**1** and **4** have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC 699085 for Complex **1** and CCDC 699086 for Complex **4** (see also Supporting Information).

### Polymerization of norbornene

In a typical procedure, 0.5 μmol of nickel(II) complex **1** in 0.5 mL of $CH_2Cl_2$, 0.94 g of NB in 1.0 mL of $CH_2Cl_2$, and 13.0 mL of fresh $CH_2Cl_2$ were added into a polymerization bottle with strong stirring under nitrogen atmosphere. After the mixture was kept at 25°C for 5 min, MAO was charged into the polymerization system by means of a syringe, and the reaction was initiated. Four minutes later, acidic ethanol ($V_{ethanol} : V_{conc.\ HCl} = 10 : 1$) was added to terminate the reaction. The solid PNB was filtered, washed with ethanol, and dried in vacuum at 100°C for 24 h. Unless otherwise stated, the total reaction volume was 15 mL, which was achieved by the variation of the amount of DCM when necessary. All the polymer samples exhibited similar IR spectral absorption. IR (KBr; cm$^{-1}$): 2946.37 (vs), 2868.91 (vs), 1473.39 (s), 1451.80 (s), 1373.83 (m), 1294.97 (m), 1257.95 (m), 1221.91 (m), 1147.70 (m), 1108.04 (m), 1042.18 (w), 942.82 (m), 892.96 (m), 754.52 (w).
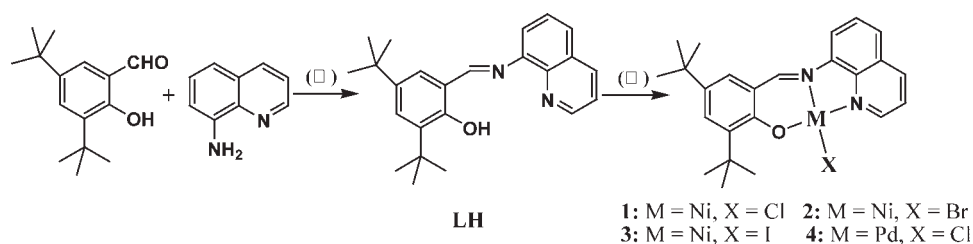
**Scheme 1** Synthesis of Complexes **1–4**.

## RESULTS AND DISCUSSION

### Ligand and complex synthesis

The synthetic routes for the new tridentate phenoxy-imine nickel(II) and palladium(II) complexes are shown in Scheme 1. The phenoxyimine ligand, LH, was efficiently prepared via the condensation reaction of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde and 8-amine-quinoline according to the literature method.[75] Treatment of the phenoxyimine ligand with $NiX_2 \cdot 6H_2O$ (X = Cl, Br, and I) or $PdCl_2$ in different solvents afforded the desired complexes in 41–76% yields. In the solid state, Complexes **1–4** are so insensitive to moisture that they can be exposed to ambient atmosphere for several days without notable change.

All synthesized compounds were characterized by elemental analysis and IR spectrometry. The elemental analysis results revealed that the components of all complexes were in accord with the formula LH or $MLX_2$ (M = Ni, Pd). The IR spectra of the ligand LH show that the C=N stretching frequency appear at 1611 cm$^{-1}$ with strong intensity; however, in Complexes **1–4**, the C=N stretching frequencies shifted toward lower values, between 1602 and 1608 cm$^{-1}$ with weak intensities. The results reveal the coordination interaction between the nitrogen atoms of the imine groups and the metal ions. In addition, ligand LH and Complex **1** were confirmed by mass spectral analysis.

To further confirm the structure of these nickel(II) and palladium(II) complexes, crystals of Complexes **1** and **4** suitable for X-ray crystallographic structure analysis were grown by slow evaporation from $CH_2Cl_2$ solution. The molecular structure of Complexes **1** and **4** are shown in Figures 1 and 2, and selected bond lengths and angles are presented in Table II.

In the solid state, Complex **1** is in the orthorhombic form and Complex **4** is in the monoclinic geometry. The geometry around the four-coordinated metal metal (Ni or Pd) atom could be described as a nearly ideal square planar where the tridentate ligand is bonded to the metal through two neutral nitrogens, N(1) from the quinoline ring and N(2) from the imino group, and the oxygen O from the phenolate group. The rest site is occupied by one chloride ligand, which lies trans to the imino nitrogen donor. These complexes are neutral owing to deprotonation of the oxygen atom of the tridentate ligand upon complexation, presumably due to the greater acidity of the phenolate protons when compared with that of the alcohol.

As shown in Figure 1, the nickel complex **1** adopts a nearly square planar geometry around nickel(II).
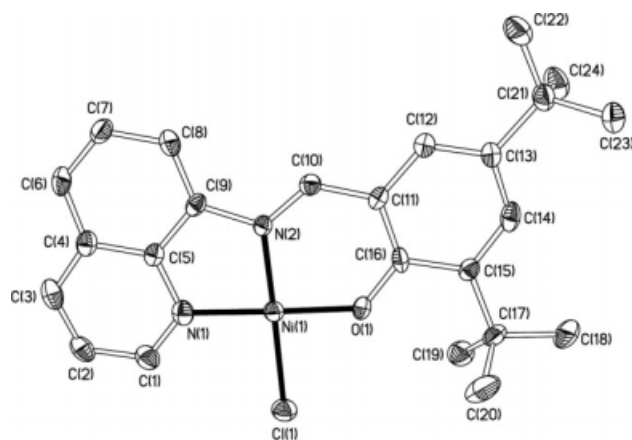


**Figure 1** Molecular structure of Complex **1**, with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.
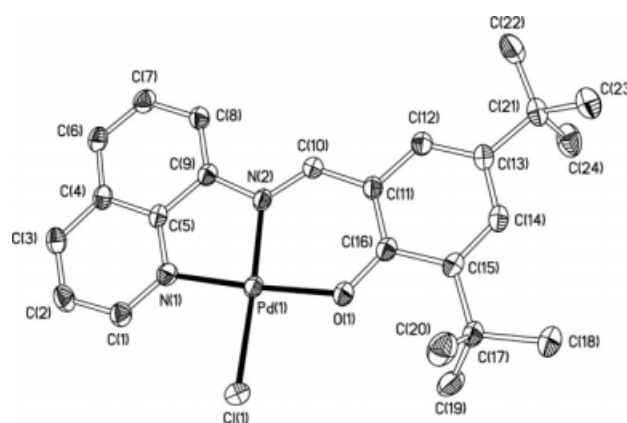


**Figure 2** Molecular structure of Complex **4**, with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.

**TABLE II**
**Selected Bond Lengths (Å) and Angles (∘)**
**for Complexes 1 and 4**

| Complex | 1, M = Ni | 4, M = Pd |
|---|---|---|
| M(1)-N(2) | 1.858(8) | 1.967(3) |
| M(1)-N(1) | 1.905(8) | 2.008(3) |
| M(1)-O(1) | 1.821(6) | 1.974(3) |
| M(1)-Cl(1) | 2.182(3) | 2.3258(13) |
| N(2)-C(10) | 1.304(12) | 1.304(5) |
| N(2)-C(9) | 1.420(11) | 1.423(5) |
| N(1)-C(1) | 1.315(13) | 1.322(5) |
| N(1)-C(5) | 1.373(13) | 1.367(5) |
| O(1)-C(16) | 1.305(12) | 1.313(5) |
| N(2)-M(1)-O(1) | 93.9(3) | 93.61(12) |
| N(2)-M(1)-Cl(1) | 177.4(3) | 177.15(9) |
| N(2)-M(1)-N(1) | 85.9(4) | 82.53(13) |
| N(1)-M(1)-O(1) | 176.8(4) | 176.04(12) |
| N(1)-M(1)-Cl(1) | 93.2(3) | 95.28(10) |
| O(1)-M(1)-Cl(1) | 87.2(2) | 88.61(9) |
| M(1)-N(1)-C(5) | 111.7(7) | 112.6(2) |
| M(1)-N(2)-C(10) | 125.6(6) | 124.4(3) |
| M(1)-N(2)-C(9) | 113.5(6) | 113.8(2) |
| M(1)-O(1)-C(16) | 129.0(6) | 125.8(2) |
| N(2)-C(10)-C(11) | 126.7(9) | 127.0(4) |
| N(2)-C(9)-C(5) | 112.5(8) | 113.5(3) |
| C(10)-N(2)-C(9) | 120.9(8) | 121.7(3) |

The N(1), N(2), O(1), and Cl(1) atoms are nearly co-planar, with Cl(1) and N(2) occupying the trans position [Cl—Ni—N(2) angles of 177.4(3)°, N(1)—Ni—O: 176.8(4)°]. The O(1)–Ni(1)–N(2), O(1)–Ni(1)–Cl(1), N(1)–Ni(1)–Cl(1), and N(1)–Ni(1)–N(2) bond angles are 93.9(3)°, 87.2(2)°, 93.2(3)°, and 85.9(4)°, respectively. It is noted that the bond lengths of Ni(1)—O(1) (1.821(6) Å) and Ni(1)—N(2) (1.858(8) Å) are shorter than that of the reported salicylaldiminato nickel(II) complex [O(1)—Ni(1) = 1.894(4) Å and Ni(1)—N(2) = 1.922(5) Å].[76] Noticeably, the Ni(1)—N(2) (in the imine group) bond and Ni—N(1) (in quinoline) bond lengths are different [Ni(1)—N(1) = 1.905(8) and Ni(1)—N(2) = 1.858(8) Å]. This is similar to that of the tridentate phenoxy-imine-based titanium complexes.[77,78] In addition, the imino N(2)—C(10) bond length is 1.304(12) Å in Complex 1, which displays distinctive double-bond character.

The two complexes are isostructural. As shown in Figure 2, the geometry in Complex 4 is very similar to that in Complex 1. In Complex 4, the Cl(1) occupies the position trans to the N(2) with a nearly linear N(2)—Pd(1)—Cl(1) angle (177.15(9)°). The N(1) attached to Pd lies in a position trans to O(1) with an O(1)1—Pd(1)—N(1) angle of 176.04(12)°. However, the bond lengths of C(1)—N(1) and C(5)—N(1) in quinoline are different from that of the corresponding bond lengths in Complex 1. With a view to obtain a better understanding of the molecular structure of Complexes 2 and 3, we attempted to grow suitable crystals of the Complexes 2 and 3 for a X-ray structure determination; however, all attempts were unsuccessful.

## Norbornene polymerization

In the presence of MAO, the nickel and palladium complexes 1–4 were completely inactive for ethylene polymerization either at 50°C, 1 atm, or at 30°C, 5 atm. However, after activation with MAO, Complexes 1–4 could promote the polymerization of NB very well. For example, it was found that PNB generated immediately after MAO was added to a mixture of NB and Complexes 1–4 in DCM or TCE.

The polymerization of NB catalyzed by Complexes 1–4 was investigated in the presence of MAO at 25°C and an Al/cat ratio of 1500. The results are listed in Table III. Under the same polymerization conditions, Complexes 1–4 display similar catalytic activities for NBE polymerization [16.75, 14.78, 10.64, and 16.23 kg PNB(mmol of M)$^{-1}$ h$^{-1}$ for 1, 2, 3, and 4, respectively].

To investigate the reaction parameters affecting vinyl polymerization of NB, the catalyst precursor 1 was typically investigated by changing the polymerization conditions. The NB polymerization results are given in Table IV.

As depicted in Table III, it was realized that the catalytic activities greatly relied on the molar ratio of NB monomer to nickel catalytic precursor.[79,80] Increasing the monomer concentration of NB with fixed amount of nickel precursor (0.5 μmol) and the

**TABLE III**
**Activity of Complexes 1–4 for Norbornene Polymerization**[a]

| Entry | Cat. | Yield (g) | Conv. (%) | Activity[b] | $M_v$ (10⁶ g/mol) | TGA (°C) |
|---|---|---|---|---|---|---|
| 1 | 1 | 0.558 | 59.40 | 16.75 | 1.67 | 461 |
| 2 | 2 | 0.493 | 52.43 | 14.78 | 1.71 | 462 |
| 3 | 3 | 0.355 | 37.72 | 10.64 | 1.76 | 462 |
| 4 | 4 | 0.541 | 57.55 | 16.23 | 1.91 | 459 |

[a] General conditions: 0.5 μmol of Complexes 1–4; MAO cocatalyst Al/cat = 1500; NB, 0.94 g; 10 mmol; $V_{total}$ 15.0 mL; DCM; 25°C, 4 min.
[b] In units of kg PNB(mmol of M)$^{-1}$ h$^{-1}$.

**TABLE IV**
**Polymerization of Norbornene with 1/MAO[a]**

| Entry | NB (g) | Solvent | $T$ (°C) | Al/cat | Yield (g) | Conv. (%) | Activity[b] | $M_v$ ($10^6$ g/mol) |
|---|---|---|---|---|---|---|---|---|
| 1 | 0.47 | DCM | 25 | 1500 | 0.347 | 73.83 | 10.41 | 1.50 |
| 2 | 0.94 | DCM | 25 | 1500 | 0.558 | 59.40 | 16.75 | 1.67 |
| 3 | 1.88 | DCM | 25 | 1500 | 0.159 | 8.46 | 4.77 | 1.89 |
| 4[c] | 0.94 | DCM | 25 | 1500 | 0.397 | 42.21 | 47.62 | 1.86 |
| 5[d] | 0.94 | DCM | 25 | 1500 | 0.677 | 71.99 | 8.12 | 1.45 |
| 6[e] | 0.94 | DCM | 25 | 1500 | 0.703 | 75.24 | 2.83 | 1.24 |
| 7 | 0.94 | DCM | 25 | 500 | 0.146 | 15.00 | 4.38 | 1.92 |
| 8 | 0.94 | DCM | 25 | 1000 | 0.392 | 41.70 | 11.76 | 1.77 |
| 9 | 0.94 | DCM | 25 | 2500 | 0.693 | 73.72 | 20.79 | 1.46 |
| 10 | 0.94 | DCM | 25 | 3000 | 0.713 | 75.88 | 21.40 | 1.25 |
| 11 | 0.94 | TCE | 0 | 1500 | 0.069 | 7.36 | 2.08 | 1.40 |
| 12 | 0.94 | TCE | 25 | 1500 | 0.500 | 53.15 | 15.01 | 1.28 |
| 13 | 0.94 | TCE | 50 | 1500 | 0.634 | 67.39 | 19.00 | 1.07 |
| 14 | 0.94 | TCE | 80 | 1500 | 0.801 | 90.53 | 25.53 | 0.82 |
| 15 | 0.94 | PhCl | 25 | 1500 | 0.027 | 2.83 | 0.798 | – |
| 16 | 0.94 | Toluene | 25 | 1500 | Trace | – | – | – |

[a] General conditions: 0.5 μmol of Complex **1**; MAO cocatalyst; NB, 0.47g, 5 mmol; 0.94 g, 10 mmol; 1.88 g, 20 mmol; $V_{total}$ 15.0 mL; 4 min.
[b] In units of kg PNB(mmol of Ni)$^{-1}$ h$^{-1}$.
[c] 1 min.
[d] 10 min.
[e] 30 min.

same solution volume, first resulted in an improvement of activity from 10.41 kg PNB(mmol of Ni)$^{-1}$ h$^{-1}$ to 16.75 kg PNB(mmol of Ni)$^{-1}$ h$^{-1}$, and then gradually decreased to 4.77 kg PNB(mmol of Ni)$^{-1}$ h$^{-1}$. In addition, the higher concentration of NB produced a higher molecular weight of PNB (entries 1–3). As expected, the polymerization yields are increasing with the prolonging reaction time, and the monomer concentration decreases as the polymerization goes on; however, the fundamental reason for the decrease of viscosity-average molecular weight ($M_v$) may probably be due to the change of active centers. It is difficult to imagine how the high-molecular-weight polymer becomes low, except we suppose the depolymerization. We can clearly observe the increase of conversion from entries 2 and 4–7. Probably, some active centers that has higher activity and produce higher molecular weight polymer deactivates more easily. Another reason may be due to the state of the polymer, as the polymer has a spherical morphology (Fig. 3), the monomer may become difficult to diffuse into the inside of the particle to propagate, thus producing lower molecular weight polymer.

Control experiments showed that no catalytic activity was observed for Complexes **1–4** in the absence of MAO. Therefore, the cocatalyst MAO, which can create an empty site for coordination and insertion of the NB, is essential for the NB polymerization catalyzed by Complexes **1–4**.[81–85] Variation of the ratio of MAO : Complex **1**, which is expressed here as the Al/Ni molar ratio, displayed significant effects on catalyst activity and the molecular weight of the resultant polymers. For example, with the increase of the ratio from 500 to 3000, the activity was enhanced nearly five times (entries 2 and 7–10). Noticeably, the catalytic activity of precatalyst **1** nearly remained steady after the Al/M molar ratio reached about 2500/1. In contrast, the viscosity-average molecular weights ($M_v$) of the polymers gradually decreased with increasing Al/M molar ratios.

Solvents also strongly influenced the activity because of the solubility of Complex **1** in the solvents. For example, PhCl gave much lower activity
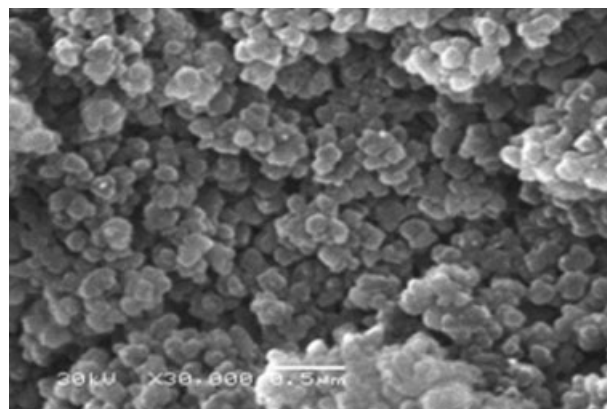


**Figure 3** The SEM images of polymer particles (Table I, entry 1).

**Activity of Complexes 1–4 for Norbornene Polymerization Under Higher Reaction Temperature[a]**

| Entry | Cat. | $T$ (°C) | Yield (g) | Conv. (%) | Activity[b] | $M_v$ ($\times 10^6$ g/mol) |
|-------|------|----------|-----------|-----------|-------------|------------------------------|
| 1 | 1 | 80 | 0.801 | 90.53 | 25.53 | 0.82 |
| 2 | 2 | 80 | 0.144 | 14.69 | 4.32 | 1.01 |
| 3 | 3 | 80 | Trace | – | – | – |
| 4 | 4 | 80 | 0.915 | 97.34 | 27.45 | 0.93 |

[a] General conditions: 0.5 μmol of Complexes **1–4**; MAO cocatalyst Al/cat = 1500; NB, 0.94 g; 10 mmol; $V_{total}$ 15.0 mL; TCE; 80°C, 4 min.
[b] In units of kg(mmol of M)$^{-1}$ h$^{-1}$.

than DCM, and only a trace amount of polymer was observed in toluene. However, when the TCE was used as solvent for NB polymerization, under similar conditions in TCE, 53.2% conversion of NB was achieved, and the activity was improved to 15.01 kg PNB(mmol of Ni)$^{-1}$ h$^{-1}$ (entries 2, 12, and 15–16). Both catalyst activity and molecular weights for the resultant polymers were also considerably influenced by reaction temperature (entries 11–14). The temperature was obtained with an external oil bath except for entry 11, in which 0°C was maintained with an ice-water bath. Accordingly, the precatalyst **1** showed better activity with increasing reaction temperature. High catalytic activity of Complex **1** up to 25.53 kg PNB(mmol of Ni)$^{-1}$ h$^{-1}$ was observed at 80°C when compared with the activity 2.08 kg PNB(mmol of Ni)$^{-1}$h$^{-1}$ at 0°C. However, the molecular weight decreased with an increased temperature. Elevated temperatures will result in higher chain propagation and chain-transfer rates, which would be expected to afford higher activity and lower molecular weight product.

Under higher reaction temperature of 80°C, the behavior of Complexes **1–4** on NB polymerization were examined (Table V). As shown in Table IV, Complexes **1** and **4** were highly active, and the anion of the complexes had a significant effect on both conversions and activities. Palladium chloride **4** proved to be the most active [27.45 kg PNB(mmol of Ni)$^{-1}$ h$^{-1}$, 97% conversion, entry 4]. In comparison, a significant reduction in activity was observed when nickel bromide **2** was used instead of the nickel chloride **1**. Nickel iodide **3** was found nearly inert toward NB polymerization probably because of thermal instability.

### Characteristics of obtained polynorbornene

All PNBs obtained from these catalytic systems showed very similar IR spectra. The IR spectra proved the absence of a double bond, which often appear at 1620–1680 cm$^{-1}$, ensuring the occurrence of vinyl-type polymerization rather than ring-opening metathesis polymerization (ROMP).[86–88] TGA investigation for all obtained polymers showed that

all of the polymer samples were very stable up to 450°C. The determination of the glass transition temperature ($T_g$) of vinyl homopolynorbornene has been described as being difficult because it is apparently located close to the temperature where decomposition tends to set in.[89] Our attempts to determine the $T_g$ of the obtained vinyl polymers also failed because DSC studies did not give an endothermic signal upon heating to the decomposition temperature. Figure 3 shows the SEM images of the PNB. The result showed that the sample had spherical morphology. The size of the regular spherical particles was 0.2–0.3 μm. All the PNBs synthesized here are easily soluble in chlorobenzene at room temperature, which indicate low stereoregularity. Indeed, analysis by WAXD shows no indication of crystallinity[90] (Fig. 4).

### CONCLUSION

The results presented in this article confirm the utility of synthesizing new nickel(II) and palladium(II) complexes with heterocyclic ligand as appropriate candidates for olefin polymerization. The X-ray diffraction studies reveal that these complexes feature a nearly square planar coordination of the central metal with the N, N, and O atoms. In the presence
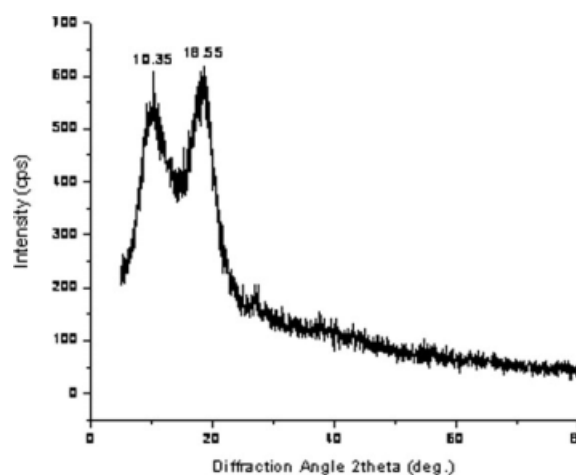


**Figure 4** WAXD diagram of polynorbornene (Table I, entry 1).

of MAO, an activity of up to 47.62 kg PNB(mmoL of Ni)$^{-1}$ h$^{-1}$ has been achieved with nickel complex **1** for the polymerization of NB. Under higher reaction temperature of 80°C, nickel chloride **1** and palladium chloride **4** exhibit high activities and significantly increases the conversions. In contrast, a significant reduction in activity was observed when nickel bromide **2** and nickel iodide **3** were used for NB polymerization probably because of thermal instability. The polymers obtained here are amorphous and soluble in chlorobenzene and stable up to 450°C. Catalytic activity, conversion yield, and polymer molecular weight could be controlled over a wide range. To the best of our knowledge, this is one of the catalysts possessing highest activities for vinyl addition polymerization of NB in reported literatures either to nickel complexes or to palladium complexes based on tridentate ligands. Further investigations into the polymerization mechanism are in progress in our laboratory.

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