Vinyl Polymerization of Norbornene with Bis(imino)pyridyl Nickel(II) Complexes

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ABSTRACT: A series of different steric hindrance nickel(II) complexes 1–6 bearing 2,6-bis(imino)pyridine ligands have been synthesized and characterized. The molecular structures of the complexes 3–5 were determined by X-ray diffraction analysis. The coordination geometry around the nickel center of the complexes is either square pyramid for complexes 3 and 4 or trigonal bipyramid for complex 5. All of the nickel complexes exhibit high catalytic activity for norbornene polymerization in the presence of MAO, although low activity for ethylene oligomerization and polymerization. The effects of the Al/Ni ratio, halogen, monomer concentration, temperature, and reaction time on activity of catalyst for norbornene polymerization and polymer microstructure were investigated. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 1486–1495, 2009

Key words: nickel complex; bis(imino)pyridine ligands; norbornene polymerization; ethylene oligomerization

INTRODUCTION

NB (norbornene) can be polymerized via three routes: ring-opening olefin metathesis (ROMP)[1,2] cationic or radical polymerization[3] and vinyl-polymerization (addition polymerization)[4,5] (Scheme 1). Each route leads to generation of different polymers in structure and properties from others.[6–8] Vinyl polymerization of NB was firstly reported by Sartori et al.[9–11] As the bicyclic structure is retained in the main chain, the NB addition polymers displays a characteristic rigid random coil conformation, which has restricted rotation about the main chain and exhibits strong thermal stability ($T_g > 350°C$). In addition, it has excellent dielectric properties, optical transparency and unusual transport properties.[9–11] So far, the NB vinyl polymerization has been widely attracted to study.[5] In recent years, the vinyl-type polynorbornene (PNB) can be prepared by nickel,[12–26] cobalt,[27–29] chromium,[30,31] titanium,[7,32,33] zirconium,[34] iron,[35,36] palladium,[37–49] and copper[21,22,24,50] complexes activated with methylaluminoxane (MAO) or cationic complexes with weakly coordinating counter ions like BF_4^- or PF_6^- (Ni, Pd).

Since the late 1990s, one of the latest breakthroughs in the olefin polymerization field has been the discovery of the neutral salicylaldiminato nickel complexes[51–56] as extremely high active catalysts for producing polyethylene and the vinyl-polymerization of NB. On the other hand, Brookhart and coworkers[57,58] and Gibson et al.[59,60] independently reported that pyridine bis(imino) iron or cobalt dichloride complexes activated with MAO led to a highly active ethylene polymerization catalysts converting ethylene to highly linear polyethylene. Our group reported the iron, cobalt, chromium, copper, and zinc complexes with bulky bis(imino)pyridine ligands and their catalytic behaviors in ethylene polymerization and vinyl polymerization of norbornene.[61] Frédéric also reported the vinyl of polymerization of NB with $CoCl_2$ and pyridine bis(imine) cobalt (II) complexes activated with MAO.[28] Yasuda and coworkers reported bis[1-(arylimino)ethyl]pyridine-$MoCl_3$/MMAO catalytic systems and their dual catalytic functions for ROMP of norbornene and linear polymerization of ethylene.[62] Mu and coworkers
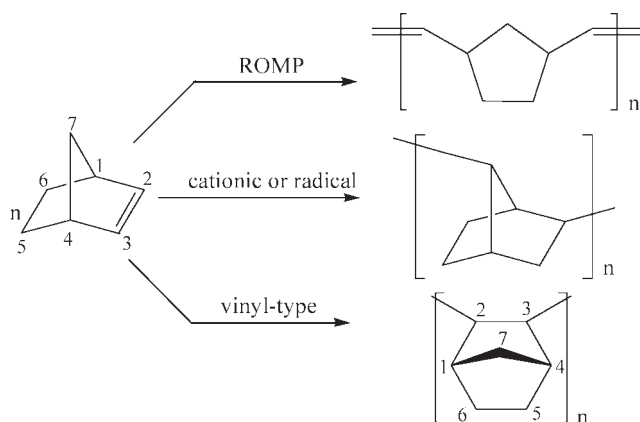
Scheme 1 Three typical types of polymerization of norbornene.

reported two nickel complexes with small steric hindrance of bis(imino)pyridine which exhibit low catalytic activities for ethylene oligomerization upon activation with MAO.[63]

In this contribution, we synthesized a series of nickel (II) complexes with different steric hindrance 2,6-bis(imino)pyridine ligands and investigated their norbornene polymerization and ethylene oligomerization behaviors. Experimental results showed that these nickel complexes displayed good activities for the vinyl polymerization of norbornene upon activation with MAO. Catalytic activities, polymer yield, molecular weight of PNB have been investigated under various reaction conditions.

EXPERIMENTAL

Materials

All manipulations involving air- and moisture-sensitive compounds were carried out under an atmosphere of dried and purified nitrogen using standard Schlenk technique. Methylaluminoxane (10% in toluene), 2,6-diacetylpyridine, 2,6-dimethylaniline, 2,6-diisopropylaniline, and 2,5-ditertbutylaniline were purchased from Aldrich. Anhydrous $NiCl_2$ and $NiBr_2$ were obtained from the corresponding hydrated salts by heating them to 220°C under vacuum condition. Solvents were dried prior to use by refluxing over and distillation from sodium (for THF, toluene and hydrocarbons) or calcium hydride (for dichloromethane, chlorobenzene and acetonitrile). Norbornene (Acros) was purified by distillation over sodium.

Synthesis of compound 2,6-diacetylpyridinebisanil (L1)

L1 was synthesized according to the published literature.[64] Yield: 78%. IR (KBr, cm^{-1}): 3055.8, 2922.4,

1952.0, 1879.0, 1752.0, 1635.4 ($v_{C = N}$), 1572.0, 1480.2, 1441.1, 1384.7, 1361.7, 1317.7, 1214.7, 1170.0, 1076.3, 990.1, 968.4, 909.0, 867.8, 818.7, 771.1, 743.7, 703.7 cm^{-1}. Elements calcd for $C_{21}H_{19}N_3$ (%): C, 80.48; H, 6.11; N, 14.41, Found: C, 80.51; H, 6.09; N, 14.48.

Synthesis of compound 2, 6-diacetylpyridinebis(2,6-dimethylanil) (L2)

L2 was synthesized according to the published literatures.[59,65] The crystal structure of **L2** has been reported by our group.[65] Yield: 82%. IR (KBr, cm^{-1}): 3067.9, 3015.9, 2917.9, 2852.8, 1640.8 ($v_{C = N}$), 1590.2, 1569.8, 1465.5, 1365.1, 1321.7, 1296.7, 1247.9, 1205.4, 1148.7, 1129.1, 1092.9, 991.6, 960.5, 915.1, 871.7, 821.2, 770.5 cm^{-1}. Elements calcd for $C_{25}H_{27}N_3$(%): C, 81.26; H, 7.37; N, 11.37. Found: C, 81.23; H, 7.32; N, 11.39.

Synthesis of compound 2,6-diacetylpyridinebis(2,6-diisopropylanil) (L3)

L3 was synthesized according to the published literature.[59] Yield: 79%. IR (KBr, cm^{-1}):3063.2, 2960.6, 2926.7, 2867.4, 1643.2 ($v_{C = N}$), 1577.56, 1457.55, 1383.5, 1364.6, 1322.5, 1240.1, 1192.4, 1118.3, 1077.6, 935.9, 875.7, 825.6, 767.5, 689.2. Elements Calcd for $C_{33}H_{43}N_3$(%): C, 82.28; H, 9.00; N, 8.72. Found: C, 82.24; H, 8.97; N, 8.69.

Synthesis of compound 2,6-diacetylpyridinebis(2,5-ditertbutylanil) (L4)

L4 was synthesized according to the literature by our group.[61] Yield: 81%. IR (KBr, cm^{-1}): 2958.8, 2866.8, 1635.6 ($v_{C = N}$), 1566, 1491, 1457.7, 1385.5, 1363.6, 1297.6, 1248.9, 1205, 1119.5, 1072, 974, 927, 886, 820, 722, 652 cm^{-1}. Elements calcd for $C_{37}H_{51}N_3$: C, 82.63; H, 9.56; N, 7.81. Found: C, 82.65; H, 9.52; N, 7.83.

Synthesis of complex (2, 6-diacetylpyridinebisanil)NiCl$_2$ (1)

L1 (0.1 mmol) was added to a solution of $NiCl_2$ (0.1 mmol) in THF (15 mL) at room temperature with stirring. The solution turned to brown immediately. After it was stirred at room temperature for 24 h, the solution volume was concentrated about 5 mL. *n*-Hexane (20 mL) was then added to the solution to lead to a precipitate of brown powder, which was subsequently washed using *n*-hexane (3 × 10 mL), filtered, and dried to obtain complex **1**. The yield for this reaction is 82%. IR (KBr, cm^{-1}): 3060, 3019, 2919, 1628 ($v_{C = N}$), 1594, 1485, 1448, 1430, 1371, 1264, 1230, 1103, 1068, 1032, 912, 862, 826, 805, 777, 759, 727, 697, 671, 587, 574, 557, 538 cm^{-1}. Elements calcd

for $C_{21}H_{19}N_3NiCl_2$(%): C, 56.94; H, 4.32; N, 9.49. Found: C, 56.98; H, 4.29; N, 9.48.

Synthesis of complex (2,6-diacetylpyridinebis(2,6-dimethylanil))NiCl₂ (2)

Synthesis of complex **2** was similar to that of complex **1** (brown solid, yield 79%). IR (KBr, cm^{-1}): 3415.9, 1625 ($v_{C=N}$), 1592, 1471, 1371, 1312, 1254, 1216, 1099, 1038, 808, 777, 620 cm^{-1}, Elements calcd for $C_{25}H_{27}N_3NiCl_2$: C, 60.16; H, 5.45; N, 8.42. Found: C, 60.12; H, 5.41; N, 8.46.

Synthesis of complex (2,6-diacetylpyridinebis(2,6-diisopropylanil))NiCl₂ (3)

The procedure was similar synthesis of complex **1**. The product was a red-brown powder with a yield of 85%. The red-brown needle crystal of complex **3** was obtained from the solution containing solvent CH_3CN by slow evaporation. IR (KBr, cm^{-1}): 3407, 2965, 2923, 2867, 1624 (m, C=N), 1585, 1464, 1382, 1320, 1262, 1206, 1087, 1057, 933, 799, 779, 563 cm^{-1}. Element calcd for $C_{33}H_{43}Cl_2N_3Ni$: C, 64.84; H, 7.09; N, 6.87. Found: C, 64.88; H, 7.12; N, 6.83.

Synthesis of complex (2,6-diacetylpyridinebis(2,6-diisopropylanil))NiBr₂ (4)

Complex **4** was synthesized by following the procedure described in synthesis of complex **1**. The red-brown needle crystal of complex **4** was obtained from the solution containing solvent CH_2Cl_2 by slow evaporation. IR (KBr, cm^{-1}): 2962.4, 2867.4, 1623.2 (versus, C=N), 1586.9, 1464.2, 1439.6, 1383.1, 1321.4, 1264.7, 1209.8, 1091.1, 1049.9, 879.6, 799.7, 776.3 cm^{-1}. Elements calcd for $C_{33}H_{43}N_3NiBr_2$: C, 56.60; H, 6.19; N, 6.00, Found: C, 56.64; H, 6.21; N, 5.99.

Synthesis of complex (2,6-diacetylpyridinebis(2,5-ditertbutylanil))NiCl₂ (5)

The brown prismatic crystal of complex **5** was obtained by following the procedure described in section 2.2.7. IR (KBr, cm^{-1}): 32960.4, 2907.2, 2869.3, 1627.5 (versus, C=N), 1589.9, 1497.8, 1467.9, 1382.7, 1265.1, 1208.2, 1136.2, 1068.6, 927.8, 896.0, 818.6, 727.2 cm^{-1}. Elements calcd for $C_{37}H_{51}N_3NiCl_2$(%): C, 66.58; H, 7.70; N, 6.30. Found: C, 66.54; H, 7.72; N, 6.26.

Synthesis of complex (2,6-diacetylpyridinebis(2,5-ditertbutylanil))NiBr₂ (6)

Complex **6** of red-brown powder was obtained in 78% yield by following the procedure described in section 2.2.5. IR (KBr, cm^{-1}): 3068.28, 2961.1, 2910.5, 2868.9, 1623.9 (versus, C=N), 1589.2, 1498.1, 1467.5, 1383.3, 1266.7, 1204.3, 1136.7, 1069.0, 1035.4, 927.5, 898.0, 820.0, 739.5 cm^{-1}. Elements calcd for $C_{37}H_{51}N_3NiBr_2$: C, 58.76; H, 6.80; N, 5.56, Found: C, 58.74; H, 6.76; N, 5.55.

Vinyl polymerization of norbornene

In a typical procedure, the precatalyst was added into a Schlenk tube with chlorobenzene then the chlorobenzene solution of norbornene was added via syringe. The polymerization started by adding MAO into the tube. After appropriate time, the polymerization was terminated by injecting 50 mL 10% acidic ethanol into the reactor. The PNB was isolated by filtration, washed with ethanol, dried in vacuum at 100°C for 48h.

Measurements

IR spectra were recorded using a Nicolet AV-360 spectrometer (KBr pellet technique) from 400 to 4000 cm^{-1}. Elemental analyses were Perkin-Elmer 240C elemental analyzer for C, H and N. The XRD diagram of the polymer powder was obtained using a Phlips X'pert MPD X-ray diffractometer with monochromatic radiation at a wavelength of 0.154 nm. Scanning was performed with 2θ ranging from 5 to 90°. The viscosity-average molar masses (M_v) of the PNB were obtained using the Mark-Houwink coefficients[26,61,66]: α = 0.56, $K = 7.78 \times 10^{-4}$ dL/g.

Crystal structure determination

Data collection for complexes **3–5** was performed at 293 K on a Rigaku *R*-AXIS RAPID Weissenberg IP diffractometer equipped with a graphite-monochromatized Mo-*K*α radiation (λ = 0.71073 Å). Lorentz-Polarization and empirical absorption corrections were applied to the data. The structures were solved by the direct methods with SHELXS-97[67] and refined on F2 using full-matrix least-squares calculations with SHELXL-97.[68] All of non-hydrogen atoms were refined with anisotropic thermal parameters, and all of the hydrogen atoms were placed at the idealized positions with isotropic *U* values of 1.2 times the equivalent isotropic *Us* of their respective parent atoms. Crystal data and refinement parameters for complexes **3–5** are summarized in Table I. The crystallographic data for complexes **3–5** have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC **293462**, **293463,** and **614307,** respectively. Copies of the data can free be obtained from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ (fax: C44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

TABLE I
Crystallographic Data for Nickel Complexes 3–5

| Complexes	$3 \cdot 0.5 H_2O$	$4 \cdot 0.88 H_2O$	$5 \cdot H_2O$
Empirical formula	$C_{33}H_{44}Cl_2N_3NiO_{0.50}$	$C_{33}H_{44.75}Br_2N_3NiO_{0.88}$	$C_{37}H_{53}Cl_2N_3NiO$
Formula weight	620.31	716.00	685.43
Crystal system	Triclinic	Triclinic	Monclinic
Space group	P-1	P-1	$P2(1)/c$
a (Å)	8.7749(3)	8.750(2)	11.617(2)
b (Å)	9.8532(3)	9.9417(18)	26.250(3)
c (Å)	21.0323(7)	20.892(3)	16.032(3)
α (°)	84.1190(11)	83.536(8)	90
β (°)	88.1025(12)	87.849(7)	108.871(6)
γ (°)	65.3378(10)	66.026(7)	90
V (Å³)	1643.81(9)	1649.9(5)	4626.3(14)
Z	2	2	4
D_{calc} (Mg m^{-3})	1.253	1.441	0.984
Crystal size(mm)	$0.48 \times 0.12 \times 0.08$	$0.28 \times 0.15 \times 0.05$	$0.35 \times 0.08 \times 0.07$
μ (mm^{-1})	0.780	3.038	0.560
$F(000)$	658	738	1464
θ_{max}, θ_{min} (°)	25.05, 2.29	27.48, 1.96	27.49, 1.55
Index range			
h	$-9 \rightarrow 10$	$-11 \rightarrow 10$	$0 \rightarrow 15$
k	$-10 \rightarrow 11$	$-12 \rightarrow 0$	$0 \rightarrow 34$
l	$-24 \rightarrow 12$	$-27 \rightarrow 26$	$-20 \rightarrow 19$
R_{int}	0.0587	0.0705	0.1585
No. of independent reflections	5351	6165	10081
No. of observed reflections	4965	2790	5917
No. of variables	361	362	396
Final R indices[$I>2\sigma(I)$]	$R_1 = 0.1271$, $wR_2 = 0.2598$	$R_1 = 0.0934$, $wR_2 = 0.1937$	$R_1 = 0.0676$, $wR_2 = 0.1062$
R indices (all data)	$R_1 = 0.1367$, $wR_2 = 0.2664$	$R_1 = 0.2149$, $wR_2 = 0.2620$	$R_1 = 0.1736$, $wR_2 = 0.1937$
Goodness of fit of F^2	1.019	1.018	1.006
Largest diff. Peak[a](hole)(e Å^{-3})	1.380 (-1.303)	0.978 (-0.538)	0.594 (-0.355)
Δ/σ	0.000, 0.000	0.000, 0.000	0.000, 0.000

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

RESULTS AND DISCUSSION

Syntheses and structures of complexes

The compounds **L1–L4** were prepared in high yield from two equivalents of aniline with one equivalent of 2,6-diacetylpyridine (Scheme 2). Compounds **L1–L4** were characterized by IR spectroscopy and elemental analyses (see experimental section). The crystal structure of **L2** has been reported by our group,[65] showing that three N atoms in **L2** are almost in a line and two imino C=N bonds have distinctive double-bond character. The complexes **1–6** were
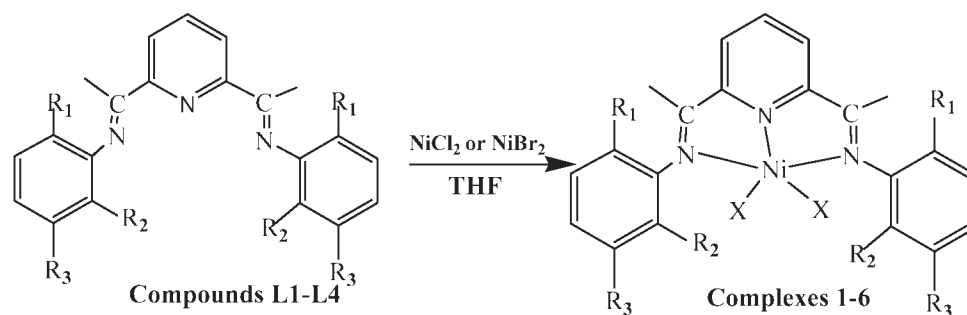
1, NiCl$_2$, R$_1$ = R$_2$ = R$_3$ = H; **2**, NiCl$_2$, R$_1$ = R$_2$ = methyl, R$_3$ = H; **3**, NiCl$_2$, R$_1$ = R$_2$ = isopropyl, R$_3$ = H; **4**, NiBr$_2$, R$_1$ = R$_2$ = isopropyl, R$_3$ = H; **5**, NiCl$_2$, R$_1$ = R$_3$= tertbutyl, R$_2$ = H; **6**, NiBr$_2$, R$_1$ = R$_3$ = tertbutyl, R$_2$ = H.

Scheme 2 Synthesis of compounds **L1–L4** and nickel complexes **1–6**.
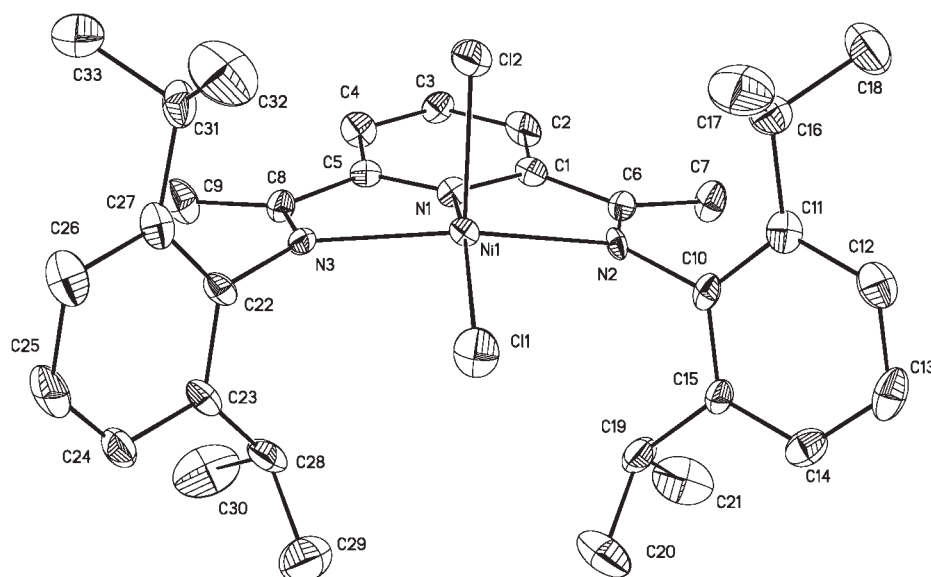
Figure 1 Thermal ellipsoid plot (30%) of complex **3** (H_2O molecule and hydrogen atoms are omitted for clarity).

prepared in high yield by treating NiX_2 (X = Cl or Br) with the compounds **L1–L4** in THF (Scheme 2). All of the complexes **1–6** were characterized by elemental analyses and IR spectroscopy (see experimental section). The elemental analysis results revealed that the compositions of these complexes were in accord with the formula $NiLX_2$(X = Cl or Br).

The IR spectra of the compounds **L1–L4** show that the C=N stretching frequency appears at a range 1635.4–1643.2 cm^{-1}. In complexes **1–6,** the C=N stretching vibrations shift toward lower frequencies and its intensity greatly reduces, which indicates the coordination interaction between the imino nitrogen atoms and the metal ions. The molecular structures of the complexes **3–5** are shown in Figures 1–3, respectively. The selected bond lengths and angles of the complexes **3–5** are presented in Tables II–IV.

Complex **3** bearing $NiCl_2$ and substituted 2,6-diisopropylanil displays an approximate C_s symmetry about a plane containing the nickel atom, the two chloro atoms, and the pyridyl nitrogen atom (Fig. 1). The dihedral angles between the phenyl rings and the plane formed by three coordinated nitrogen

atoms are 79.20(37) and 79.21(26)°, respectively. The dihedral angle of the two phenyl rings is 79.30(30)°. The Cl1 and Cl2 atoms deviate from the plane formed by three nitrogen atoms by 0.0312 and 0.6036 Å, respectively. The nickel atom deviates by 0.1731 Å from the plane formed by the three N atoms and Cl1 atom. The coordination geometry of the central nickel can be best described as distorted square pyramidal [Fig. 4(a)]. As previously observed,[63] the Ni-N(imino) bonds [2.156(6) and 2.161(7) Å] are longer than the Ni-N(pyridyl) bond [1.996(7) Å]. The two imino C=N bonds have distinctive double-bond character because two C—N distances are1.291(11) and 1.297(11) Å. The N(2)-Ni(1)-N(3) angle is 149.1(3)°. Two N (1)-Ni(1)-Cl angles are unsymmetrical: one is 154.9(2)°, whereas another one is 91.5(2)° (Table II).

The structure of complex **4** bearing $NiBr_2$ andsubstituted 2,6-diisopropylanil is isostructural with that of complex **3** (Table III, Fig. 2). Complex **5** bearing substituted 2,5-ditertbutylanil displays an approximate C_2 symmetry about a plane containing the nickel atom, the two chloro atoms, and the pyridyl

TABLE II
Selected Bond Lengths (Å) and Angles (°) for Complex 3

Ni(1)-N(1)	1.996 (7)	Ni(1)-N(2)	2.156 (6)
Ni(1)-N(3)	2.161 (7)	Ni(1)-Cl(1)	2.233 (3)
Ni(1)-Cl(2)	2.289 (3)	N(2)-C(6)	1.291 (11)
N(2)-C(10)	1.438 (11)	N(3)-C(8)	1.297 (11)
N(1)-Ni(1)-N(3)	76.7 (3)	N(1)-Ni(1)-N(2)	76.7 (3)
N(1)-Ni(1)-Cl(1)	154.9 (2)	N(2)-Ni(1)-N(3)	149.1 (3)
N(3)-Ni(1)-Cl(1)	98.9 (2)	N(2)-Ni(1)-Cl(1)	98.6 (2)
N(2)-Ni(1)-Cl(2)	97.8 (2)	N(1)-Ni(1)-Cl(2)	91.5 (2)
Cl(1)-Ni(1)-Cl(2)	113.59 (12)	N(3)-Ni(1)-Cl(2)	98.3 (2)

TABLE III
Selected Bond Lengths (Å) and Angles (°) for Complex 4

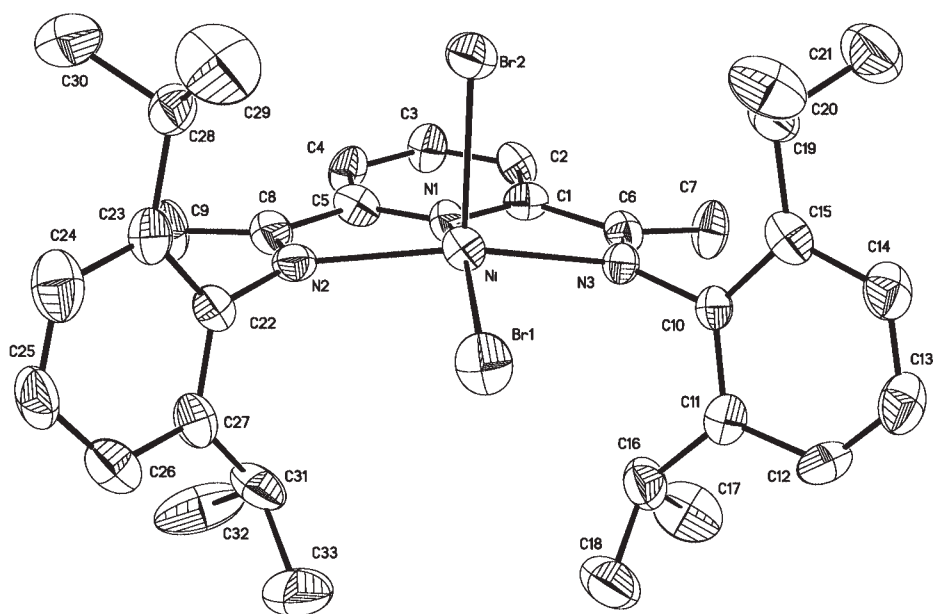|			
Ni-N(1)	1.938 (9)	Ni-N(2)	2.179 (9)
Ni-N(3)	2.184 (8)	Ni-Br(1)	2.3525 (19)
Ni-Br(2)	2.4262 (19)	N(2)-C(8)	1.265 (15)
N(2)-C(22)	1.425 (14)	N(3)-C(6)	1.264 (13)
N(3)-C(10)	1.432 (12)	N(1)-Ni-N(2)	76.4 (4)
N(1)-Ni-N(3)	76.4 (3)	N(2)-Ni-N(3)	148.8 (3)
N(1)-Ni-Br(1)	155.7 (3)	N(2)-Ni-Br(1)	99.7 (2)
N(3)-Ni-Br(1)	98.7 (2)	N(1)-Ni-Br(2)	91.9 (3)
N(2)-Ni-Br(2)	98.6 (2)	N(3)-Ni-Br(2)	97.3 (2)
Br(1)-Ni-Br(2)	112.44 (7)		

Figure 2 Thermal ellipsoid plot (30%) of complex **4** (H_2O molecule and hydrogen atoms are omitted for clarity).

nitrogen atom (Fig. 3). The Ni(1)-N (pyridyl) bond [2.032(2) Å] is significantly shorter than the Ni-N (imino) bonds [2.249(2) and 2.292(2) Å]. The planes of the phenyl rings are orthogonally oriented to the plane formed by the three N atoms. The dihedral angle of the two phenyl rings is 79.69(9)°. The nickel atom deviates by 0.0295 Å from the plane formed by three coordinated nitrogen atoms. The Cl(1)-Ni(1)-Cl(2) angle is 116.22(4)°. Two N (1)-Ni(1)-Cl angles are unsymmetrical: one is 113.42(8)°, while another one is 130.30(9)°. The N(3)-Ni(1)-N(2) bond angle is

149.88(8)° (Table IV). The coordination geometry of the central nickel can be best described as distorted trigonal bipyramidal, with the pyridyl nitrogen atom and the two chloro atoms forming the equatorial plane (Fig. 4c), which is similar to that with 2,5-tert-butylphenyl substituted Co complex.[61] The corresponding bond lengths and angles are also close to those of Co complex.

The crystal structure of complex **1** bearing 2,6-diacetylpyridinebisanil has been reported in the literature.[63] The co-ordination geometry of the central
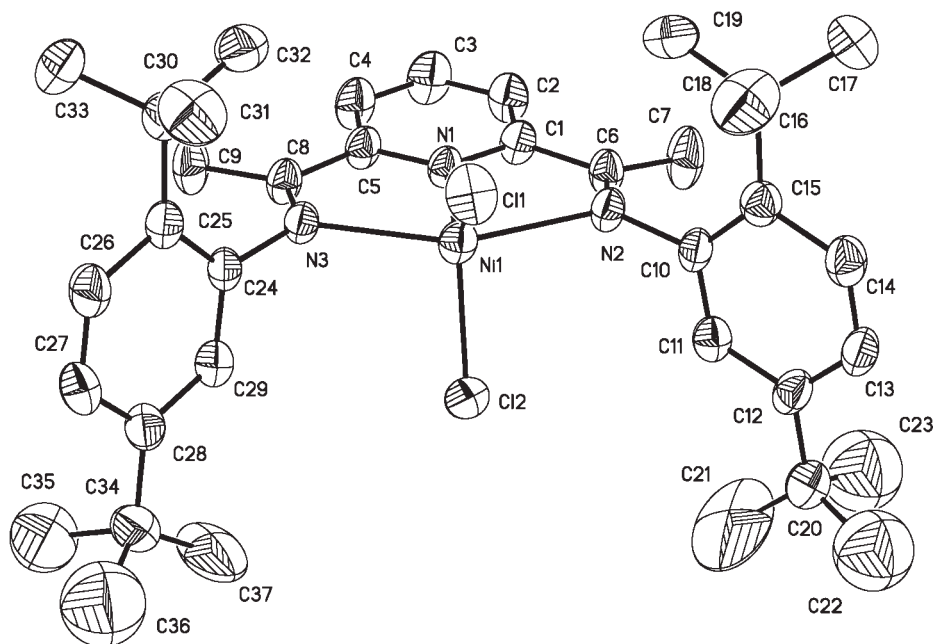

Figure 3 Thermal ellipsoid plot (30%) of complex **5** (H_2O molecule and hydrogen atoms are omitted for clarity).

TABLE IV
Selected Bond Lengths (Å) and Angles (°) for Complex 5

Ni(1)-N(1)	2.032 (2)	Ni(1)-Cl(1)	2.2326 (10)
Ni(1)-N(3)	2.249 (2)	Ni(1)-Cl(2)	2.2621 (11)
Ni(1)-N(2)	2.292 (2)	N(2)-C(6)	1.275 (4)
N(2)-C(10)	1.444 (4)	N(3)-C(8)	1.277 (4)
N(3)-C(24)	1.446 (4)		
N(1)-Ni(1)-N(3)	75.22 (9)	N(1)-Ni(1)-Cl(1)	130.30 (9)
N(1)-Ni(1)-Cl(2)	113.42 (8)	Cl(1)-Ni(1)-N(3)	98.81 (7)
N(3)-Ni(1)-Cl(2)	99.12 (7)	Cl(1)-Ni(1)-Cl(2)	116.22 (4)
Cl(1)-Ni(1)-N(2)	98.03 (7)	N(1)-Ni(1)-N(2)	74.83 (9)
Cl(2)-Ni(1)-N(2)	95.55 (7)	N(3)-Ni(1)-N(2)	149.88 (8)

nickel in complex **1** is described as distorted trigonal bipyramidal, which is similar to that in complex **5**, but different from those in complexes **3** and **4**. In complex **1**, the nickel atom deviates from the plane formed by the three N atoms by 0.045 Å. The Ni-N(imino) bonds [2.134(12) and 2.109(14) Å] are also

longer than the Ni-N(pyridyl) bond [1.960(4) Å]. The two imino C=N bonds also have typical double bond character as C=N bond lengths are 1.310(20) and 1.240(30) Å, respectively.

Norbornene polymerization

The nickel complexes bearing bulky steric hindrance 2,6-bis(imino)pyridine ligands were similar to the iron and cobalt complexes of 2,6-bis(imino)pyridine, which are good candidates for catalytic ethylene polymerization reactions. However, all of the Ni complexes **1–6** can not catalyze ethylene to produce high molecular weight polyethylene at atmospheric pressure of ethylene when activated with MAO.

Preliminary experiments have indicated that neither Ni(II) complexes nor MAO alone was able to catalyze norbornene polymerization. However, in

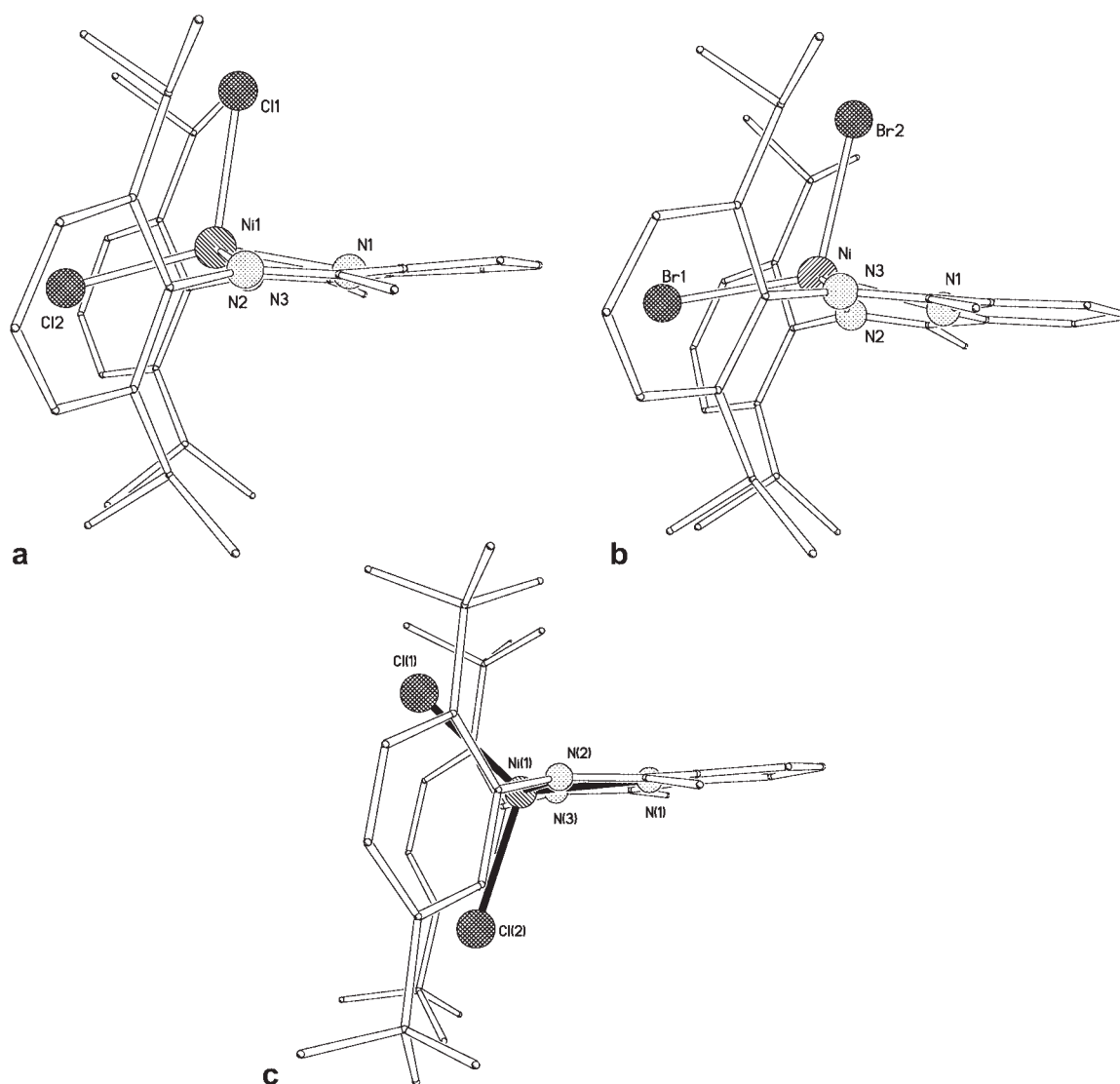**Figure 4** Side-on view, perpendicular to the plane of the three ligands nitrogen atoms of the complex **3** (a), **4** (b) and **5** (c), showing the pronounced differences in coordination geometry and the deviation of the metal centers from the ligand plane.

TABLE V
Different Nickel Complexes on Polymerization of Norbornene[a]

Entry	Complex	Yield (g)	Activity[b]	$M_v (\times 10^5$ g/mol)
1	**1**	0.95	1.9	5.5
2	**2**	1.40	2.8	5.4
3	**3**	2.35	4.7	3.5
4	**4**	2.15	4.3	3.2
5	**5**	2.20	4.4	3.1
6	**6**	2.10	4.2	3.2

[a] Polymerization conditions: 0.5 µmol catalyst; Al/Ni = 500; NB/Ni = 100000; Solvent: chlorobenzene; total volume, 15 mL; 30°C; reaction time: 1 h.
[b] [$\times 10^6$ g PNB/(mol Ni h)].

TABLE VII
Influence of the Reaction Temperature on Catalytic Activity of Complex 3 and the Molecular Weight of the PNB[a]

Entry	T(°C)	Yield (g)	Activity[b]	$M_v (\times 10^5$ g/mol)
13	0	1.90	3.8	0.99
14	30	2.35	4.7	3.5
15	50	2.25	4.5	2.1
16	70	2.30	4.6	0.41

[a] Polymerization conditions: 0.5 µmol catalyst; Al/Ni = 500; NB/Ni = 100000; Solvent: chlorobenzene; total volume, 15 mL; reaction time: 1 h.
[b] [$\times 10^6$ g PNB/(mol Ni h)].

combination with MAO, these Ni complexes **1–6** exhibit high catalytic activity for norbornene polymerization under moderate conditions. The polymerization results using Ni (II) complexes **1–6** activated with MAO are summarized in Table V. It showed that all of Ni (II) complexes can catalyze the polymerization of norbornene to produce polymer with high activities ($1.9–4.7 \times 10^6$ g PNB/(mol Ni h),) and high molecular weights (M_v up to 10^5 g/mol). In these experiemts, chlorobenzene was used as solvent because catalytic activities increased with increasing polarity of the solvent in the catalyst system of Ni (II)/MAO for norbornene polymerization.

A comparison in Table V reveals that the structures of the complexes evidently affect the polymer yields, molecular weight and the catalyst activity. With increasing the steric hindrance of the precatalysts, the polymer yields and the activity increase while the molecular weight decreases. The activity of complexes **3** bearing 2,6-diisopropy substituent is up to 4.7×10^6 g PNB/(mol Ni h) (Entry 3, Table V) which is similar to that of complex **5** bearing 2,5-ditertbutyl substituent (4.4×10^6 g PNB/(mol Ni h) Entry 5, Table V).

To examine the effect of the halide substituent on the precatalyst in the polymerization, four complexes **3–6,** with identical metal centers and bis(imino)pyridine ligands, but with chloride for **3** and **5** and bromide for **4** and **6,** were prepared. The activity of the dibromide precatalyst **4** (4.3×10^6 g PNB/(mol Ni h)) is slightly lower than the dichloride **3** (4.7×10^6 g PNB/(mol Ni h)). The complexes **5** and **6** have the similar trends. The molecular weights of polymer obtained from the complexes **3–6** were in the same order ($3.1–3.5 \times 10^5$ g/mol, Table V).

To systematically investigate the effects of reaction parameters on vinyl-polymerization of NB, the complex (2, 6-diacetylpyridinebis(2,6-diisopropylanil))-NiCl$_2$ (**3**) was studied by changing the reaction parameters such as the Al/Ni ratio, reaction temperature and time. The results of polymer yield, catalytic activity as well as the molecular weight are listed in Tables VI–VIII, respectively, along with the reaction parameters.

The MAO amount is essential for the polymerization of norbornene. Polymer yield, catalytic activities and molecular weight increased with increasing the Al/Ni molar ratio from 500 to 100. When the Al/Ni

TABLE VI
The Relationship of Al/Ni Ratio, Polymer Yield, Catalytic Activity of the Complex 3 and the Molecular Weight of the PNB[a]

Entry	Al/Ni	Yield (g)	Activity[b]	$M_v (\times 10^5$ g/mol)
7	100	1.82	3.64	3.3
8	500	2.35	4.7	3.5
9	1000	2.20	4.4	2.9
10	1500	2.25	4.5	2.5
11	2000	2.40	4.8	1.5
12	2500	2.30	4.6	0.42

[a] Polymerization conditions: 0.5 µmol catalyst; NB/Ni = 100000; Solvent: chlorobenzene; total volume, 15 mL; 30°C; reaction time: 1 h.
[b] [$\times 10^6$ g PNB/(mol Ni h)].

TABLE VIII
The Relationship of Reaction Time and Catalytic Activity of Complex 3 and the Molecular Weight of the PNB[a]

Entry	Time (h)	Yield (g)	Activity[b]	$M_v (\times 10^5$ g/mol)
17	0.25	0.30	2.40	1.9
18	0.50	0.87	3.50	3.8
19	1	2.35	4.70	3.5
20	4	3.02	1.51	4.2
21	8	3.86	0.96	3.5
22	12	4.38	0.73	3.6
23	24	4.65	0.38	3.8

[a] Polymerization conditions: 0.5µmol catalyst; Al/Ni = 500; NB/ Ni = 100000; Solvent: chlorobenzene; total volume, 15 mL; 30°C; reaction time: 1 h.
[b] [$\times 10^6$ g PNB/(mol Ni h)].

molar ratio is in the range 1000 to 2500, variation of the Al/Ni had little effects on parameters tested.

The reaction temperature also considerably affects the catalytic activities and molecular weight (Table VII). With increasing reaction temperature to 30°C, the catalytic activity reached the highest value at 4.7 $\times 10^6$ g PNB/(mol Ni h). When the temperature further increased, the activity remained constant value, indicating that the activity center was stable in temperature range of 30–70°C. However, the molecular weight of PNB increased to 3.5×10^5 g/mol at 30°C, it is then drastically decreased to 0.41×10^5 g/mol at 70°C.

The results of norbornene polymerization with time are presented in Table VIII. The yield of polymer increased with the reaction time. The catalytic activity increased in the first one hour, then decreased dramatically due to a significant decrease in the monomer concentration of the reaction mixture. The M_v of the polymer increased in the first 30 min then tended to remain constant.

All of the IR spectra and ^{1}H-NMR spectra of the obtained PNB were similar and characteristic of the addition-type PNB. In FTIR spectra (IR (KBr): 2946, 2868, 1474, 1451, 1372, 1296, 1258, 1221, 1190, 1148, 1108, 1041, 942, 893, 806, 728 cm^{-1}), there are no absorptions at 1680–1620 cm^{-1}, as well as at 960 cm^{-1} and 735 cm^{-1}, which are assigned to the *trans* and *cis* form of double bonds, respectively, are characteristic of the ROMP structure of PNB.[69] ^{1}H-NMR spectra confirmed the above conclusions. ^{1}H-NMR spectra [^{1}H-NMR: δ 0.9–3.0 (maxima at 1.14, 1.21, 1.56, 2.30, 2.37 ppm)] show signals in the 0.9–3.0 ppm range, which indicate the *cis* and *trans* form of double bonds when no resonances are displayed at about 5.1 and 5.3 ppm.[55] This indicates the presence of the ring-opening metathesis polymerization (ROMP) structure. Our attempts to determine the glass transition temperature (T_g) of PNB failed, and the DSC studies did not give an endothermic signal upon heating to the decomposition temperature (above 450°C). All the polymer samples obtained were soluble in chlorobenzene and cyclohexane at room temperature which indicated low stereoregular.[26] Figure 5 shows the X-ray diffraction (XRD) spectra of the obtained PNB. The spectra display two broad halos at 2θ of ∼ 11° and 18° that can be attributed to a short range order, or pseudoperiodicity of the arrangement of the bicycle units along the chain. This is almost in agreement with the results reported in the literatures.[70–74] No traces of Bragg refractions are revealed at crystalline regions. Therefore, the PNB herein is amorphous.

In general, these complexes showed good activities for norbornene polymerization in the presence of MAO. Several parameters, including the nature of catalytic precursors, concentration of MAO, reaction
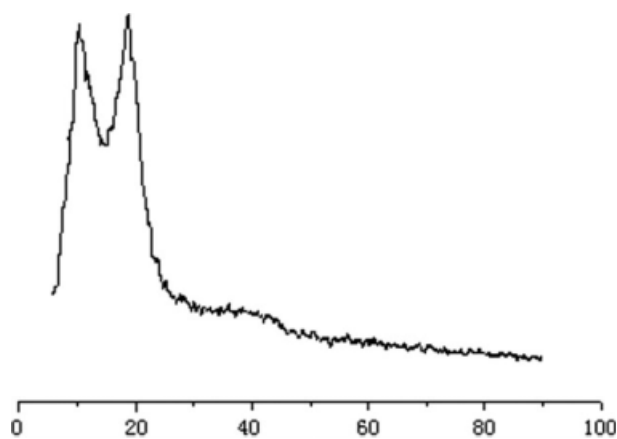

Figure 5 XRD diagram of PNB obtained with **3**/MAO.

temperature and reaction time have some effect on the activities of the complexes and the molecular weight of the PNB. Compared to the 2,6-bis(imino)-pyridyl iron, cobalt, and chromium complexes[28,61] and other nickel- and palladium-based complexes activated with MAO,[75–77] these nickel complexes have less activity than the above complexes having activities up to 10^7 g/mol h.[12–26]

CONCLUSIONS

We have synthesized and characterized 2,6-bis(imino)pyridyl nickel complexes **1–6** and determined molecular structures of complex **3–5** from single X-ray diffraction data. The experimental results show that these complexes display high catalytic activities to the vinyl polymerization of norbornene when activated with MAO. Activities, polymer yield and molecular weight can be optimized by reaction conditions such as temperature, time and the Al/Ni ratio. The PNB obtained is amorphous and soluble in halogenated aromatic hydrocarbons at room temperature.

References

1. Aguero, A.; Kress, J. J. Chem Soc Chem Commun 1985, 12, 793.
2. Dragutan, V.; Balaban, A. T.; Dimonie, M.; Olefin Metathsis and Ring Opening Polymerization of Cyclo-olefins, Wiley Interscience: Chichester, 1985; p 1.
3. Gaylord, N. G.; Deohande, A. B.; Mandal, B. M.; Martan, M. J. Macromol Sci 1977, 5, 1053.
4. Sartori, G. F.; Ciampelli, F.; Cameli, N. Chim Ind 1963, 45, 1479.
5. Gibson, V. C.; Spitzmesser, S. K. Chem Rev 2003, 103, 283.
6. Rush, S.; Reinmuth, A.; Risse, W. Macromolecules 1997, 30, 7375.
7. Seehof, N.; Mehler, C.; Breunig, S.; Risse, W. J Mol Catal 1992, 76, 219.
8. Janiak, C.; Lassahn, P. G. J Mol Catal A Chem 2001, 166, 193.
9. Sartori, G.; Ciampelli, F. C.; Cameli, N. Chim Ind (Milan) 1963, 45, 1478.

10. Koinzer, J. P.; Langbein, U.; Taeger, E. Ger. Offen. 2,421,838 (1975).VEB Leuna-Werke (GDR), Chem Abstr 1976, 84, 60227y.

11. Tsujino, T.; Saegusa, T.; Furukawa, J. Makromol Chem 1965, 85, 71.

12. Berchtold, B.; Lozan,V.; Lassahn, P. G.; Janiak, C. J Polym Sci A 2002, 40, 3604.

13. Zhu, Y.-Z.; Liu, J.-Y.; Li, Y-S; Tong, Y.-J. J Organomet Chem 2004, 689, 1295.

14. Hou, J.-X.; Sun; W.-H. Zhang, D.-H.; Chen, L.–Y. J Mol Catal A Chem 2005, 231, 221.

15. Gui, G.-Q.; Bao, F.; Gao, H.-Y.; Zhu, F.-M.; Wu, Q. Appl Organomet Chem 2005, 19, 627.

16. Bao, F.; Lu, X. Q.; Qiao, Y. Q.; Gui, G. Q.; Gao, H. Y.; Wu, Q. Appl Organomet Chem 2005, 19, 957.

17. Chang, F.; Zhang, D.; Xu, G.-Y.; Yang, H.-J.; Li, J.-T.; Song, H.-B.; Sun, W.-H. J Organomet Chem 2004, 689, 936.

18. Suzuki, H.; Matsumura, S.; Satoh, Y.; Sogoh, K.; Yasuda, H. Reac Funct Polym 2004, 58, 77.

19. Wang, H.-Y.; Zhang, J.; Meng, X.; Jin, G.-X. J Organomet Chem 2006, 691, 1275.

20. Wang, H.-Y.; Meng, X.; Jin, G.-X. Dalton Trans 2006, 21, 2579.

21. Chen, F. T.; Tang, G. R.; Jin, G.-X. J Organomet Chem 2007, 692, 3435.

22. Tang, G. R.; Lin, Y. J.; Jin, G.-X. J Organomet Chem 2007, 692, 4106.

23. He, X.-H.; Chen, Y.-W.; Liu, Y.-M.; Yu, S.-X.; Hong, S.-G.; Wu, Q. J Polym Sci A: Polym Chem 2007, 45, 4739.

24. Huang, Y.-B.; Tang, G.-R.; Jin, G.-Y.; Jin, G.–X. Organmometalics 2008, 27, 259.

25. Yang, H.-J.; Li, Z.-L.; Sun, W.-H. J Mol Cata A Chem 2003, 206, 23.

26. Mast, C.; Krieger, M.; Dehnicke, K.; Greiner, A. Macromol Rapid Commun 1999, 20, 232.

27. Yasuda, H.; Nakayama, Y.; Sato, Y. J Organomet Chem 2004, 689, 744.

28. Frédéric, P.; Pierre, J. L.; Marcel, W.; Jacky, K. Macromol Rapid Commun 2003, 24, 768.

29. Alt, F. P.; Heitz, W.; Macromol Chem Phys 1951 1998, 199.

30. Peuckert, U.; Heitz, W. Macromol Rapid Commun 1998, 19, 159.

31. Woodman, T. J.; Sarazin, Y.; Garratt, S.; Fink, G.; Bochmann, M. J Mol Catal A Chem 2005, 235, 88.

32. Yoshida, Y.; Matsui, S.; Fujita, T. J Organomet Chem 2005, 690, 4382.

33. Tang, L.-M.; Hu, T.; Bo, Y.-J.; Li, Y.-S.; Hu, N.-H. J Organomet Chem 2005, 690, 3125.

34. Kaminsky, W.; Noll, A. Polym Bull 1993, 31, 175.

35. Sacchi, M. C.; Sonzogni, M.; Losio, S.; Forlini, F.; Locatelli, P.; Tritto, I.; Licchelli, M. Macromol Chem Phys 2001, 2052, 202.

36. Lassahn, P. G.; Lozan, V.; Timco, G. A.; Christian, P.; Janiak, C.; Winpenny, R. E. P. J Catal 2004, 222, 260.

37. Lassahn, P. G.; Lozan, V.; Wu, B.; Weller, A. S.; Janiak, C. Dalton Trans 2003, 37, 4437.

38. Haselwander, T. F. A.; Heitz, W.; Maskos, M. Macromol Rapid Commun 1997, 18, 689.

39. Surrah, A. S. A.; Thewalt, U.; Rieger, B. J Organomet Chem 1999, 587, 58.

40. Puech, L.; Perez, E.; Rico-Lattes, I.; Bon, M.; Lattes, A. Colloids Sur A 2000, 167, 123.

41. Wang, L.-Y.; Li, Y.-F.; Zhu, F.-M.; Wu, Q. Eur Polym Mater 2006, 42, 322.

42. Myagmarsuren, G.; Lee, K.-S.; Jeong, O.-Y.; Ihm, S.–K. Catal Commun 2003, 4, 615.

43. Surrah, A. S. A.; Lappalainen, K.; Repo, T.; Klinga, M.; Leskela, M. H.; Hodali, A. Polyhedron 2000, 19, 1601.

44. Kiesewetter, J; Arikan, B. A.; Kaminsky, W. Polymer 2006, 47, 3302.

45. Myagmarsuren, G.; Lee, K.-S.; Jeong, O.-Y.; Ihm, S.–K. Polymer 2005, 46, 3685.

46. Abu-Surrah, A. S.; Rieger, B. J Mol Catal A Chem 1998, 128, 239.

47. Shin, D.-M.; Son, S.-U.; Hong, B.-K.; Chung, Y.-K.; Chun, S.-H. J Mol Catal A Chem 2004, 210, 35.

48. Kang, M.; Sen, A. Organometallics 2004, 23, 5396.

49. Funk, J. K.; Andes, C. E.; Sen, A. Organometallics 2004, 23, 1680.

50. Lu, X. Q.; Bao, F.; Kang, B. S.; Wu, Q.; Liu, H. Q.; Zhu, F. M. J Organomet Chem 2006, 691, 821.

51. Carlini, C.; Giaiacopi, S.; Marchetti, F.; Pinzino, C.; Galletti, A. M. R.; Sbrana, G. Organometallics 2006, 25, 3659.

52. Wang, C.; Friedrich, S.; Younkin, T. R.; Li, R. T.; Grubbs, R. H.; Bansleben, D. A.; Day, M. W. Organometallics 1998, 17, 3149.

53. Younkin, T. R.; Connor, E. F.; Henderson, J. I.; Friedrich, S. K.; Grubbs, R. H.; Bansleben, D. A. Science 2000, 287, 460.

54. Hicks, F. A.; Brookhart, M. Organometallics 2001, 20, 3217.

55. Hicks, F. A.; Jenkins, J. C.; Brookhart, M. Organometallics 2003, 22, 3533.

56. Jenkins, J. C.; Brookhart, M. Organometallics 2003, 22, 250.

57. Small, B. L.; Brookhart, M. J Am Chem Soc 1998, 120, 7143.

58. Small, B. L.; Brookhart, M.; Bennett, A. M. A. J Am Chem Soc 1998, 120, 4049.

59. Britovsek, G. J. P.; Bruce, M.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; Mastroianni, S.; McTavish, S.; Redshaw, J. C.; Solan, G. A.; Strömberg, S.; White, A. J. P.; Williams, D. J. J Am Chem Soc 1999, 121, 8728.

60. Gibson, V. C.; Redshaw, C.; Solan, G. A. Chem Rev 2007, 107, 1745.

61. Chen, J.-X.; Huang, Y.-B.; Li, Z.-S.; Zhang, Z.-C.; Wei, C.-X.; Lan, T.-Y.; Zhang, W.-J. J Mol Catal A Chem 2006, 259, 133.

62. Hiya, K.; Nakayama, Y.; Yasuda, H. Macromolecules 2003, 36, 7916.

63. Fan, R.-Q.; Zhu, D.-S.; Mu, Y.; Li, G.-H.; Feng, S.-H. Chem J Chin Univ 2005, 26, 1215.

64. Sacconi, L.; Morassi, R.; Midollini, S. J. Chem Soc A 1968, 14, 1510.

65. Huang, Y.-B.; Ma, X.-L.; Zheng, S.-N.; Chen, J.-X.; Wei, C.-X. Acta Cryst E 2006, 62, o3044.

66. Wang, W.-H.; Jin, G.-X. Inorg Chem Commun 2005, 8, 109.

67. Sheldrick, G. M. SHELXL-97, Program for X-ray Crystal Structure Refinement. University of Göttingen: Göttingen, Germany, 1997.

68. Sheldrick, G. M. SHELXS-97, Program for X-ray Crystal Structure Solution. University of Göttingen: Göttingen, Germany, 1997.

69. Haselwander, T. F. A.; Heitz, W.; Krügel, S. A.; Wendorff, J. H. Macromolecules 1997, 30, 5345.

70. Haselwander, T. F. A.; Heitz, W.; Krügel, S. A.; Wendor, J. H. Macromol Chem Phys 1996, 197, 3435.

71. Zhao, C. T.; Ribeiro, M. R.; Pinho, M. N.; Subrahmanyam, V. S.; Gil, C. L.; Lima, A. C. Polymer 2001, 42, 2455.

72. Wang, H.-Y.; Jin, G.-X. Eur J Inorg Chem 2005, 9, 1665.

73. Wang, X.; Jin, G.-X. Organometallics 2004, 23, 6319.

74. Wang, X.; Liu, S.; Jin, G.-X. Organometallics 2004, 23, 6002.

75. Li, X.-F.; Li, Y.-S J Polym Chem 2002, 40, 2680.

76. Lasshn, P. G.; Janiak, C.; Oh, J. S. Macromol Rapid Commun 2002, 23, 16.

77. Gao, H.-Y.; Pei, L.-X.; Li, Y.-F.; Zhang, J.-K.; Wu, Q. J Mol Catal A Chem 2008, 280, 81.