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Vinyl polymerization of norbornene catalyzed by a new bis(β-ketoamino)nickel(II) complex–methylaluminoxane system

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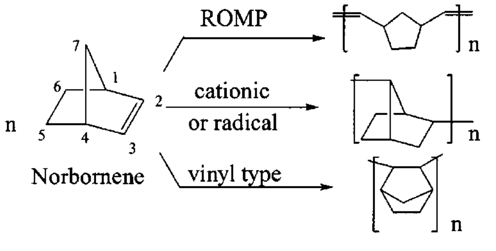
A new β-ketoimine ligand was prepared through traditional condensation of 2-acetylcyclohexanone with 1-naphthylamine. Consequently, the new moisture- and air-stable bis(β-ketoamino)nickel(II) complex $Ni[2\text{-}CH_3C(O)C_6H_8(=NAr)]_2$ (Ar = naphthyl) was synthesized and characterized. The solid-state structures of the ligand and complex have been determined by single-crystal X-ray diffraction. Additionally, the new complex is a highly active catalyst precursor for polymerization of norbornene in combination with methylaluminoxane. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: late-metal catalyst; β-ketoimine; nickel complex; norbornene polymerization

INTRODUCTION

Norbornene (bicyclo[2.2.1]hept-2-ene; NBE) and its derivatives can be homo-polymerized via ring-opening olefin metathesis (ROMP), cationic (or radical) polymerization and vinyl (or addition) polymerization (see Scheme 1). Each route leads to its own polymer type that is different in structure and properties from the other two. Since the first report in 1954 by Andersen and Merkling,[1] ROMP has been well studied. This type of polymerization can be carried out by a variety of transition-metal complexes with high oxidation states. The corresponding polymers, containing one double bond in each repeating unit, following vulcanization or hydrogenation of the double bonds in the polymer backbone have been commercialized. The cationic and the radical polymerization of NBE were first described in 1967,[2] and the polymers obtained via these kinds of route show a 2,7-linkage. Little is known about cationic or radical polymerization of NBE, which mostly result in low molecular weight materials (molecular weight <1000) with low yields because of rearrangements and transfer reactions.[3,4]

The vinyl polymerization of NBE was first reported by Sartori *et al.*[5] in 1963. The NBE addition polymer with 2,3-insertion displays a characteristic rigid random coil conformation, which shows 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.[6–8] Therefore, NBE addition polymers and their derivatives are attractive materials for the manufacture of microelectronic and optical devices. The vinyl-type polynorbornene (PNBE) can be prepared catalytically using metal complexes, such as nickel,[9–13] palladium,[14–19] cobalt,[20,21] zirconium,[22–25] chromium,[26] titanium[27] and iron.[28] Generally, these precatalytic metal complexes require a cocatalyst (like methylaluminoxane (MAO)) for their activation. In order to explore the possibility of obtaining this interesting class of polymers with new structures, the design of new catalysts for vinyl polymerization of NBE is still required.



Scheme 1. Three different types of polymerization for NBE.

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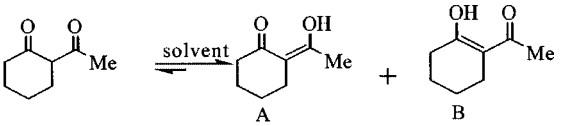
β-Ketoimines are common Schiff bases that can be obtained from traditional 1 : 1 (50 mol% excess) condensation of *β*-diketones with primary amines.[29] These bases are capable of existing in any of three tautomeric forms: Schiff base, ketoamine and enimine. The interchange between the last two tautomers involves a small displacement in the equilibrium position of the acidic proton. In most solvents (acetone is always an exception), these compounds are virtually completely tautomerized to the ketoamine form.[30] As a result, through removing the acid proton with a strong base, like KOC(CH_3)$_3$, some metal complexes bearing *β*-ketoamino ligands, including bis(*β*-ketoamino)nickel(II) complexes, bis(*β*-ketoamino)cobalt(II) complexes and bis(*β*-ketoamino)titanium(IV) complexes, have been prepared and studied.[31–36]

As promising alternatives to both traditional Ziegler–Natta and metallocene catalysts for the polymerization of olefins, late-metal catalysts for the polymerization of olefins are becoming a research priority (see Refs 37–42 for recent reviews). Many significant advances, especially involving nickel catalysts, have been made during last decade. Recently, bis(*β*-ketoamino)nickel(II) complexes have sparked new interest in developing late-metal catalysts for olefin polymerization. Recently, bis(*β*-ketoamino)nickel(II) complexes prepared through KOC(CH_3)$_3$ deprotonation, which can serve as active catalyst precursors for methyl methacrylate (MMA) polymerization, were first reported.[43] The related nickel complexes prepared using NaH-promoted deprotonation were found to be active precatalysts for NBE polymerization.[44] In this paper, with *n*-BuLi as base, we report the synthesis, structural characterization, and NBE polymerization behavior of a new nickel complex bearing two *β*-ketoamino ligands.

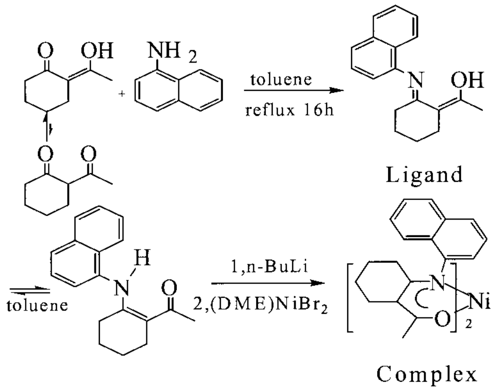
RESULTS AND DISCUSSION

Ketoimine ligand and bis(*β*-ketoamino)nickel(II) complex syntheses

One *N*-aryl-substituted *β*-ketoimine ligand, 2-(naphthyl) amino-1-cyclohexyl methyl ketone, was prepared by conventional Schiff-base condensation of 2-acetylcyclohexanone and 1-naphthylamine in 1 : 1 molar ratio by refluxing in toluene with removal of water. When the molar ratio of the diketone to the amine was changed from 1 : 1 to 1 : 2, or even to 1 : 3, we could not obtain the corresponding *β*-diimine ligand; the final compound was still the same *β*-ketoimine ligand, just like other *β*-diketones.[45] Moreover, condensation only occurs at the cyclohexanone carbonyl rather than at the acetyl carbonyl due to steric hindrance. Given the well-known keto–enol tautomerism, most *β*-diketones transform easily to enols in solution. Here, 2-acetylcyclohexanone can form two enols (see Scheme 2), A and B in acid solutions.[46] Compared with enol A, the steric hindrance of enol B makes it difficult to obtain nucleophilic addition of the amine of the acetyl carbonyl owing to the methyl group. The subsequent reaction of the ligand with (DME)NiBr$_2$ (DME = 1, 2-dimethoxyethane) in the presence of *n*-BuLi leads to formation of the corresponding bis(*β*-ketoamino)nickel(II) complex in moderate yield (as shown in Scheme 3).



Scheme 2. Keto–enol tautomerism of 2-acetylcyclohexanone.



Scheme 3. Synthesis route of the complex.

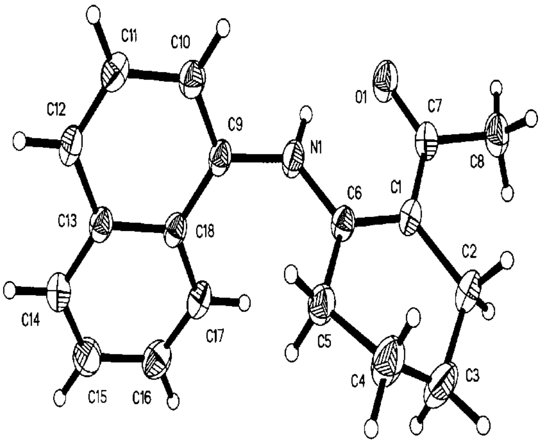


Figure 1. Molecular structure of the ligand.

Crystals of the ligand and complex suitable for single-crystal X-ray diffraction analysis were grown from their toluene solutions. The molecular structures of the ligand and complex are shown in Figures 1 and 2 respectively. Table 1 lists the selected bond lengths and angles, and the crystallographic data are summarized in Table 2. Owing to the special cyclohexyl moiety, all six carbon atoms are not coplanar. The single-crystal structures show this clearly.

From Figure 1, we can see the ketoamine is still a stable form in the solid state, like in most solutions. For the complex, Figure 2 shows that the coordination geometry of complex

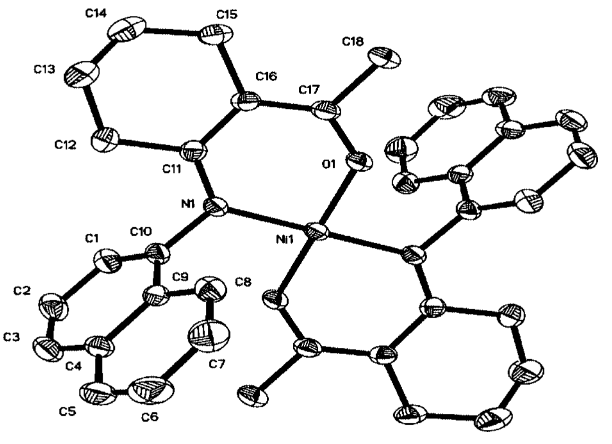


Figure 2. Molecular structure of the complex.

Table 1. Selected bond lengths (Å) and angles (°) for the ligand and complex

Ligand ($C_{18}H_{19}$ N O)		Complex ($C_{36}H_{36}N_2NiO_2$)	
Bond length			
C(1)–C(6)	1.383(2)	C(11)–C(16)	1.415(3)
C(1)–C(7)	1.435(2)	C(16)–C(17)	1.379(3)
C(1)–C(2)	1.524(2)	C(15)–C(16)	1.524(3)
C(2)–C(3)	1.515(3)	C(14)–C(15)	1.493(5)
C(3)–C(4)	1.475(3)	C(13)–C(14)	1.435(5)
C(4)–C(5)	1.508(3)	C(12)–C(13)	1.485(4)
C(5)–C(6)	1.506(2)	C(11)–C(12)	1.521(3)
C(6)–N(1)	1.3487(19)	C(11)–N(1)	1.326(3)
C(7)–O(1)	1.249(2)	C(17)–O(1)	1.283(3)
C(7)–C(8)	1.515(2)	C(17)–C(18)	1.511(3)
C(9)–N(1)	1.4266(19)	C(10)–N(1)	1.440(3)
Bond angle			
C(6)–C(1)–C(7)	120.59(14)	C(17)–C(16)–C(11)	120.7(2)
C(6)–C(1)–C(2)	120.88(14)	C(11)–C(16)–C(15)	121.0(2)
C(7)–C(1)–C(2)	118.51(14)	C(17)–C(16)–C(15)	118.3(2)
C(3)–C(2)–C(1)	113.13(15)	C(14)–C(15)–C(16)	113.7(2)
C(4)–C(3)–C(2)	112.19(18)	C(13)–C(14)–C(15)	113.5(3)
C(3)–C(4)–C(5)	111.16(19)	C(14)–C(13)–C(12)	113.6(3)
C(6)–C(5)–C(4)	113.54(15)	C(13)–C(12)–C(11)	116.1(2)
N(1)–C(6)–C(5)	116.60(14)	N(1)–C(11)–C(12)	118.3(2)
O(1)–C(7)–C(1)	123.54(14)	O(1)–C(17)–C(16)	125.9(2)

is mononuclear and nearly ideally a four-coordinate, square-planar configuration. Interestingly, the anticipated formation of tetrahedral complexes, although sterically possible, was not observed. The nickel ion is arranged in a nearly perfect square-planar coordination environment where β-ketoamino acts as a monoanionic bidentate *N*,*O*-chelator, and lies in the trans-configuration to create two stable six-membered metallacyclic chelate rings (NiOCCCN). In addition, after removing the proton, the β-ketoimine ligand changes to the β-ketoamino ligand, a conjugate-base anion. Owing to this effective conjugation, the bond length of bonds on the chelate ring (NiOCCCN) becomes averaged. The double bond becomes longer and the single bond shorter (see Table 1).

NBE polymerization

This complex can effectively catalyze NBE polymerization in the presence of MAO. The PNBEs were separated as white solids and characterized by gel-permeation chromatography (GPC) in chlorobenzene using polystyrene standards as the reference. All polymers are soluble in chlorobenzene, *o*-dichlorobenzene and cyclohexane at room temperature, which indicates low stereoregularity. The M_n of all PNBEs is between 10^5 and 10^6 g mol^{-1}, which means that the polymerization is not cationic or free-radical-promoted polymerization.

The ^{1}H NMR spectrum of PNBE at 80 °C indicates that all protons appear in $\delta = 0$–3; no vinyl hydrogen atoms ($\delta > 4$) are observed, indicating the absence of ROMP with this complex (see Figure 3). This also suggests that the PNBEs obtained are vinyl addition products. Moreover, from the polymerization results, we find that yield, molecular weight and polydispersity index (PDI), as well as catalytic activity, depend significantly on the polymerization parameters, such as the Al/Ni molar ratio, polymerization time, temperature and the amount of the precatalyst (complex).

The amounts of MAO used are essential for this polymerization. As shown in Table 3, variations in the Al/Ni molar ratio result in different catalytic activities. The optimized Al/Ni was 1000. Higher or lower Al/Ni leads to decreases in the catalytic activity. In addition, the Al/Ni molar ratio also affects the molecular weight and PDI of the PNBE. GPC results showed lower M_n values and higher PDIs with increase in the Al/Ni ratio.

With polymerization time increasing under certain polymerization conditions, more polymer was obtained, but the catalytic activity decreased all the time. In the first 15 min, the catalyst system exhibits the highest activity, 3.08×10^6 g h^{-1} of polymer per mole of nickel, but after 60 min the catalytic activity drops to 1.59×10^6 g h^{-1} of polymer per mole of nickel, which is not a dramatic decrease, suggesting that this catalyst system has good stability at 30 °C (see Table 4). At the same time, M_n drops and the PDI increases.

From Table 5, we can see this catalytic system shows good activities over a wide range temperature from 20 to 80 °C. With increasing temperature, the catalytic activity first increases at 40 °C, and then decreases. Meanwhile, the M_n decreases and PDI increases.

The data in Table 6 show that the amounts of the complex (catalyst precursor) have a considerable effect on the polymerization reaction under certain reaction conditions. With an increasing amount of the complex, the catalytic activity grows first and then declines. The optimized amount of catalyst precursor is 0.1 mg of complex in this polymerization (highest catalytic activity). In addition, the

Table 2. Crystallographic data for the ligand and complex

	Ligand	Complex
Empirical formula	$C_{18}H_{19}NO$	$C_{36}H_{36}N_2NiO_2$
Formula weight	265.34	587.38
Crystal color	Light yellow	Green
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system, space group	Monoclinic, $P2_1/c$	Triclinic
Unit cell dimensions		
a (Å)	11.5160(15)	6.7148(9)
b (Å)	10.7374(13)	9.9659(14)
c (Å)	13.866(2)	12.2323(17)
α (°)	90	66.514
β (°)	124.634(2)	74.434
γ (°)	90	85.465
Volume (Å^3)	1410.7(3)	722.86(17)
Z, calculated density (Mg m^{-3})	4, 1.249	1, 1.349
Absorption coefficient (mm^{-1})	0.077	0.707
F(000)	568	310
Crystal size (mm^3)	0.50 × 0.47 × 0.38	0.48 × 0.38 × 0.14
θ range for data collection (°)	2.15 to 27.03	1.88 to 27.06
Limiting indices	$-14 \le h \le 11, -11 \le k \le 13, -17 \le l \le 17$	$-8 \le h \le 8, -12 \le k \le 12, -15 \le l \le 15$
Max. and min. transmission	0.9714 and 0.9626	0.9075 and 0.7278
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3052/0/182	3118/0/188
Goodness-of-fit on F^2	1.041	1.076
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0505, wR_2 = 0.1360$	$R_1 = 0.0437, wR_2 = 0.1110$
R indices (all data)	$R_1 = 0.0650, wR_2 = 0.1486$	$R_1 = 0.0535, wR_2 = 0.1180$
Largest diff. peak and hole (e$^-$ Å^{-3})	0.565 and −0.269	0.771 and −0.420

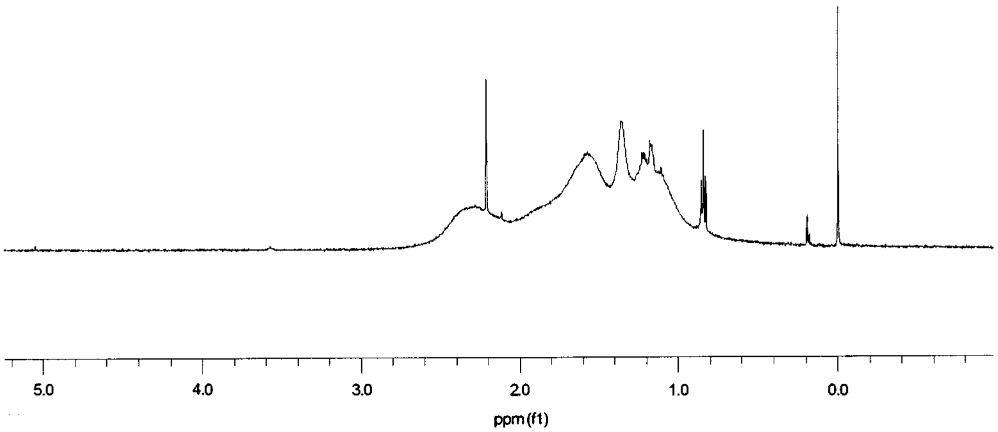


Figure 3. ^{1}H NMR spectrum of PNBE by the complex.

M_n decreases and the PDI becomes wider with increasing amount of the complex. The reason is that a greater amount of catalyst precursor can speed up polymerization and result in high viscosity in a very short time (shorter gel time), and high viscosity can stunt the chain propagation reaction by slowing down the diffusion of the monomer to the catalytically active nickel species.

CONCLUSIONS

In summary, we have prepared a new β-ketoimine ligand from 2-acetylcyclohexanone and 1-naphthylamine and a corresponding bis(β-ketoamino)nickel(II) complex and examined this complex's catalytic behavior for the vinyl (or addition) polymerization of NBE. The complex with

Table 3. Influence of the Al/Ni molar ratio

Run	Al/Ni[a]	Yield (g)	Activity × 10^{-6} (g h^{-1})[b]	$M_n \times 10^{-5}$ (g mol^{-1})	PDI
1	250	0.1028	0.60		
2	500	0.1809	1.06		
3	1000	0.2814	1.65	8.31	1.54
4	1500	0.2348	1.38		
5	2000	0.1922	1.13		
6	3000	0.1361	0.79	4.87	2.19

[a] Conditions: 0.1 mg nickel complex; 0.05 mol NBE; reaction volume, 25 ml; temperature, 30 °C; polymerization for 1 h.
[b] Of polymer per mole of nickel.

Table 4. Influence of the polymerization time

Run	*t* (min)[a]	Yield (g)	Activity× 10^{-6} (g h^{-1})[b]	$M_n \times 10^{-5}$ (g mol^{-1})	PDI
1	15	0.1310	3.08	8.05	1.61
2	30	0.1862	2.18	11.73	1.24
3	45	0.2237	1.75	8.26	1.54
4	60	0.2717	1.59	8.25	1.55

[a] Conditions: 0.1 mg nickel complex; 0.05 mol NBE; reaction volume, 25 ml; temperature, 30 °C; [Al]/[Ni] = 1000.
[b] Of polymer per mole of nickel.

Table 5. Influence of the polymerization temperature

Run	*T* (°C)[a]	Yield (g)	Activity× 10^{-6} (g h^{-1})[b]	$M_n \times 10^{-5}$ (g mol^{-1})	PDI
1	20	0.1763	1.04	8.31	1.54
2	40	0.2945	1.72	4.86	2.19
3	60	0.2929	1.71	3.96	2.29
4	80	0.2821	1.66	2.78	2.80

[a] Conditions: 0.1 mg nickel complex; 0.05 mol NBE; [Al]/[Ni] = 1000; reaction volume, 25 ml; polymerization for 1 h.
[b] Of polymer per mole of nickel.

Table 6. Influence of the amounts of catalyst precursor (complex)

Run	Complex (mg)[a]	Yield (g)	Activity× 10^{-6} (g h^{-1})[b]	$M_n \times 10^{-5}$ (g mol^{-1})	PDI
1	0.05	0.0857	0.50		
2	0.1	0.2755	1.62	8.37	1.51
3	0.2	0.4067	1.19		
4	0.4	0.8989	1.31		
5	1	2.1438	1.25	3.61	3.00
6	2	1.8764	0.55		

[a] Conditions: reaction volume, 25 ml; 0.05 mol NBE; temperature, 30 °C; [Al]/[Ni] = 1000; polymerization for 1 h.
[b] Of polymer per mole of nickel.

cocatalyst MAO exhibited relatively higher activity. The polymers obtained here have high molecular weight and narrow molecular weight distributions (PDI <3 for all polymers). To some extent, we can control the M_n and PDI of PNBE through regulating the polymerization parameters.

EXPERIMENTAL

General procedures and materials

All manipulations involving air- and moisture-sensitive compounds were carried out under an atmosphere of dried and purified nitrogen using standard Schlenk techniques. Solvents were purified using standard procedures. 2-Acetylcyclohexanone (97%), MAO solution, *n*-BuLi solution and 1-naphthylamine were bought from Aldrich and used without further purification. (DME)$NiBr_2$ was prepared following the published procedure with minor modification.[47] NBE was purified by drying with potassium at 60 °C for 8 h and distilled, then dissolved in toluene to make a 5.0 mol l^{-1} solution. Elemental analyses (carbon, hydrogen, and nitrogen) of the ligand and complex were obtained using a Vario EL microanalyzer. ^1H NMR spectra were obtained using an INOVA 500 Hz at room temperature in $CDCl_3$ (for ligand and complex) or *o*-$C_6D_4Cl_2$ (for PNBE) solution using tetramethylsilane as internal standard. GPC analyses of the molecular weight and molecular weight distribution of the polymers were performed on a Waters Breeze instrument using chlorobenzene as the eluent at 40 °C and standard polystyrene as the reference.

[2-PhC(O)C_6H_9(=NAr)] (ligand, Ar=naphthyl)

2-Acetylcyclohexanone (3.4 ml, 0.025 mol), 1-naphthylamine (3.6 g, 0.025 mol) and a catalytic amount of *p*-toluenesulfonic acid were combined in toluene (50 ml), and then the mixture was refluxed for 16 h in a Dean–Stark apparatus to remove water. The resulting solution was evaporated under vacuum to remove the residual toluene. The remaining residue was then crystallized twice in hexane, to give light-yellow crystals 2.5 g (yield: 37.7%; m.p.: 153 °C). Anal. Found: C, 81.38; H, 7.11; N, 5.35. Calc. for $C_{18}H_{19}NO$: C, 81.49; H, 7.22; N, 5.28%. ^1H NMR ($CDCl_3$), δ (ppm): 13.2 (w, 1H, –N*H*); 7.99 (1H, –naphthyl); 7.84 (1H, –naphthyl); 7.71 (H, –naphthyl); 7.3–7.5 (3H, –naphthyl); 7.2 (1H, –naphthyl); 2.5 (2H, $-CH_2-$); 2.3 (s, 3H, $-CH_3$); 1.7 (2H, $-CH_2-$); 15 (2H, $-CH_2-$).

[2-PhC(O)C_6H_8(=NAr)]$_2$Ni (complex, Ar=naphthyl)

The ketoimine ligand (1.2 g, 0.0045 mol) in toluene (40 ml) was added to a 100 ml flask equipped with a magnetic stirrer. The solution was cooled to −78 °C, and then the *n*-BuLi (1.7 ml, 2.8 mol l^{-1}) in hexane was added dropwise. The reaction mixture was stirred overnight and warmed to room temperature. Then, the (DME)$NiBr_2$ (0.7 g, 0.0023 mol) was added to the resulting yellow solution over a pale yellow precipitate. The new mixture was stirred at 40 °C for 1 day;

the mixture became a dark-green solution with some gray precipitate. After filtering, the solvent was evaporated under vacuum to about 5 ml, and then 60 ml hexane was added to the dark residue; a green solid appeared. The solid was washed with hexane (three times) after filtering. Drying in vacuum afforded 0.65 g of a yellowish green product (yield: 16.4%; m.p.: 317 °C). Anal. Found: C, 73.51; H, 6.32; N, 4.59. Calc. for $C_{36}H_{36}N_2NiO_2$: C, 73.62; H, 6.18; N, 4.77%. ^{1}H NMR ($CDCl_3$), δ (ppm): 8.4–8.6 (2H, –naphthyl); 7.1–7.7 (12H, –naphthyl); 1.8–2.5 (8H, 4 $-CH_2-$); 1.5 (6H, 2 CH_3-); 1.0–1.3 (4H, $-CH_2-$); 0.5 (4H, $-CH_2-$).

NBE polymerization

The toluene (5–10 ml), 10 ml of NBE (0.05 mol), and the appropriate amount of MAO solution were introduced into a 50 ml round-bottom glass flask in order, then an appropriate amount of nickel (II) complex in toluene solution was syringed into the well-stirred solution (total reaction volume is about 25 ml). The contents were continuously stirred for a certain time period at the polymerization temperature. The polymerizations were stopped by addition of excess 10% HCl–EtOH. The resulting precipitated PNBE was collected and treated by filtering, washing with EtOH several times, and drying in vacuum at 60 °C/12 h to a constant weight.

Crystal structure determination

The crystals were mounted on a glass fiber using the oil drop scan method. Data obtained with the $\omega-2\theta$ scan mode were collected on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 293 K. The structures were solved using direct methods, and further refinement with full-matrix least squares on F^2 was obtained with the SHELXTL program package.[48,49] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in calculated positions with the displacement factors of the host carbon atoms.

Supplementary materials

The X-ray crystallographic data for the structures reported here have been deposited at the Cambridge Crystallographic Data Centre, CCDC No. 251 151 for the ligand and no. 251 152 for the complex. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax +44(1223)336-033 or e-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

Acknowledgements

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