

Olefin Homopolymerization Catalyzed over Asymmetric and Symmetric Ni(II) Diimine Complexes

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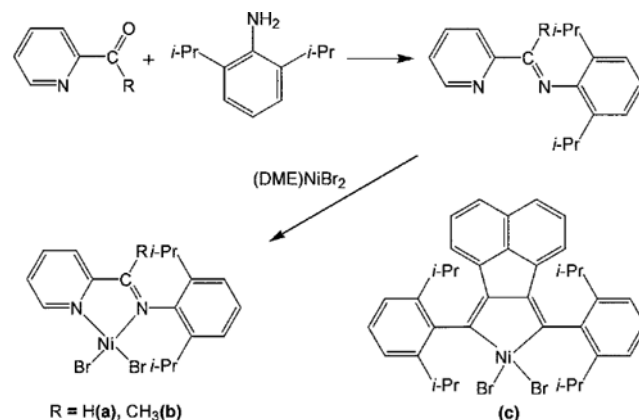
Abstract—Symmetric and asymmetric Ni(II) diimine complexes such as 2-[(2,6-diisopropylphenylimino)methyl]pyridine nickel(II) dibromide (**a**), 2-[1-(2,6-diisopropylphenylimino)ethyl]pyridine nickel(II) dibromide (**b**) and [1,2-bis(2,6-diisopropylphenylimino)]acenaphthene nickel(II) dibromide (**c**) were synthesized. For olefin homopolymerization, asymmetric Ni(II) diimine complexes [(**a**) & (**b**)] were compared with symmetric system (**c**). Asymmetric Ni(II) diimine complexes exhibited less catalytic activity and thermal stability as well as more β -hydride elimination than a symmetric diimine complex (**c**). The activity of (**a**) was larger than that of (**b**), which indicates that methyl group has a contribution to the instability of catalyst by σ bond vibration rather than the stabilization of the active site by electron releasing property.

Key words: Olefin, Polymerization, Asymmetric, Ni(II) Diimine Complexes

INTRODUCTION

Since the 1980s, Zeigler-Natta catalysts have evolved further with the development of a series of homogeneous metallocenes based on early transition metals such as titanium, zirconium and hafnium [Kaminsky et al., 1985; Kaminsky, 1996; Brintzinger et al., 1995; Yoon et al., 1998; Kim et al., 2002; Cho et al., 2000]. Brookhart et al. reported that high molecular weight poly(α -olefins) were synthesized with Ni(II) and Pd(II) diimine derivatives activated by MAO or other ionizing reagents [Johnson et al., 1995; DuPont, 1996]. These are the first late transition metal systems which polymerized ethylene and α -olefins to high molar weight polymers of unique microstructure. The properties of ethylene homopolymers prepared by using nickel(II) diimine catalysts range from strictly linear, semi-crystalline polymers to highly branched amorphous polymers by the variations in catalyst structure, reaction temperature and ethylene pressure [Brookhart et al., 1996, 1997]. The general type of ligands is [(ArN=C(R)C(R)=NAr)] (Ar=phenyl or substituted phenyl, R=hydrocarbyl, substituted hydrocarbyl or substituted hydrocarbylene to form a ring, etc.). Nearly all of the ligands involved in the above Ni(II) and Pd(II) catalysts were symmetric α -diimines [DuPont, 1996; Koten et al., 1982]. Recently, Li et al. reported asymmetric features of the ligands, their metal complexes, reaction and structurally characterization [Li et al., 2001].

In this study we report the synthesis of two asymmetric Ni(II) diimine complexes (**a**) and (**b**) (Scheme 1) as well as symmetric Brookhart type Ni(II) complex (**c**). In addition, the polymerization behaviors of Ni(II) complexes were examined for olefin homopolymerization.



Scheme 1. Synthesis for asymmetric Ni(II) diimine complexes.

lymerization.

EXPERIMENTAL SECTIONS

1. Materials

All operations were performed under inert atmosphere of nitrogen using standard Schlenk tube techniques or inside a drybox.

Polymerization-grade ethylene, propylene (donated from Daelim Ind. Co., Korea) and extra-pure-grade nitrogen were further purified by passing through columns of Fisher RIDOX and 5A/13X molecular sieves. Toluene (J. T. Baker) was distilled from Na-benzophenone ketyl and CH₂Cl₂ from CaH₂ in a nitrogen atmosphere before use. MMAO-4 was purchased from Akzo Co. as a toluene solution and used without further purification. Methanol, 2-pyridinecarboxaldehyde, 2,6-diisopropylaniline and 2-acetylpyridine (Aldrich) were used as received.

2. Synthesis of Ligands and Complexes

2-1. 2-[(2,6-diisopropylphenylimino)methyl]pyridine nickel(II) dibromide (**a**)

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*This paper is dedicated to Professor Wha Young Lee on the occasion of his retirement from Seoul National University.

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Table 1. Results of ethylene polymerization with [(Py-2-CH=N-2,6-di-*i*PrPh)NiBr₂] (a) and [(Py-2-C(CH₃)=N-2,6-di-*i*PrPh)NiBr₂] (b)^a

Catalyst system	T _p (°C)	Yield (g)	Activity [kg-PE/(mol-Ni·atm·h)]	T _m (°C)	M _w ×10 ⁻⁵	MWD	Form
(a)	-20	5.59	155	127.7	1.44	3.1	Powder
	0	13.8	383	-	-	-	Wax
	30	12.6	350	-	-	-	Oil
(b)	-20	3.68	102	123.5	1.06	5.09	Powder
	0	10.5	291	-	-	-	Wax

^aOther conditions: Cat.=20 μmol; MMAO-4=20 mmol; 200 ml Toluene solvent, Pressure=1.2 atm; Polymerization time=90 min.

The mixture of 2-pyridinecarboxaldehyde (4.94 ml, 51.43 mmol) and 2,6-diisopropylaniline (10 ml, 51.43 mmol) in 50 mL methanol was stirred at room temperature for 27 h. Then the mixture was concentrated and the resulting yellowish crystals (Py-2-CH=N(*i*Pr)₂Ph ligand) were recrystallized with methanol in a yield of 80% (10.94 g). mp=72–73 °C. ¹H NMR (500 MHz, CDCl₃): δ 1.16 (d, 12H, ³J=6.9 Hz, CH₃), 2.95 (heptet, 2H, ³J=6.9 Hz, CHCH₃), 7.17–7.18 (m, 3H, Ph), 7.38–7.42 (m, 1H, H_b), 7.81–7.86 (m, 1H, H_c), 8.25 (d, 1H, ³J=7.9 Hz, H_d), 8.29 (s, 1H, HC=N), 8.70–8.72 (m, 1H, H_a). MS (70 eV): m/z 266 (M⁺). Anal. Calcd. for C₁₈H₂₀N₂: C, 81.15; H, 8.32; N, 10.52. Found: C, 81.04; H, 8.35; N, 10.77. A solution of ligand (1.00 g, 3.75 mmol) in 20 ml CH₂Cl₂ was cannulated to a suspension of NiBr₂(DME) (1.13 g, 3.65 mmol, DME=dimethoxyethane [Ward, 1972]) in 50 mL CH₂Cl₂. After overnight stirring at room temperature, the resulting orange-red precipitate was filtered out and washed with hexane and then was dried *in vacuo*, in 46% yield. Anal. Calcd. for C₁₈H₂₂Br₂N₂Ni: C, 44.58; H, 4.57; N, 5.78. Found: C, 44.94; H, 4.68; N, 5.66.

2-2-[1-(2,6-diisopropylphenylimino)ethyl]pyridine nickel(II) dibromide (b)

Py-2-C(CH₃)=N(*i*Pr)₂Ph ligand was synthesized by the condensation reaction of 2-acetylpyridine and 2,6-diisopropylaniline catalyzed by small amount of formic acid, in 92% yield. mp=78–80 °C. ¹H NMR (500 MHz, CDCl₃): δ 1.13 (d, 12H, ³J=6.9 Hz, CHCH₃), 2.19 (s, 3H, CH₃), 2.73 (heptet, 2H, ³J=6.9 Hz, CHCH₃), 7.05–7.16 (m, 3H, Ph), 7.37–7.39 (m, 1H, H_b), 7.79 (m, 1H, H_c), 8.34 (d, 1H, ³J=8.0 Hz, H_d), 8.66 (d, 1H, ³J=4.8 Hz, H_a). MS (70 eV): m/z 280 (M⁺). Anal. Calcd. for C₁₉H₂₄N₂: C, 81.34; H, 8.63; N, 9.99. Found: C, 81.24; H, 8.74; N, 10.01. Metallation proceeded by a similar method to that of [Py-2-CH=N(*i*Pr)₂Ph]NiBr₂ in 52% yield. MS (70 eV): m/z 498 (M⁺), 280 (M⁺ of ligand). Anal. Calcd. for C₁₉H₂₄Br₂N₂Ni: C, 45.74; H, 4.85; N, 5.61. Found: C, 45.73; H, 4.91; N, 5.28. [1,2-bis(2,6-diisopropylphenylimino)]acenaphthene nickel(II) dibromide (c) was synthesized according to the literature [Svoboda et al., 1980].

3. Polymerization

The polymerization was carried out at the monomer pressure of 1.2 atm in a 500 mL round bottom flask reactor by using a Teflon magnetic spin bar. After toluene (200 mL) was introduced into the reactor, the temperature was fixed to the polymerization temperature, and then toluene was saturated with the monomer. A prescribed amount of MMAO and Ni catalysts dissolved in toluene were injected into the reactor by a tuberculin syringe, and then the polymerization was carried out for a certain time. The polymerization rate was acquired at 0.01-s intervals from the rate of monomer consumption measured by a hot-wire flow meter (model 820 from Sierra Instrument) connected to a personal computer through an A/

D converter. After being quenched in acidified methanol, the precipitated polymer was recovered by filtration and then washed with fresh methanol and dried *in vacuo*. The detailed procedures for the polymerization were described elsewhere [Han et al., 1999].

4. Analysis of Polymer

¹³C NMR spectra of the polymers were recorded at 120 °C using a Bruker AMX-300 FT-NMR spectrometer. The solution was made up in 1,2,4-trichlorobenzene/benzene-d₆ up to a concentration of 15 wt%. Molecular weight and molecular weight distribution (MWD) were measured at 145 °C by means of gel-permeation chromatography (Waters Associates; model ALC-GPC-150C) using *o*-dichlorobenzene as a solvent. Differential scanning calorimetry measurements were conducted by using DuPont Analyst 2000 at a heating rate of 5 °C/min.

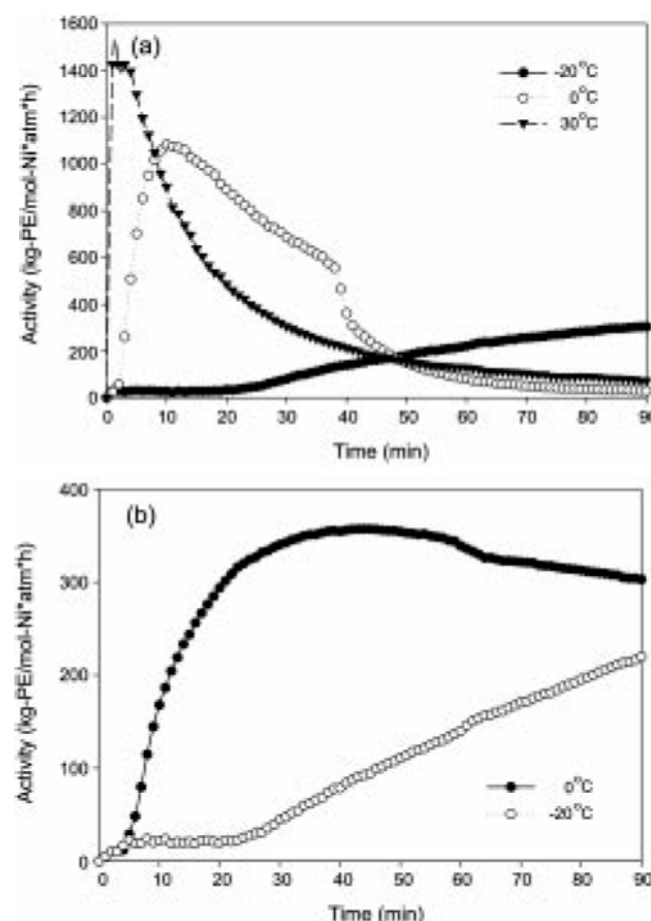


Fig. 1. Kinetic behavior of ethylene polymerization with (a) [(Py-2-CH=N-2,6-di-*i*PrPh)NiBr₂]/MAO and (b) [(Py-2-C(CH₃)=N-2,6-di-*i*PrPh)NiBr₂]/MAO.

Table 2. Branch concentrations and distributions determined by ^{13}C NMR

Catalyst system	T_p ($^{\circ}\text{C}$)	$n\text{CH}_3/1000\text{C}$	B_1	B_2	B_3	B_4	B_5	B_n ($n \geq 6$) ^a
(a)	-20	7.7	4.9 (64.1) ^b	0.7 (8.6)	-	-	-	2.1 (27.3)
	0	40.7	4.8 (11.7)	3.7 (9.0)	3.0 (7.3)	1.9 (4.6)	2.4 (5.9)	25.0 (61.5)
(b)	-20	15.0	13.0 (86.6)	-	-	-	0.6 (4.2)	1.4 (9.2)
	0	48.2	11.0 (22.8)	4.2 (8.7)	3.6 (7.4)	2.1 (4.3)	4.1 (8.6)	23.2 (48.2)

^a B_1 : methyl branch, B_2 : ethyl branch, B_3 : propyl branch, B_4 : butyl branch, B_5 : amyl branch, B_n : long branch.

^bRelative portion of each branch based on total branches (%).

Table 3. Results of ethylene and propylene homopolymerization with [(2,6-di-*i*-PrPh)₂DABAn]NiBr₂(c)/MAO^a

Ni (μmol)	MAO (mmol)	Monomer ^b	T_p ($^{\circ}\text{C}$)	t_p (min)	Yield (g)	Activity ^c	T_m ($^{\circ}\text{C}$)	ΔH_f (J/g)	$M_w \times 10^{-5}$	MWD
9	18	E	-30	60	4.25	387	136	124	11.43	1.4
9	18	E	0	30	22.9	4184	110	59.2	34.13	2.4
9	18	E	30	60	15.3	1392	39.5	5.66	5.41	2.6
9	18	E	50	60	10.2	924	37.4	2.98	2.89	2.5
15	30	P ^d	-50	360	1.4	12.9	46.4	2.23	2.19	1.3
15	30	P	0	120	5.1	142	37.2	1.70	7.16	1.7
15	30	P	50	120	1.6	43.6	23.7	0.90	1.68	2.3

^aPolymerization condition: 200 ml toluene solvent, 1.2 atm pressure. ^bE=Ethylene, P=Propylene. ^cUnit=kg-polymer/(mol-Ni·atm·h). ^d50 mL liquid propylene.

RESULTS AND DISCUSSION

The results of ethylene polymerization with asymmetric Ni(II) diimine complexes (a) and (b) activated with MAO are summarized in Table 1. At -20 $^{\circ}\text{C}$, induction period was very long and the activity was low in ethylene polymerization. The maximum activity was obtained at 0 $^{\circ}\text{C}$ with (a) and as temperature increased, the polymerization rate decreased quickly as shown in Fig. 1(a). This phenomenon was also observed in Brookhart type catalyst (c)/MAO system. However, the absolute magnitude of activity with (a) and the molecular weight of polyethylene prepared with (a) are much smaller than those of (c). It seems that asymmetry and less bulkiness of diimine ligand and the difference in the character of double bond between -CH=N- and -C=N- in pyridine increased pseudo-five member ring strain resulting in the reduced stability of the active site especially at high polymerization temperature. In the case of (b), polymerization activity at 0 $^{\circ}\text{C}$ is larger than that at -20 $^{\circ}\text{C}$ [Fig. 1(b)], but the absolute magnitude is smaller than that of (a), indicating that methyl group of (b) has a contribution to the instability of catalyst by σ bond vibration rather than the stabilization of the active site by electron releasing property.

The degree of branching could be estimated from ^{13}C NMR integration of the methyl, ethyl, and so on [Usami et al., 1984]. The number of branches of polyethylene obtained by (a) and (b) is larger than that of polyethylene prepared by symmetric (c) (Tables 2, 4). The form of polyethylene was powder at -20 $^{\circ}\text{C}$, wax at 0 $^{\circ}\text{C}$ and oil at 30 $^{\circ}\text{C}$, respectively, indicating that the extent of branching and the molecular weight of polymer was greatly affected by polymerization temperature. When polymerized at -20 $^{\circ}\text{C}$, polyethylene has methyl branches as a main branch, whereas long branches predominate at 0 $^{\circ}\text{C}$ as shown in Table 2. Higher temperature enhanced the mobility of the less bulky and asymmetric backbone and the macromonomer could be formed more easily by β -hydride elimi-

Table 4. Branch concentrations and distributions determined by ^{13}C NMR calibration method

Monomer	$n\text{CH}_3/1000\text{C}$	B_1	B_2	B_3	B_4	B_5	B_n ($n \geq 6$)
Ethylene at 0 $^{\circ}\text{C}$	30.2	22.3 (73.9) ^a	2.3 (7.6)	1.3 (4.1)	0.9 (3.0)	1.1 (3.8)	2.3 (7.6)
Ethylene at 50 $^{\circ}\text{C}$	94.7	59.0 (62.3)	11.9 (12.6)	5.4 (5.7)	3.8 (4.0)	2.8 (3.0)	11.8 (12.4)

^aRelative portion of each branch based on total branches (%).

nation, so the portion of long branches increased.

The experimental results of ethylene and propylene homopolymerizations for (c)/MAO system are given in Table 3. In this catalyst system, the optimum temperature for the most stable active site was 0 $^{\circ}\text{C}$. At -30 $^{\circ}\text{C}$, the induction period was long and the activity was low. A maximum activity was obtained at 0 $^{\circ}\text{C}$, and as the polymerization temperature increased up to 0 $^{\circ}\text{C}$, the activity reduced drastically. When ethylene polymerization was carried out at -30 $^{\circ}\text{C}$ and 0 $^{\circ}\text{C}$, polyethylene was formed as powder, whereas amorphous and sticky polyethylene was produced at 30 $^{\circ}\text{C}$ and 50 $^{\circ}\text{C}$. As can be seen in Table 4, the number of branchings increased from 30 to 95 when the polymerization temperature increased from 0 $^{\circ}\text{C}$ to 50 $^{\circ}\text{C}$. As the polymerization temperature increased, β -hydride elimination reaction occurred frequently and the resulting macromonomer was inserted again into the main chain, which produced various kinds and the large number of branchings [Killian et al., 1997]. Various kinds of branches obtained at 50 $^{\circ}\text{C}$ prevented a chain folding, so the melting point reduced drastically to 37.4 $^{\circ}\text{C}$. The main branch is a methyl branch and the portion of long branches increased as the polymerization temperature increased.

Fig. 2(a) shows the kinetic profile of ethylene homopolymerization with (c)/MAO system. When the polymerization was conducted

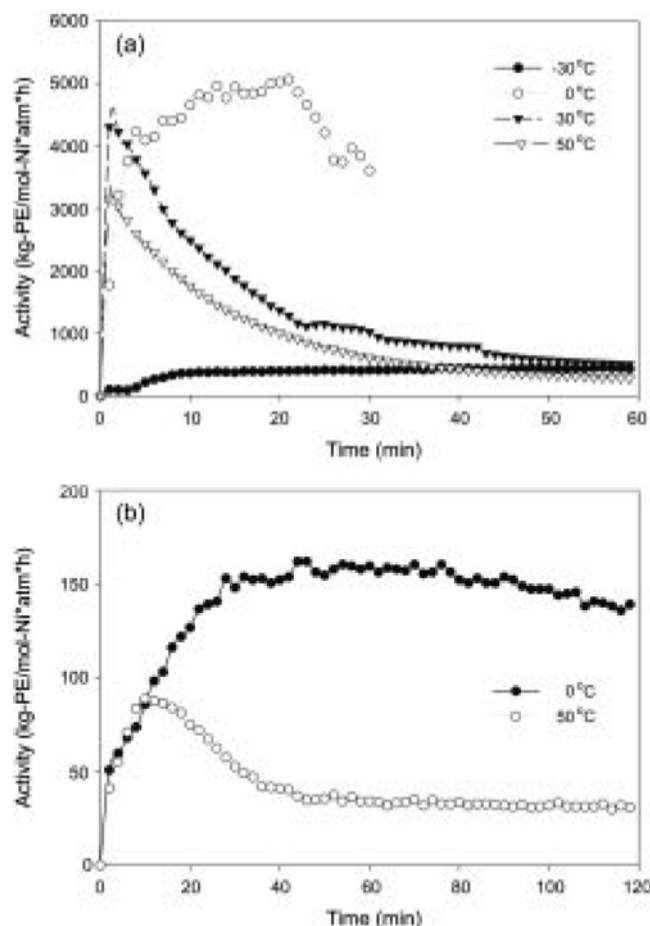


Fig. 2. Polymerization rate profile of ethylene (a) and propylene (b) homopolymerization with [(2,6-di-*i*-PrPh)₂DABAN]NiBr₂ (c)/MAO.

at $-30\text{ }^{\circ}\text{C}$, the activity increased slowly with polymerization time. At $30\text{ }^{\circ}\text{C}$ and $50\text{ }^{\circ}\text{C}$, a maximum activity was obtained within 1 min, but catalytic activity was quickly decreased later on. However, a maximum activity at $0\text{ }^{\circ}\text{C}$ was obtained within 15 min and polymerization rate was slightly decreased later on. It seems that the rapid deactivation at high temperature is due to the thermal instability of active sites [Johnson et al., 1995]. Especially at $0\text{ }^{\circ}\text{C}$, polyethylene obtained with (c) has high molecular weight ($M_w \approx 3,413,000$) and narrow polydispersity ($MWD \approx 2.4$). The high molecular weight polymer can be arising from the extreme steric bulkiness of the symmetric diimine ligands which retard the rate of associative displacement of the growing chain resulting in the increase of propagation rate [Johnson et al., 1995].

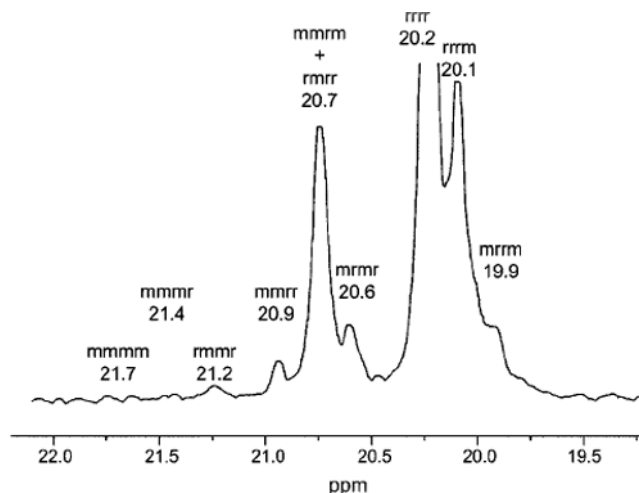


Fig. 3. ^{13}C NMR spectra of polypropylene obtained at $-50\text{ }^{\circ}\text{C}$.

The catalytic activity of (c) in propylene polymerization is about 1/30 of that of (c) in ethylene polymerization. The trend of polymerization activity with respect to polymerization temperature is similar to that of ethylene homopolymerization. The maximum activity of $142\text{ kg-PP/mol-Ni}\cdot\text{atm}\cdot\text{h}$, which is in good agreement with the results reported [Johnson et al., 1995], was observed at $0\text{ }^{\circ}\text{C}$. Prepared polypropylene has high molecular weight and narrow MWD (Table 3). Catalytic activity at $50\text{ }^{\circ}\text{C}$ decreased rapidly after reaching the maximum activity, whereas a high activity maintained for long time at $0\text{ }^{\circ}\text{C}$ as shown in Fig. 2(b). In particular, polypropylene obtained at $-50\text{ }^{\circ}\text{C}$ showed a syndiotactic sequence with 75% rr triad content (Table 5). The pentad assignments shown in Fig. 3 are based on those proposed by Zambelli et al. [Zambelli et al., 1975]. Pentad analysis indicates that intense resonances of the rrrr and the mrrm sequences, in approximately 1 : 1 ratio, suggesting that polymerization proceeded by chain-end mechanism [Inoue et al., 1984]. Syndiotactic specific polymerization of propylene with (N-N)NiBr₂/MAO (N-N=1,2-bis(2,6-di-*isopropylphenyl*)ethylene diimine) [Pellecchia et al., 1996] has been reported. Polymerization of propylene at $-78\text{ }^{\circ}\text{C}$ produced a syndiotactic crystalline poly(propylene) (rr triad content $\approx 80\%$). However, the absolute magnitude of activity is smaller than that of (c) because of the reduced bulkiness of a diimine ligand.

In summary, asymmetric diimine Ni(II) complexes (a) and (b) have been synthesized. The complexes showed less catalytic activity for ethylene polymerization, thermal stability and more β -hydride elimination than symmetric diimine complex (c). The presence of rigid naphthyl group in the diimine ligand backbone of (c) effect

Table 5. ^{13}C NMR data for polypropylene at $-50\text{ }^{\circ}\text{C}$ with [(2,6-di-*i*-PrPh)₂DABAN]NiBr₂ (c)/MAO

Pentad distribution								
Mmmm	mmmr	mmr	mmrr	mmrm+rmrr	mrrr	rrrr	rrrm	mrrm
0.026	0.031	0.278	0.402	4.365	1.155	10	5.760	1.192
Triad distribution				Regioirregularity				
mm	mr	rr		2,1-insertion		1,3-insertion		
0.335 (1.4%)	5.675 (24.2%)	17.45 (74.4%)		13.5%		0.5%		

increase of the catalytic activity and the molecular weight of obtained polyethylene arising from the enhanced planarity of square planar structure of the complex and the less displacement of vibrational motion of the diimine ligand.

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