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Steric and Electronic Effects of Tetradentate Nickel(II) and Palladium(II) Complexes toward the Vinyl Polymerization of Norbornene

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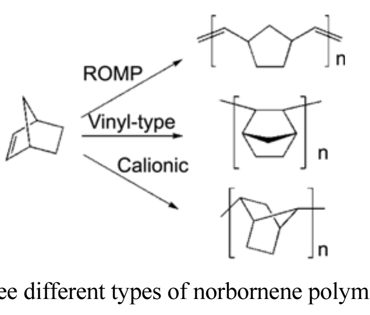
A series of Ni(II) and Pd(II) complexes bearing N4-type tetradentate ligands, [Ni(X^1X^2-6-Me_2bpb) **1**] and [Pd(X^1X^2-6-Me_2bpb) **2**]; 6-Me_2bpb = *N,N'*-(*o*-phenylene)bis(6-methylpyridine-2-carboxamidate), X^1 = Cl, H, or CH_3, X^2 = NO_2, Cl, F, H, CH_3, or OCH_3) were designed, synthesized, and characterized to investigate electronic and steric effects of ligand on the norbornene polymerization catalysts. Using modified methylaluminoxanes as an activator, the complexes exhibited high catalytic activities for the polymerization of norbornene and the nickel complexes exhibited better catalytic activity the palladium complexes. Ni complex **1a** with NO_2 group on the benzene ring showed the highest catalytic activity of 4.9×10^6 g of PNBEs/$mol_{Ni} \cdot$ h and molecular weight of 15.28×10^5 g/mol with PDI < 2.30. Complexes with electron-withdrawing groups are more thermally stable (> 100 °C), and tend to afford higher polymerization productivities than the ones having electron-donating groups. Amorphous polynorbornenes were obtained with good solubility in halogenated aromatic solvents. A vinyl addition mechanism has been proposed for the catalytic polymerization.

Key Words: Ni(II) and Pd(II) complexes, N4-type tetradentate ligands, Norbornene polymerization, Electronic effect, Steric effect

Introduction

Norbornene (NBE) (bicycle-[2,2,1]hept-2-ene) can be polymerized *via* three pathways: ring-opening metathesis polymerization (ROMP),[1] cationic or radical polymerization,[2] and vinyl addition polymerization[3] (Scheme 1). Each pathway leads to polymers with different structures and properties. Of these processes, polynorbornenes (PNBEs) *via* vinyl addition polymerization are polymer materials with special properties, such as high thermal stability, high glass transition temperatures ($T_g > 350$ °C), excellent optical transparency, high chemical resistance, large refractive index and low birefringence because of the constrained nature of the saturated carbon.[4] The vinyl-type PNBEs can be prepared using metal complexes based on chromium,[5] titanium,[6] zirconium,[7] iron,[5b,5c,8] cobalt,[9] copper,[10] nickel,[11] and palladium[12] as catalyst. However, most of the obtained PNBEs are insoluble in common solvents and show poor process ability due to high crystallinity.[3b] Therefore, it is still necessary to develop new catalysts for preparation of high molecular weight polymers which are soluble in common solvents.



Scheme 1. Three different types of norbornene polymerization.

During the past few years, our group has focused our attention on nickel and palladium complexes bearing N4-type tetradentate ligands due to easy preparation by one-step-reaction.[11n,13] Importantly, the Ni(II) and Pd(II) complexes have shown high catalytic activity and good thermal stability toward norbornene polymerization.[11n,13d] Especially, some structural modification with the methyl groups of pyridyl rings and the strong electron-withdrawing substituents on the benzene ring induced a great improvement in solubility, thermal stability and catalytic activity.[13d] We proposed that this high reactivity might be based on the stabilities of the starting complexes and polymerization intermediates due to increased chelate effect.

As a part of our continued interests in the syntheses, structures, and reactivities of neutral Ni(II) and Pd(II) complexes with rigid N4-type tetradentate ligands, and with the aim to fully understand electronic and steric effects of the complexes toward norbornene polymerization in order to find more efficient catalysts that could be carried out under mild reaction conditions, we synthesized a series of neutral Ni(II) and Pd(II) complexes with various substituents on the benzene ring of the tetradentate ligand. Here we report the synthesis, characterization and catalytic reactivity of a series of nickel and palladium complexes containing rigid N4-type tetradentate ligands. These complexes show high chemical and thermal stability and catalytic activity towards norbornene polymerization with high molecular weight and good solubility. The catalytic reaction mechanism is also discussed.

Experimental

General Measurements. Diamines, 6-methyl-2-picolinic acid, pyridine, acetonitrile, diethyl ether, chloroform, palladium(II) acetate, nickel(II) acetate, and triphenylphosphite were purchased from Aldrich and were used as received. All the works involving moisture-sensitive compounds were carried out using standard Schlenk or dry-box techniques. Toluene was dried over sodium metal and distilled under nitrogen. Dichloromethane and chlorobenzene were dried over phosphorus pentoxide. Other reagents, purchased from Aldrich Chemical Co., were used without further purification. ^{1}H and ^{13}C NMR spectra were recorded on Oxford Unity 300 spectrometer at ambient temperature. IR spectra were measured on a BIO RAD FTS 135 spectrometer as KBr pellets. Elemental analyses were performed with EA-1110 (CE Instruments). Molecular weight measurements were made on a gel permeation chromatography (GPC) system (Waters 150C) equipped with a refractive index detector in Samsung Atofina Co. Polymer samples were dissolved in chlorobenzene (50 mg/15 mL) and filtered through a 0.45 Teflon filter. All molecular weights are relative to polystyrene standards. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements of the polymers were performed under a nitrogen atmosphere at a heating rate of 10 °C/min of pristine samples using a Dupont 9900 analyzer.

Syntheses of Ligands (a-g). Ligands **a-f** were obtained from the previous study.[11n,13,14] Ligand **g** (H_26-Me_2-MeObpb) was prepared by the reaction of 4-methoxydiaminobenzene (10 mmol) with 6-methyl-2-picolinic acid (20 mmol) in pyridine in the presence of triphenylphosphite (20 mmol) according to the literature method (Scheme 1).[13,14] For **g**, yield was 1.26 g (33.5%). ^{1}H NMR (300 MHz, DMSO-d_6, δ) 10.85 (s, 2H, N-H), 8.65 (s, 1H, the one pyridyl ring-H (3-position)), 8.18 (s, 1H, the other pyridyl ring-H (3-position)), 7.96 (m, 4H, benzene ring-H (3,6-positions) and pyridyl ring-H (4-positions)), 7.67 (d, 1H, benzene ring-H (2-position)), 7.50 (m, 2H, pyridyl ring-H (5-position)), 3.92 (s, 3H, OCH3), 2.64 (s, 3H, CH_3), and 2.60 (s, 3H, CH_3) ppm. IR (KBr): (N-H) 3331, (C=O) 1679 cm^{-1}. Anal. Calcd for $C_{21}H_{20}N_4O_3$ (376.41): C, 67.01; H, 5.36; N, 14.88. Found: C, 67.34; H, 5.41; N, 15.02.

Syntheses of Complexes (1a-1g) and (2a-2g). The Ni complexes **1a-1f** and, the Pd complexes **2a**, **2c**, **2d**, and **2f**, were obtained from the previous study.[13,14] The Ni complex **1g** and the Pd complexes **2b**, **2e**, and **2g**, were prepared from the reaction of each ligand (0.5 mmol) with nickel(II) acetate or palladium(II) acetate (0.5 mmol) in CH_3CN (20 mL) in good yields, according to the literature method (Scheme 1).[13,14]

[Ni(6-Me$_2$-MeObpb)] 1g: Yield was 75.1%. ^{1}H NMR (300 MHz, $CDCl_3$, δ) 8.03 (d, 2H, pyridyl ring-H (3-position)), 7.80 (m, 2H, pyridyl ring-H (4-position)), 7.70 (m, 2H, benzene ring-H (2,3-positions)), 7.18 (2d, 2H, pyridyl ring-H (5-position)), 6.47 (q, 1H, benzene ring-H (1-position)), 3.78 (s, 3H, OCH_3), 2.35 (s, 6H, $2CH_3$). IR (KBr): (C=O) 1620 cm^{-1}. Anal. Calcd for $C_{21}H_{18}N_4NiO_3$ (433.09): C, 58.24; H, 4.19; N, 12.94. Found: C, 57.85; H, 4.10; N, 12.81.

[Pd(6-Me$_2$-bpc)] 2b: Yield was 64.2%. ^{1}H NMR (300 MHz, DMSO-d_6, δ) 2.41 (s, 6H, $2CH_3$), 8.14 (s, 2H, benzene ring-H), 7.95-7.97 (d, t, each 2H, pyridyl ring-H (3- and 4-positions)), and 7.56 (d, 2H, pyridyl ring-H (5-position)). IR (KBr): (C=O) 1635 cm^{-1}. Anal. Calcd for $C_{20}H_{16}N_4PdO_2$ (450.79): C, 53.2; H, 3.58; N, 12.43. Found: C, 53.54; H, 3.16; N, 12.63.

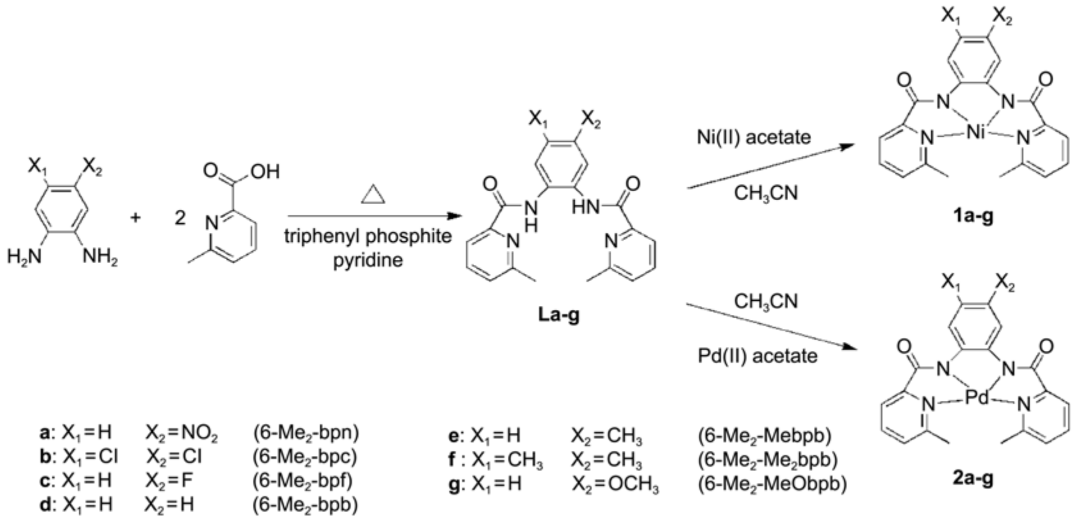
[Pd(6-Me$_2$-Mebpb)] 2e: Yield was 80.4%. ^{1}H NMR (300 MHz, DMSO-d_6, δ) 8.10 (t, 2H, pyridyl ring-H (3-position)), 8.04 (t, 2H, pyridyl ring-H (4-position)), 7.72 (t, 2H, benzene ring-H (2,4-positions)), 7.65 (d, 2H, pyridyl ring-H (5-position)), 6.68 (d, 2H, benzene ring-H (3-position)), 2.52 (s, 3H, CH_3), 2.50 (s, 3H, CH_3), 2.22 (s, 3H, CH_3). IR (KBr): (C=O) 1626 cm^{-1}. Anal. Calcd for $C_{18}H_{12}N_4PdO_2$ (422.73): C, 51.14; H, 2.86; N, 13.25. Found: C, 51.13; H, 2.51; N, 13.43.

[Pd(6-Me$_2$-MeObpb)] 2g: Yield was 63.1%. ^{1}H NMR (300 MHz, DMSO-d_6, δ) 8.76 (d, 2H, pyridyl ring-H (3-position)), 8.12 (m, 2H, pyridyl ring-H (4-position)), 8.10 (d, H, benzene ring-H (3-position)), 7.80 (d, 2H, pyridyl ring-H (5-position)), 7.72 (d, H, benzene ring-H (2-position)), 7.68 (s, H, benzene ring-H (6-position)), 3.90 (s, 3H, OCH_3), 2.62 (s, 6H, $2CH_3$). IR (KBr): (C=O) 1622 cm^{-1}. Anal. Calcd for $C_{20}H_{18}N_4PdO_3$ (468.78): C, 51.24; H, 3.88; N, 11.95. Found: C, 51.40; H, 3.57; N, 11.91.

Polymerization of Norbornene. In an inert (N_2) atmosphere, MMAO (catalyst:cocatalyst = 1:1500 equiv.) was placed into a small vial. To this, approximately 10 mL of chlorobenzene was added and the mixture was gently stirred to dissolve the solids. This solution was then transferred to a 30 mL-vial with a stirring bar containing 20 μmol of **1a**, 5 g of norbornene and 10 mL of chlorobenzene. The solution was stirred rapidly for about 30 minutes. The reaction was quenched with acidic methanol (methanol/conc. HCl = 50/1) and the solids were filtered and dried under vacuum at 80 °C for 12 h. ^{1}H NMR (400 MHz, $CDCl_3$, δ) 3-0 (broad). ^{13}C NMR (100 MHz, o-$C_6D_4Cl_2$, δ) 54.0-47.5, 43.0-38.5, 37.8-36.0, 34.0-29.7.

Results and Discussion

We prepared ligands **a-g** in moderate yields (30-60%) by the reactions between appropriate diamines with 6-methyl-2-picolinic acid in pyridine in the presence of triphenylphosphite according to the literature method (Scheme 2).[13,14] The Ni(II) and Pd(II) complexes, **1a-1g** and **2a-2g**, were obtained from the reaction of each ligand with nickel(II) or palladium(II) acetate dihydrate in CH_3CN in good yields (60-80%). The complexes were isolated as yellow solids, which are soluble in DMSO and DMF. Both Ni(II) and Pd(II) complexes were stable for several months in air. They were characterized by ^{1}H-NMR, FT-IR spectroscopies and elemental analyses. The crystal structures of **1a**, **1c**, **1f**, **2c**, **2d**, and **2f** were previously reported.[13b,14]



Scheme 2. Syntheses of ligands (**a**-**g**), and their nickel (**1a**-**1g**) and palladium complexes (**2a**-**2g**).

Norbornene polymerization was carried out with **1a**-**1g** and **2a**-**2g** in the presence of modified methylaluminoxane (MMAO). The polymerization was run with relatively long reaction time (30 min) to achieve the maximum molecular weights of the polymers. Control experiments showed that norbornene polymerization did not occur in the absence of either the complex or MMAO. The PNBEs were white solids and all polymers were soluble in 1,3,5-trichlorobenzene, 1,2-dichlorobenzene and chloroform at 50 °C, which indicates low stereoregularity. The results are summarized in Table 1. In general, the identity of the metal has an important influence on the catalytic activity of polymerization. The nickel complexes exhibited better catalytic activity than the palladium complexes. The change of the substituent on N4-type tetradentate chelating ligands had an important influence on catalytic activities of norbornene polymerization. Relatively low M_w/M_n (1.81-2.68) results clearly show that these polymerizations proceed *via* homogeneous catalysis and electron-withdrawing substituents on 4 or 5 positions of benzene ring induce higher activities than electron-donating ones. The activity orders of polymerization activities at 50 °C are as follows; (**1a**, **2a**) > (**1b**, **2b**) > (**1c**, **2c**) > (**1f**, **2f**) > (**1e**, **2e**) > (**1d**, **2d**) > (**1g**, **2g**).

Table 1. Polymerization of norbornene with Ni and Pd complexes[a]

Catalyst	Yield (g)	Activity[b] (10^3 g/mol$_{cat}$·h)	M_w[c] (10^5 g/mol)	PDI[c] (M_w/M_n)
1a	4.12	4120	11.84	2.21
1b	3.68	3680	11.17	1.98
1c	3.42	3420	10.32	2.11
1d	2.81	2810	9.01	1.81
1e	2.88	2878	8.81	1.97
1f	3.01	3010	9.82	2.10
1g	2.46	2462	8.24	2.04
2a	2.65	2650	8.81	2.64
2b	2.43	2430	8.31	2.68
2c	2.35	2350	7.75	2.54
2d	1.83	1830	5.87	2.32
2e	2.09	2090	6.72	2.49
2f	2.19	2190	6.98	2.43
2g	1.81	1810	6.32	2.41

[a]Polymerization conditions: norbornene: 5.0 g, catalyst: 20 μmol, Al/Ni or Al/Pd = 1500, solvent: 20 mL chlorobenzene, reaction temperature: 50 °C, reaction time: 30 min. [b]Activity (10^3 g PNBEs/mol$_{Ni}$·h) or (10^3 g PNBEs/mol$_{Pd}$·h). [c]M_w and M_w/M_n values were determined by GPC.

To examine the electronic influence on the catalyst, the Hammett plot was constructed from the correlation of the relative rates with σp for a series of *para*-substituted benzene ring *p*-X_2-$C_6H_4NC_4H_4$ (X_2=OMe, CH_3, H, F, NO_2), which led to positive ρ values of 0.47 for **1**/**Ni** (r = 0.90) and 0.39 for **2**/**Pd** (r = 0.93) (Fig. 1). The Hammett positive ρ values imply that there is the build up of a partial positive charge in the rate-limiting transition state for the polymerization.

Most importantly, steric hindrance of the pyridyl substituent of the complex affects the molecular weights (M_w) of the PNBEs. The nickel and palladium complexes with the methyl group at the ortho-position of the pyridyl groups exhibited significantly higher M_w polymers (M_w = 11.84,

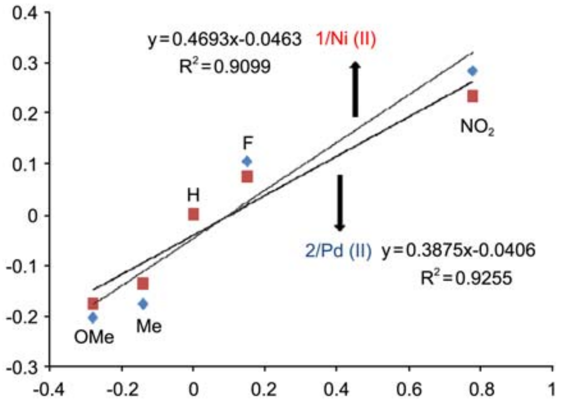


Figure 1. Hammett plots for relative catalytic reactivities of norbornene polymerization versus substituted ligands of **1**/Ni and **2**/Pd.

8.81×10^5 g/mol) than the complexes without methyl group ($M_w = 6.18, 3.91 \times 10^5$ g/mol).[11n,13d] A significant dependence on substituent can be seen in the data, with an overall trend of higher M_w polymers produced from catalysts bearing more electron-withdrawing substituents. It should be noted that these trends might be partially implicated by the catalyst stability. Generally, the more electron-poor catalysts are more thermally stable and tend to afford higher polymerization productivities.[3b,15] The polymer M_W is the result of complex interplay of monomer insertion, chain transfer, and potential catalyst decomposition.[15] High catalytic activity means a fast rate of chain propagation, while the fast chain propagation is often associated with faster chain transfer reaction. Therefore, the polymer M_w decreases with the increase of catalytic activities. In case of N4-type tetradentate complexes, a similar trend in the dependence of M_w and polymerization rate on ligand substituent suggests that the influence of ligand electronic effects on M_w is primarily through the effect on insertion rate. For a stable catalyst, the polymer M_w is primarily controlled by the relative rates of monomer insertion and chain transfer, due to CH_3 groups on the pyridyl groups. A more electron-withdrawing ligand may better stabilize the transition state for monomer insertion than for chain transfer, resulting in a more productive catalyst that produces higher M_w. Consequently, Ni complex **1a** with NO_2 group on the benzene ring showed the highest catalytic activity and molecular weight. The M_w of all PNBEs were between 5.87 and 11.84×10^5 g/mol, and molecular weight distributions (M_w/M_n) of the polymers (about 1.81-2.64) obtained by the complexes indicate the presence of a single active species in the polymerization process. The ^1H NMR spectrum of PNBEs showed absence of any double bonds (C=C, 5-6 ppm, Figure S1, Supporting information).[8,16] The ^{13}C NMR spectrum was similar to those reported by Li's and Wu's groups.[16,17] The resonances of methylenes and methines appear as follows; for C5/C6 carbons at 29.7-34.0 ppm, 36.0-37.8 ppm for C7 carbon, 38.5-43.0 ppm for C1/C4 carbons, and 47.5-54.0 ppm for C2/C3 carbons (Figure S2, Supporting Information). Moreover, FT-IR spectra of the polymers showed no absorptions at 1620-1680 cm^{-1} and especially at about 960 cm^{-1} (Figure S3, Supporting information), which is assigned to the characteristic trans form of stretching of the C=C double bond of the ROMP structure of PNBEs.[1,3b] These results suggest that the catalytic reaction occurs *via* vinyl addition polymerization.

Next, we have chosen Ni complexes **1a** having electron-withdrawing group ($-NO_2$) on the benzene ring and **1f** having electron-donating group (2Me) on the benzene ring, to study the effects of various reaction parameters such as reaction temperature, Al/Ni molar ratio, the molar monomer ratio, reaction time and solvent.

The reaction temperature strongly affected the catalytic activities, and the results of norbornene polymerization over a wide range of temperatures from 0 to 100 °C are listed in Table 2. For **1a/Ni** catalytic system, with an increase in the reaction temperature from 0 to 100 °C, the catalytic activity increased consistently, which means that it has a good thermal stability possibly due to the chelate effect of the ligand even at higher temperature. In comparison, for **1f/Ni** catalytic system, with increasing reaction temperature, the catalytic activity increased up to 70 °C and then somewhat decreased with further temperature increment. A higher temperature (> 70 °C) caused a decrease in the catalytic activity for norbornene polymerization due to the instability or decomposition of the active species. During the polymerization, the formation of metal black or metal agglomeration was not detected, because N4-type chelating ligands are probably able to stabilize compounds in an unusually early stage of molecular agglomeration. **1a/Ni** with a nitro substituent is more thermally robust than **1f/Ni** with two methyl substituents on 4 and 5 positions of the benzene ring, indicating that there is a strong electron-withdrawing effect of the NO_2 group. Thus, **1a/Ni** may have the enhanced catalytic activity and durability under the reaction conditions. The polymerization temperature also affected the M_w of the polymers. M_w decreased from 15.28 to 7.81×10^5 g/mol with increasing temperature (Table 2, **1a**/Ni), while M_w/M_n increased from 1.84 to 3.61 as expected. Also, the **1f/Ni** catalytic system showed the same tendency of decreasing M_w and increasing M_w/M_n consistently (Table 2, **1f/Ni**). The rate of chain-transfer was more sensitive to temperature relative to that of chain growing, and at higher temperature, chain-transfer was in the predominant state.[11n,13d] Therefore, the M_w of polymer decreased with the increasing temperature. These results were similar to those of all the complexes with the tetradentate N4-type ligands in catalytic activity for norbornene polymerization.

Table 2. Effect of the reaction temperature on polymerization of norbornene with **1a**/Ni and **1f**/Ni[a]

Catalyst	Solvent	T (°C)	Activity[b] (10^3 g/mol$_{Ni}$·h)	M_w[c] (10^5 g/mol)	PDI[c] (M_w/M_n)
1a/Ni	PhCl	0	2140	15.28	1.84
	PhCl	30	3320	13.12	2.02
	PhCl	50	4120	11.84	2.21
	PhCl	70	4870	9.38	2.94
	PhCl	100	4950	7.81	3.61
1f/Ni	PhCl	0	1560	13.23	1.88
	PhCl	30	2530	10.16	2.01
	PhCl	50	3010	9.82	2.10
	PhCl	70	3890	7.32	3.11
	PhCl	100	3230	6.46	3.92

[a]Polymerization conditions: norbornene: 5.0 g, catalyst **1a** or **1f**/Ni: 20 μmol, Al/Ni = 1500, solvent: 20 mL chlorobenzene. [b]Activity (10^3 g PNBEs/mol$_{Ni}$·h). [c]M_w (10^5 g/mol) and PDI (M_w/M_n) values were determined by GPC.

In Figure 2 is shown the catalytic kinetic system over a wide temperature range from 0 to 100 °C. The polymer yields increased with increased reaction time, and two distinct periods could be observed in the polymerization process. In the first period, about 5-30 min, the polymer yields increased rapidly. In the second period, the polymer yields increased slightly and leveled off, possibly due to deactivation of the active species. It is notable that the initial

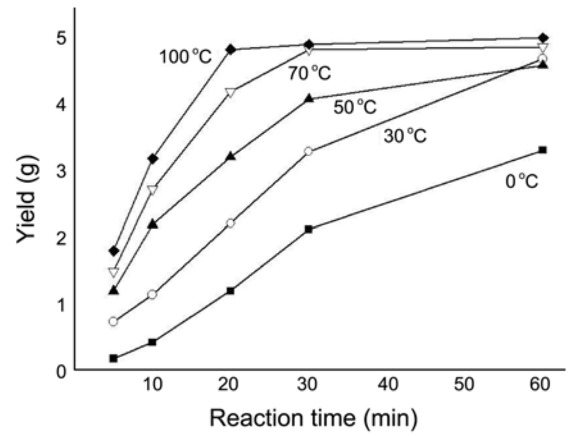


Figure 2. Kinetic study of the norbornene polymerization catalyzed by the complex **1a**/**Ni** at 0, 30, 50, 70 and 100 °C. Polymerization conditions: norbornene, 5.0 g; catalyst **1a**/**Ni**: 20 μmol, **Al**/**Ni** = 1500, solvent: 20 mL chlorobenzene.

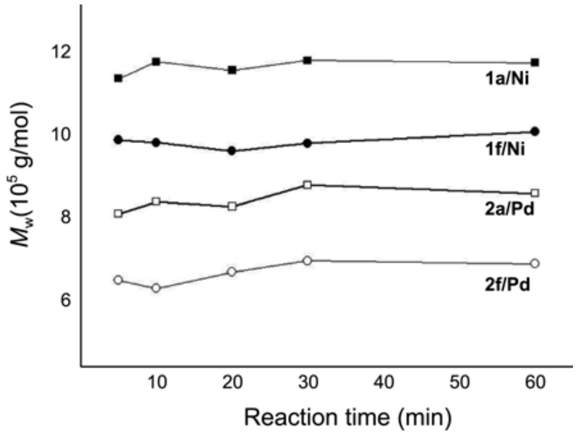


Figure 3. Time dependence of M_w on the norbornene polymerization with **1a**/**Ni**, **1f**/**Ni**, **2a**/**Pd** and **2f**/**Pd**. Polymerization conditions: norbornene, 5.0 g; catalyst: 20 μmol, reaction temperature: 50 °C, Al/Ni or Al/Pd = 1500, solvent: 20 mL chlorobenzene.

polymerization rate was higher at a high polymerization temperature (< 70 °C) than that at a low temperature (< 30 °C). And with the prolongation of polymerization time, the polymer yield was higher at the high polymerization temperature. These results imply that the active species was stable and highly activated at the high temperature. Most importantly, the observed M_w was independent of the reaction time (Fig. 3). As reported by Wu's groups,[11f,11o] the polymerization was initiated instantaneously at the beginning, the molecular chain grew rapidly, and then a constant ratio between chain propagation and chain transfer was reached in a few minutes. The catalytic activities decreased continuously due to the decreasing monomer concentration during the longer reaction time, but the increased polymer yields were obtained.

Al/M (M = Ni or Pd) mole ratio also played an important role in affecting the catalytic activities. Thus, **1**/**Ni** or **2**/**Pd** were chosen to investigate influence of Al/M ratio at the optimized temperature (50 °C). As shown in Figure 4, for **1a**/**Ni** or **2a**/**Pd** catalytic systems, with the change of Al/M

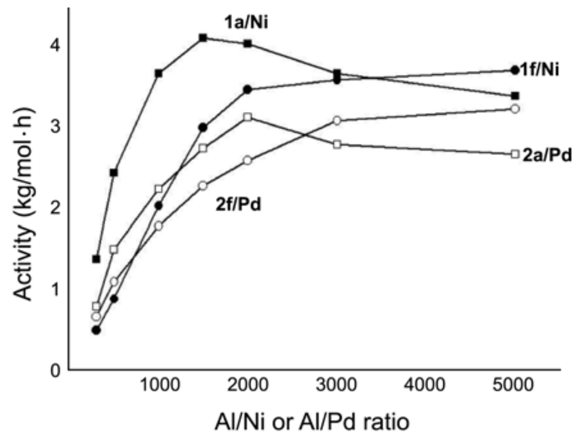


Figure 4. Influence of Al/Ni or Al/Pd ratio on catalytic activity of the norbornene polymerization with **1a**/**Ni**, **1f**/**Ni**, **2a**/**Pd** and **2f**/**Pd**. Polymerization conditions: norbornene, 5.0 g; catalyst: 20 μmol, reaction temperature: 50 °C, reaction time: 30 min, solvent: 20 mL chlorobenzene.

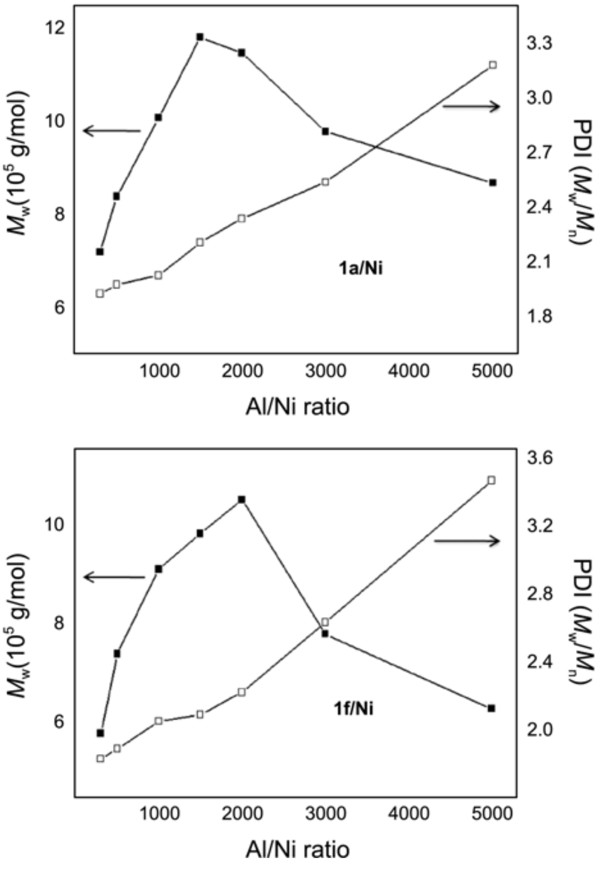


Figure 5. Influence of Al/Ni ratio on M_w and M_w/M_n obtained from the norbornene polymerization with **1a**/**Ni** and **1f**/**Ni**. Polymerization conditions: norbornene, 5.0 g; catalyst: 20 μmol, reaction temperature: 50 °C, reaction time: 30 min, solvent: 20 mL chlorobenzene.

ratio from 300 to 5000, the catalytic activity increased with an increase of MMAO amount until the Al/M molar ratio reached 1500-2000, and then decreased with further increase of the Al/M ratio. When the MMAO ratios were 1500 for **1a**/**Ni** and 2000 for **2a**/**Pd**, the highest catalytic activities of

Table 3. Solvent effect on polymerization of norbornene with **1a/Ni**, **1f/Ni**, **2a/Pd** and **2g/Pd**[a]

Catalyst	Solvent	Activity[b] (10^3 g/mol$_{Ni}$·h)	M_w[c] (10^5 g/mol)	PDI[c] (M_w/M_n)
1a/Ni	CH_2Cl_2	3110	11.80	2.10
	PhCl	3320	13.12	2.02
	PhMe	1730	5.48	1.94
1f/Ni	CH_2Cl_2	2410	9.54	2.13
	PhCl	2530	10.16	2.01
	PhMe	1340	4.98	1.87
2a/Pd	CH_2Cl_2	2140	8.45	2.63
	PhCl	2380	9.84	2.54
	PhMe	1210	4.76	1.92
2f/Pd	CH_2Cl_2	1820	6.98	2.51
	PhCl	2170	7.83	2.63
	PhMe	940	3.88	1.84

[a] Polymerization conditions: norbornene: 5.0 g, catalyst: 20 μmol, Al/Ni or Al/Pd = 1500, solvent: 20 mL and reaction temperature: 30 °C. [b] Activity (10^3 g PNBEs/mol$_{Ni}$·h). [c] M_w (10^5 g/mol) and PDI (M_w/M_n) values were determined by GPC.

4.12 and 3.14×10^6 g of PNBEs/mol·h were observed, respectively. However, **1f/Ni** or **1f/Pd** catalytic systems showed a little different tendency. With an increase in Al/M ratio, the catalytic activities for norbornene polymerization increased consistently even though they were levelled in the high ratio.

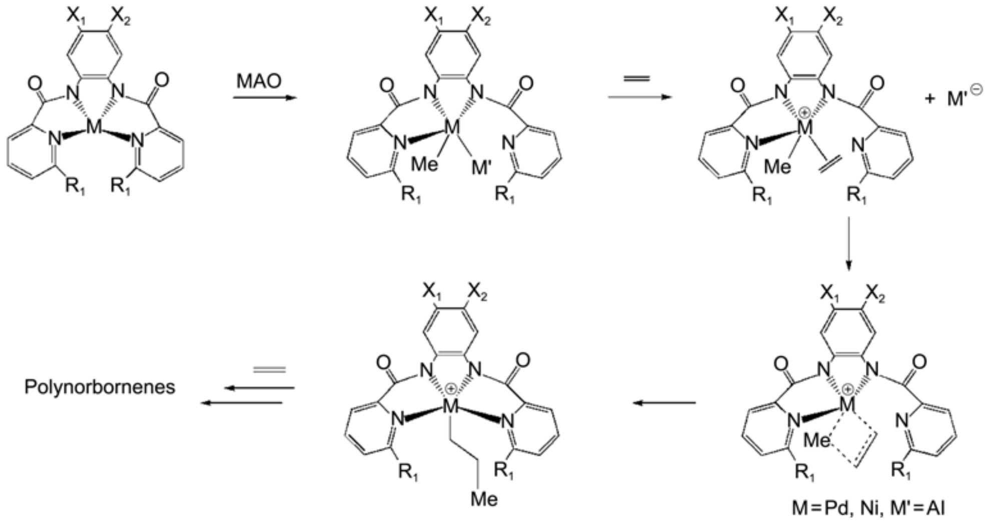
In addition, the Al/Ni molar ratio affected the molecular weight and M_w/M_n of the PNBEs (Fig. 5). All of the catalytic systems showed the same tendency. With an increase in Al/Ni ratio, the M_w of PNBEs increased until the Al/M molar ratio reached 1500-2000, and then decreased, while M_w/M_n increased consistently (from 1.80 to 3.61) in the ranges we tested. Possibly, excess MMAO might give rise to an easy chain transfer due to the action of $AlMe_3$.

The effect of solvent on the catalytic activities is shown in Table 3. All of the catalytic systems showed the same tendency. The higher activities were generally observed in polar solvents (PhCl > CH_2Cl_2 > PhMe at 30 °C), suggesting a complex cation/MMAO anion pair as an active species that is possibly generated by the removal of the moiety of the amide-pyridyl group of the complexes by MMAO as shown in Scheme 3. The decrease of activity in toluene is accompanied by a decrease in polymer molar mass and a slight increase in molecular weight distribution.

Although the mechanism of the polymerization reaction is not obvious, at the initiation step, the complex activated with MAO would produce the active species LM-CH_3. The norbornene monomer occupies the coordination site, and the norbornene would insert into the M-carbon bond if a new monomer is ready to complex (Scheme 3). The repetition of the coordination insertion steps leads to polymer chain growth. More electron-withdrawing catalysts would decrease electron density on the imido N atom, leading to rapider insertion of monomer. On the other hand, the complexes with the methyl group at 6-position of the pyridyl group have shown higher reactivity than the complexes without the methyl group,[13d] as we proposed in the previous study with N4-type Ni and Pd complexes. The methyl group in the *ortho*-position of the pyridyl group would induce an easy dissociation of the pyridyl group to produce a vacant site for the coordination of norbornene, owing to a steric effect. Therefore, more polar solvents allow better ion-pair separation, increasing the accessibility of monomer and active cation. In conclusion, both electronic and steric effects of the substituents on the ligand play a significant role in norbornene polymerization.

Conclusion

Ni(II) and Pd(II) complexes bearing N4-type tetradentate ligands were designed, synthesized, and characterized to investigate electronic and steric effects of ligand toward the norbornene polymerization reactions with MMAO. The ligand structure had an important influence on catalytic activies and polynorbornene productivities. The steric bulky hindrance of nickel complexes resulted in higher catalytic activity; ligands led to different electrophilicity of the nickel



Scheme 3. Proposed polymerization mechanism.

metal center, and a relatively higher positive nickel metal center would exhihibit high catalytic activities. Complexes with the methyl groups of pyridyl rings and the strong electron-withdrawing groups are more thermally stable (> 100 °C), and tend to afford higher polymerization productivities than the complexes having electron-donating groups. Polymerization temperature, Al/M (M = Ni or Pd) ratio, molar monomer ratio, reaction time and solvent also played important roles in affecting catalytic activities and productivities for norbornene polymerization. The PNBEs obtained were amorphous and showed good solubility in halogenated aromatic hydrocarbons for the determination of M_w. FT-IR, ^{1}H, and ^{13}C NMR analyses of the polymers suggest that the catalytic polymerization occurs *via* vinyl addition mechanism. To the best of our knowledge, this is one of the catalysts possessing highest activities for vinyl addition polymerization of norbornene in reported literatures either to nickel or palladium complexes based on high tetradentate ligands.

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