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Novel nickel(II)-based catalysts for the polymerization of ethylene

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Abstract

A series of Ni(II)-based bidentate α-diimine complexes bearing two alkyl (alkyl = methyl, ethyl and isopropyl) substituents on each imine aryl group were studied as precatalysts for the polymerization of ethylene. These new catalysts were observed to show high activity in combination with methyl aluminoxane (MAO) and produced high molecular weight polyethylenes. The effects of the steric bulk of *ortho*-aryl substituents of the ligand on the catalytic activity and the resulting polyethylene microstructure were investigated. Kinetics of polymerization was also studied by changing important parameters such as temperature and MAO concentration. The polymerization activity, polymer molecular weight and resulting polymer microstructure were drastically changed according to the catalyst structure modification and polymerization parameters.

Keywords: Catalysis; Nickel; Polyethylene; Polymerization; Transition metals

1. Introduction

Olefin polymerization and oligomerization catalyzed by transition metal complexes have attracted great attention in both academic and industrial research [1–3]. Although olefin polymerization has been the domain of early metal catalysts, in the past decade there has been growing interest in late transition metal catalysts. In the past late transition metal catalysts were generally accepted that they produced only oligomers because of the accelerated β-hydride elimination. An industrial process, Shell Higher Olefin Process (SHOP), is an example of oligomer production by using homogeneous chelate Ni(II) complexes. However, Brookhart in 1995, in which they produced high molecular weight polyethylene for the first time with cationic Ni(II) α-diimine complexes, has revived the investigation of late transition metal complexes as potential catalyst precursors [4]. Most late metal systems produce highly branched and low molecular weight polymers from ethylene [5]. The key to high polymer production using the aryl-substituted α-diimine systems is the incorporation on the aryl rings of bulky *ortho* substituents that greatly retard the rate of chain transfer [2–6].

Considering these previous findings, we were interested in exploring and synthesizing some new ligands in order to develop new late-transition metal complexes for olefin polymerization catalysis. We report here the synthesis of novel nickel complexes bearing ligands with aryl rings of different *ortho* substituents, resulting in highly active catalysts for the polymerization of ethylene.

2. Experimental

2.1. Material

All reactions were performed under a purified nitrogen atmosphere using standard glove box and Schlenk technique. Polymerization grade of ethylene (SK Co., Korea) was purified by passing it through columns of Fisher RIDOX catalyst and molecular sieve 5 Å/13×. Organic solvents were distilled from Na/benzophenone and stored over molecular sieves (4 Å). All other reagents were purchased from Aldrich and used without further purification. Methyl aluminoxane (MAO) was purchased from Akzo Chemical as 8.4 wt.% total Al solution in toluene.

2.2. Synthesis of ligand precursors

The synthetic route of newly designed nickel complexes bearing ligands with aryl rings of different *ortho* substituents is shown in Scheme 1.

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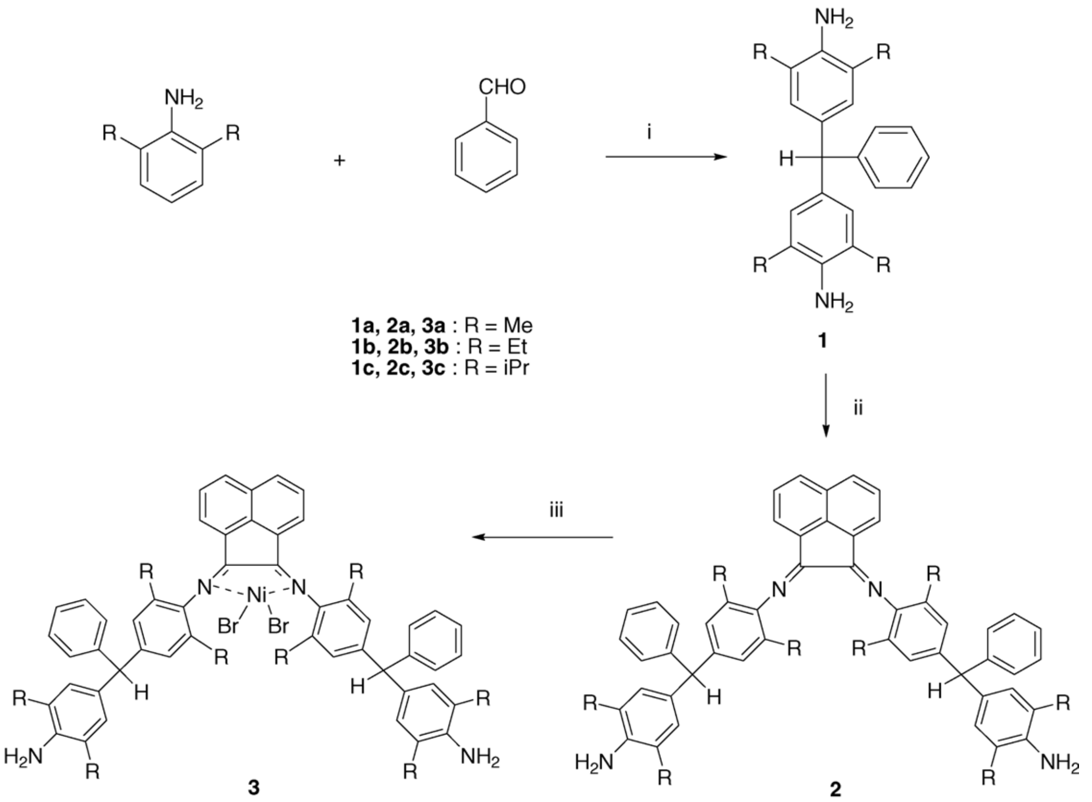

Scheme 1. Synthesis of ligands and catalyst precursors: (i) HCl; (ii) acenaphthenequinone, MeOH; (iii) (DME)NiBr$_2$, CH$_2$Cl$_2$.

2.2.1. *α,α-Bis(4-amino-3,5-dimethylphenyl)toluene (**1a**)*

2,6-Dimethylaniline (1.4 ml, 11 mmol) was heated at 120 °C in nitrogen to which *para*-substituted benzaldehyde (0.6 g, 5 mmol) dissolved in concentrated HCl was added dropwise over a period of 1 h as a modification from the reported procedure [7]. The reaction mixture was continually refluxed for 24 h. After cooling to room temperature, it is basified with aqueous sodium hydroxide was added. The organic materials were extracted with CHCl$_3$, and the combined organic layers were washed with water and brine. The solution was dried over MgSO$_4$, and was concentrated in a vacuum oven. The product was purified by silica gel chromatography (ethyl acetate (EA):hexane = 1:3) to give a product as a white solid 1.0 g (yield 61%). ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.11 (s, 12H), 3.47 (s, 4H), 5.26 (s, 1H), 6.69 (s, 4H), 7.12–7.24 (m, 5H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 17.92, 55.66, 121.62, 125.77, 128.20, 129.38, 134.08, 140.81, 145.06. Anal. Calcd. for C$_{23}$H$_{26}$N$_2$: C, 83.59; H, 7.93; N, 8.48. Found: C, 83.55; H, 7.90; N, 8.50.

2.2.2. *α,α-Bis(4-amino-3,5-diethylphenyl)toluene (**1b**)*

The **1b** compound was prepared according to the similar procedures employed for the preparation of **1a** compound to get a blue solid as a 60% yield. ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.15 (t, 12H), 2.45 (quart, 8H), 3.50 (s, 4H), 5.31 (s, 1H), 6.75 (s, 4H), 7.14–7.24 (m, 5H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 13.45, 24.68, 56.23, 125.58, 125.83, 127.96, 129.40, 134.58, 128.08, 146.38. Anal. Calcd. for C$_{27}$H$_{34}$N$_2$: C, 83.89; H, 8.87; N, 7.25. Found: C, 83.81; H, 8.92; N, 7.28.

2.2.3. *α,α-Bis(4-amino-3,5-diisopropylphenyl)toluene (**1c**)*

The **1c** compound was prepared according to the similar procedures employed for the preparation of **1a** compound to get a blue solid as a 60% yield. ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.35 (s, 24H), 2.88 (sep, 4H), 3.61 (s, 4H), 5.31 (s, 1H), 6.78 (s, 4H), 7.10–7.22 (m, 5H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 22.24, 28.15, 56.83, 124.04, 125.58, 127.95, 129.73, 132.28, 132.54, 135.75, 138.42, 146.00. Anal. Calcd. for C$_{31}$H$_{42}$N$_2$: C, 84.11; H, 9.56; N, 6.33. Found: C, 84.10; H, 9.58; N, 6.31.

2.3. *Synthesis of ligands*

2.3.1. *Ligand **2a** (Scheme 1)*

Acenaphthenequinone (0.38 g, 2.1 mmol) and α,α-bis(4-amino-3,5-dimethylphenyl)toluene (excess) were dissolved in 50 ml of CH$_3$OH in a round-bottom flask. Five drops of formic acid were added, and the sealed solution was stirred at 50 °C overnight. After filtration, the red solid was washed with hot methanol and dried to give an orange powder 1.2 g in 65% yield. ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.19 (d, 24H), 3.57 (s, 4H), 5.43 (s, 2H), 6.81–7.02 (d, 8H), 7.22–7.39 (m, 12H), 7.91 (t, 4H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 18.20, 31.64, 47.52, 55.97, 121.93, 122.89, 124.73, 126.00, 131.51, 134.10, 138.75, 139.78, 141.56, 141.75, 145.11, 146.77, 161.12. Anal. Calcd.

for $C_{58}H_{54}N_4$: C, 86.31; H, 6.74; N, 6.94. Found: C, 86.33; H, 6.72; N, 6.97.

2.3.2. Ligand **2b**

The **2b** was prepared by the similar procedure with **2a** except for using α,α-bis(4-amino-3,5-diethylphenyl)toluene. The resulting product was an orange solid (yield = 62%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.10–1.22 (t, 24H), 2.52 (quart, 16H), 3.61 (s, 4H), 5.57 (s, 2H), 6.81–7.02 (d, 8H), 7.22–7.39 (m, 12H), 7.91 (t, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.28, 14.21, 24.56, 25.05, 56.48, 123.47, 127.27, 128.93, 129.63, 130.61, 131.12, 134.57, 139.74, 140.16, 140.75, 145.11, 145.58, 146.99, 161.12. Anal. Calcd for $C_{66}H_{70}N_4$: C, 86.23; H, 7.68; N, 6.09. Found: C, 86.26; H, 7.70; N, 6.03.

2.3.3. Ligand **2c**

The **2c** was prepared by the similar procedure with **2a** except for using α,α-bis(4-amino-3,5-diisopropylphenyl)toluene. The resulting product was an orange solid (yield = 60%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.95–1.10 (d, 48H), 2.98 (sep, 8H), 3.69 (s, 4H), 5.59 (s, 2H), 6.81–7.02 (d, 8H), 7.22–7.39 (m, 12H), 7.91 (t, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.75, 23.91, 28.77, 29.51, 31.85, 56.92, 123.57, 124.78, 125.94, 127.54, 128.12, 128.54, 129.89, 131.69, 132.15, 134.49, 135.97, 138.54, 140.16, 141.75, 145.18, 146.73, 160.92. Anal. Calcd. for $C_{74}H_{86}N_4$: C, 86.16; H, 8.40; N, 5.43. Found: C, 86.19; H, 8.44; N, 5.40.

2.4. Synthesis of catalysts

A 1.1 equiv. of the ligand (**2a**, **2b** or **2c**) and (DME)$NiBr_2$ (DME = 1,2-domethoxyethane) were added together in a Schlenk flask under nitrogen. Stirring was begun and continued overnight. Diethylether was added to the reaction to precipitate the complex, and the resultant solids were filtered, washed with ether, and dried in vacuo. All of the complexes were prepared in high yield (>90%) in this manner. The paramagnetic character of the resulting catalysts makes NMR analysis impossible.

2.4.1. Catalyst precursor **3a**

Isolate as a dark brown power. Anal. Calcd. for $C_{58}H_{54}N_4Br_2Ni$: C, 67.92; H, 5.31; N, 5.46. Found: C, 67.81; H, 5.40; N, 5.41.

2.4.2. Catalyst **3b**

Isolate as a brown power. Anal. Calcd. for $C_{66}H_{70}N_4Br_2Ni$: C, 69.67; H, 6.20; N, 4.92. Found: C, 69.74; H, 6.32; N, 4.85.

2.4.3. Catalyst **3c**

Isolate as a brown power. Anal. Calcd. for $C_{74}H_{86}N_4Br_2Ni$: C, 71.10; H, 6.93; N, 4.48. Found: C, 71.15; H, 6.87; N, 4.54.

2.5. Polymerization and characterization

Ethylene polymerizations were performed in a 250 ml round-bottom flask equipped with a magnetic stirrer and a thermometer [8]. The catalyst was added to the flask and the reactor was charged with toluene (80 ml) via a syringe. The reactor was immersed in a constant temperature bath previously set in a desired temperature. When the reactor temperature had been equilibrated to the bath temperature, ethylene was introduced into the reactor after removing argon gas under vacuum. When no more absorption of ethylene into toluene was observed, a prescribed amount of MAO was injected into the reactor and then the polymerization was started. Polymerization rate was determined at every 0.01 s from the rate of consumption, measured by a hotwire flowmeter (model 5850 D from Brooks Instrument Div.) connected to a personal computer through an A/D converter. Polymerization was quenched by the addition of methanol containing HCl (5 vol.%) and then the unreacted monomer was vented. The polymer was washed with an excess amount of methanol and dried under vacuum at 50 °C.

^{1}H NMR, ^{13}C NMR spectra were recorded on a Varian Gemimi 2000 (300 MHz). All chemical shifts are reported in parts per million relative to tetramethylsilane. Elementary analysis was determined with Vario EL. Analytical thin layer chromatography (TLC) was conducted using Merck 0.25 mm silica gel 60F precoated aluminium plates with fluorescent indicator UV_{254}. Thermal analysis of polyethylene was carried out by using a differential scanning calorimeter (Perkin-Elmer DSC, model: Pyris 1) at 10 °C/min heating rate under nitrogen atmosphere. The results of the second scan are reported to eliminate difference in sample history. The intrinsic viscosity was measured in decalin at 135 °C using an Ubbelohed viscometer and the average of molecular weight was calculated by following relation [9]: $[\eta] = 6.2 \times 10^{-4} \bar{M}_v^{0.7}$.

3. Results and discussion

The general structure of bidentate α-diimine ligands used in this study is shown in Scheme 1. They were prepared by the conventional Schiff-base condensation of 2 equiv. of the desired 2,6-dialkyl-substituted anilines with acenaphthenequinine. The pre-catalysts were formed by addition of the ligands to (DME)$NiBr_2$. The reactions were complete in all cases in less than 6 h, and the products are isolated by filtration or evaporation and washed with ether to yield the desired catalyst precursors in quantitative yields.

The catalyst precursors were tested in solution polymerization runs at 1.3 bar of ethylene pressure in toluene at temperature (T_p) between 10 and 50 °C and the results are summarized in Table 1. The active catalysts are generated in situ in toluene by the addition of MAO to the catalyst precursor in the presence of ethylene. Methyl-substituted catalyst (**3a**/MAO) showed the highest activity while isopropyl homologue (**3c**/MAO) showed the lowest activity. The **3a**/MAO catalyst exhibited a two-fold higher activity than **3c**/MAO at low T_p (say 10 °C). However, as T_p increased to 50 °C, the reverse order was observed between them. Obviously these results come from the difference in steric bulk of the bidentate α-diimine ligands.

In ethylene polymerizations by Ni(II)-based α-diimine catalysts, the aryl groups are roughly perpendicular to the coordination plane, so the bulky substituents on the aryls are positioned at the axial directions to retard associative chain transfer reactions [10–12]. At elevated temperatures, the aryl

Table 1
Results of ethylene polymerizations by Ni(II) α-diimine catalyst precursors combined with MAO[a]

Entry	Catalyst	Loading (μmol)	T_p (°C)	[Al]/[Ni][b]	$\bar{R}_{p,avg}$[c] ($\times 10^{-7}$ g PE/mol Ni h bar)	$\bar{M}_v$[d] ($\times 10^{-3}$)	Branches/1000C[e]
1	**3a**	7.5	10	500	93.39	204.5	20
2			30	500	65.13	160.0	37
3			50	500	21.05	77.9	79
4	**3b**	7.5	10	500	57.20	231.3	30
5			30	500	61.97	179.7	45
6			50	500	18.71	81.0	81
7	**3c**	7.5	10	500	47.76	261.6	39
8			30	500	43.28	191.3	109
9			50	500	51.28	95.3	131
10	**3a**	7.5	30	25	18.30	75.6	27
11			30	50	58.96	67.8	28
12			30	100	40.61	73.2	30
13			30	300	100.06	170.5	44
14			30	500	65.13	160.0	37

[a] A 250 ml reactor, 80 ml of toluene, 30 min runs, atmospheric pressure, MAO as cocatalyst.

[b] Al/Ni, the molar ratio of MAO and Ni catalyst.

[c] Average rate of polymerization for 30 min of polymerization.

[d] Viscosity average molecular weights calculated from the equation [9]: $[\eta] = 6.2 \times 10^{-4} \bar{M}_v^{0.7}$.

[e] Total branching was determined by ^{1}H NMR spectroscopy [5,6].

groups may freely rotate away from the perpendicular orientation, resulting in increased associative chain transfers and a subsequent decrease in molecular weight of the PE. In addition such free rotation at elevated temperature (say 50 °C) makes the structure of the cationic active species more unstable, resulting in fast decrease of activity. This trend was more evident for the less bulky compound, say **3a** and **3b** catalyst.

As expected from the above explanation, the polymer molecular weights (as M_v) vary dramatically with the modification of ligand structure. Reducing the steric bulk of the diimine ligands by substituting methyl groups for isopropyl groups resulted in a decreased molecular weight (Table 1). Similar results have been reported for Ni(II) and Pd(II) systems and Fe(II) and Co(II) systems [2–6]. These results demonstrate that steric bulk around the active metal centers is a key to retarding chain transfer in order to obtain high molecular weight polymer. The M_v value was also decreased monotonously as T_p increased.

In order to investigate the effect of MAO on the kinetic behavior of polymerization, we have run ethylene polymerizations at 30 °C by using a wide range of MAO concentrations ([Al]/[Ni] = 25–500), even though this range is still narrow considering the MAO concentration needed to activate metallocene complexes [1]. Catalytic activity increases with increases in the concentration of MAO, and the highest activity was found around [Al]/[Ni] = 300 (Table 1). This value to achieve the maximum activity is much lower than that needed in conventional metallocene catalyst systems [1], in which a gross excess (>10,000) of MAO is frequently needed. In addition, **3a** catalyst affords polyethylenes with high molecular weights (M_v ranging from 67,800 to 170,500). It is interesting to note that the M_v value does not decrease as MAO concentration increases, which is different from conventional metallocene and Ziegler–Natta catalysts. It means that, within our experimental range ([Al]/[Ni] = 25–500), transfer to MAO cocatalyst is not a major factor controlling molecular weight.

β-Elimination from the growing polymer chain seems to be a main termination reaction in this catalyst system. The resulting oligomer and polymer chains bearing unsaturation bond at their chain ends lead to chain branching or chain transfer. The formation of high molecular weight polymers is possible because the steric protection of the vacant axial coordination sites reduces the rate of associative displacement from β-eliminated olefin-hydride complexes, and thus reduces chain transfer rates. A range of polyethylene materials with high molecular weights and degrees of branching from linear to over 100 branches per 1000 carbon atoms was accessible by simple variation of temperature and ligand architecture as shown in Table 1. At higher temperatures, unsaturated oligomer and polymer chains resulting from activated β-elimination are polymerized to yield highly branched materials as expected because of β-elimination and activated reinsertion mechanisms leading to chain branching.

4. Conclusions

A series of newly designed Ni(II) complexes bearing β-diimine ligands with different steric bulk were demonstrated to be very active catalyst systems in ethylene polymerizations combined with MAO. The activity, polymer molecular weight and polymer microstructure could be tuned by modifying the catalyst architecture and by controlling polymerization parameters such as temperature and MAO concentration. In general both polymer molecular weight and number of branches increased as steric bulk of the catalyst and polymerization temperature increased. A relatively small amount of MAO cocatalyst (say [Al]/[Ni] = 300) was needed to fully activate the catalyst, and the chain transfer to MAO was a minor termination.

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