Symmetric and Asymmetric Binuclear
α-Diimine Nickel(II) Complexes for Ethylene Polymerization

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ABSTRACT: *A series of symmetric and asymmetric binuclear α-diimine nickel(II) complexes toward ethylene polymerization were successfully synthesized and characterized by ^{1}HNMR. All the catalysts were typically activated with MAO and displayed good activity at room temperature under 1atm ethylene pressure. The symmetric catalyst containing isopropyl on ligand activated with 500 equiv MAO produced high molecular weight polyethylene with a PDI=1.75, while the symmetric catalyst containing methyl on ligand produced relatively low molecular weight polyethylene with a PDI=1.74. By contrast, the molecular weight, branching density of resultant polymer produced by asymmetric catalyst decrease roughly somewhere between that of polymers prepared by two symmetric catalysts.*

KEYWORDS: *α-Diimine nickel complexes; Ethylene polymerization; Symmetric catalyst; Asymmetric catalyst.*

INTRODUCTION

Compared to corresponding mononuclear complexes, multinuclear catalysts toward olefin polymerization display unique performances in selective polymerization, catalytic activity, thermal stability, the molecular weight and branching density of the resulting polymers [1-3]. *Cui* and *co-workers* [4] synthesized a series of binuclear rare-earth metal bis(alkyl) complexes for isoprene polymerization and their results showed that the binuclear catalyst showed relatively lower cis-1,4-selectivity and higher 3,4-selectivity, produced polyolefin with a much higher molecular weight in comparison with the mononuclear complexes. Marks' research group [5] reported that the closer the distance of two metal active centers, (η^5-indenyl)

[1-Me$_2$Si (tBuN) TiCl$_2$]-3-C$_n$H$_{2n}$-[N,N-bis(2-(ethylthio) ethyl)-amine]CrCl$_3$ produced polyethylenes with higher activity, the molecular weight, and branch density under identical ethylene polymerization conditions due to very large cooperative effects. It is worth noting that multinuclear catalysts also showed good thermal stability. Besides the higher activity, biphenyl-bridged bis(imino) pyridylcobalt catalyst exhibited better thermal stability and longer lifetimes than did the mononuclear bis(imino)pyridyl cobalt catalyst[6]. Takeuchi and co-workers [7] synthesized Dinuclear Fe complex with a double-decker structure for ethylene polymerization, and its activity was up to 975 g/(mmol Fe).h.atm at 100 °C.

M$_1$N$_4$Ni$_2$:R$_1$=R$_2$=-CH(CH$_3$)$_2$, M$_2$N$_4$Ni$_2$:R$_1$=R$_2$=- CH$_3$
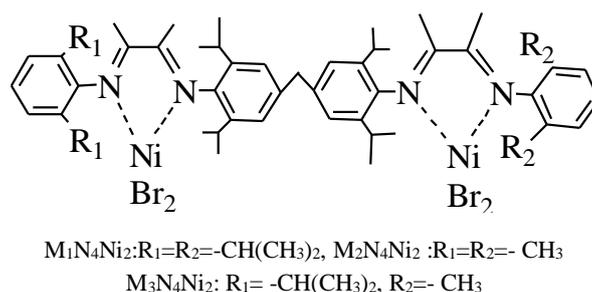M$_3$N$_4$Ni$_2$: R$_1$= -CH(CH$_3$)$_2$, R$_2$=- CH$_3$

Fig. 1: Different architectures of symmetric and asymmetric binuclear diimine nickel complexes

Nickel and palladium α-diimine catalysts for olefin polymerization have been a topic of significant interest since they produce polyolefin with various topologies ranging from highly linear to hyperbranched alone from ethylene [8-15]. Through elaborate modification in substituents on the ortho-position of the aniline and backbone groups, α-diimine nickel and palladium catalysts show excellent catalytic performance for olefin homo-polymerization [16-19], copolymerization of an olefin with polar monomer [20-25] and living polymerization [26-28]. Considering catalytic advantages of multinuclear catalysts and α-diimine catalysts, we designed and synthesized a series of novel symmetric and asymmetric binuclear α-diimine nickel(II) catalysts and investigated the influence of the catalyst structure on catalytic properties for ethylene polymerization in the presence of methylaluminoxane (MAO)(Fig.1.).

EXPERIMENTAL SECTION
Materials

4,4′-methylene-bis(2,6-diisopropylaniline), 2,6-diisopropylaniline, 2,6-di -methylaniline, NiBr$_2$(DME) was purchased from Aldrich was purchased from Alfa Aesar Chemical. Methylaluminoxane (MAO) was purchased as 10 wt % in toluene from Aldrich. 3-((2,6-diisopropylphenyl)imino)-2-butanone,3-((2,6–di methylphenyl) imino)-2-butanone were synthesized according to the literature[29.30]. Polymerization–grade ethylene was further purified by passing through two columns of pre-activated molecular sieves 4Å. Toluene was refluxed over sodium with benzophenone as an indicator and distilled under nitrogen atmosphere.

Ethylene Polymerization

The nickel catalysts were obtained from an in situ reaction of the ligand with (DME)NiBr$_2$ in toluene for 12 h.

Then, the catalyst solutions were directly activated by MAO and the homogeneous solutions were immediately used for the polymerization experiments. Polymerization was conducted in a 100-mL glass reactor equipped .with a stirrer, an ethylene inlet, and a vacuum outlet was purged three times with argon. At a selected polymerization temperature, toluene was introduced into the reactor and saturated with ethylene monomer. Subsequently, the required solution of the activated catalyst was injected into glass reactor to start the polymerization. The polymerization was terminated at a fixed time by the addition of acidified ethanol. The precipitated polymer was collected and treated by filtering, washing with ethanol several times, and then drying in vacuum at 50 °C to a constant weight [31.32].

Characterization

Molecular weights and molecular weight distributions for polyethylene were determined by the high-temperature Gel Permeation Chromatography (GPC) method with a PL-220 apparatus (Polymer Laboratories Co., UK), using 1,2,4-trichloro-benzene as the eluent at 150 °C. Narrow standard polystyrene was used for GPC calibration. ^{13}C NMR spectra and ^{1}H NMR of polyethylene were recorded with a 400 MHz AVANCE NMR spectrometer (Model DMX500) using TMS as the standard.

Synthesis of ligand
M$_1$N$_4$

In a 100 mL flask, 4,4′-methylene-bis(2,6-diisopropylaniline) (3.5g, 9.7mmol), 3-((2,6 -diisopropylphenyl)imino) 2-butanone (5.4g, 22.0 mmol) were dissolved in 60mL benzene,and and 0.05g p-toluenesulfonic acid monohydrate was added. The flask was connected to a water separator and a reflux condenser. After refluxing the mixture overnight,

the solvent was evaporated. The crude product was purified via column chromatography (15% ethyl acetate/ petroleum ether, 200 mm silica gel) to give a white powder (7.5 g, 85%). ^{1}H NMR(CDCl$_3$): δ7.20(4H,o-H-Ar), 7.12(2H,m-H-Ar), 6.98 (4H,o-H-(Ar)$_2$), 4.03(2H,CH$_2$-(Ar)$_2$), 2.75(8H, Ar-CH(CH$_3$)$_2$), 2.06(12H,Ar-N=CCH$_3$),1.20(48H,Ar-CH(CH$_3$)$_2$)(Fig.2).

M$_2$N$_4$

Using a procedure similar to that described in the preparation of LS1-N4. 4,4′-methylene-bis(2,6-diisopropylaniline) (3.5g, 9.7mmol), 3-((2,6 –dimethyl -phenyl)imino)-2-butanone (5.2g, 22.0 mmol) were dissolved in 60mL benzene,and and 0.05g p-toluenesulfonic acid monohydrate was added (7.3g,82%).^{1}H NMR(CDCl$_3$): δ7.18(4H,o-H-Ar), 7.10(2H,m-H-Ar), 6.98 (4H,o-H-(Ar)$_2$), 4.02(2H, CH$_2$-(Ar)$_2$) ,2.71(2H,Ar-CH(CH$_3$)$_2$), 2.08(12H,Ar-N=CCH$_3$), 1.58(12H,Ar-CH$_3$), 1.19 （ 24H,Ar-CH (CH$_3$)$_2$) (Fig.3.).

M$_3$N$_4$

In a 100 ml flask, 4,4′-methylene-bis(2,6-diisopropylaniline) (3.5g, 9.7mmol), 3-((2,6 -diisopropylphenyl)imino) 2-butanone (2.2g, 9.0mmol) were dissolved in 60mL benzene,and and 0.05g p-toluenesulfonic acid monohydrate was added. The flask was connected to a water separator and a reflux condenser. After refluxing the mixture overnight, the solvent was evaporated. The crude product was purified via column chromatography (25% ethyl acetate/ petroleum ether, 200 mm silica gel) to give a white powder (compound 5). Then, in a 100 mL flask, compound 5 (3.16g, 5.30mmol), and 3-((2,6–dimethyl -phenyl)imino) 2-butanone (1.42g, 6.0 mmol) were dissolved in 60mL benzene,and and 0.05g p-toluenesulfonic acid monohydrate was added. The flask was connected to a water separator and a reflux condenser. After refluxing the mixture overnight, the solvent was evaporated. The crude product was purified via column chromatography (15 % ethyl acetate/ petroleum ether, 200 mm silica gel) to give white powder(2.2g,50%). ^{1}HNMR(CDCl$_3$): δ7.20(4H,o-H-Ar), 7.10(2H, m-H-Ar), 6.98 (4H,o-H-(Ar)$_2$), 4.03(2H,CH$_2$-(Ar)$_2$), 2.75(2H,Ar-CH(CH$_3$)$_2$), 2.06(12H,Ar-N=CCH$_3$), 1.58(6H,Ar -CH$_3$), 1.20(36H,Ar-CH(CH$_3$)$_2$)(Fig.4.)。
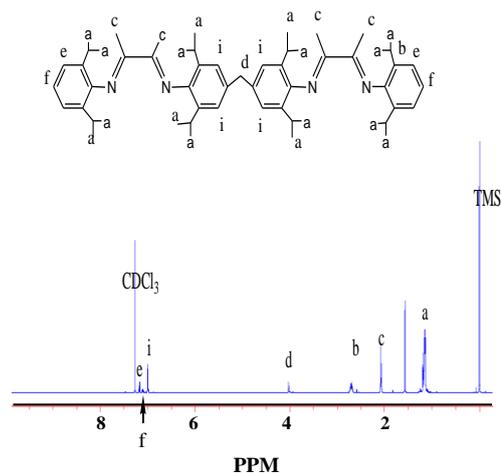
Fig. 2: ^{1}HNMR spectrum of M$_1$N$_4$ ligand.
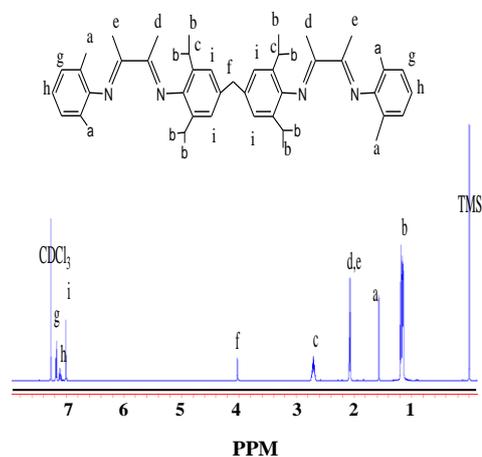

Fig. 3: ^{1}HNMR spectrum of M$_2$N$_4$ ligand.
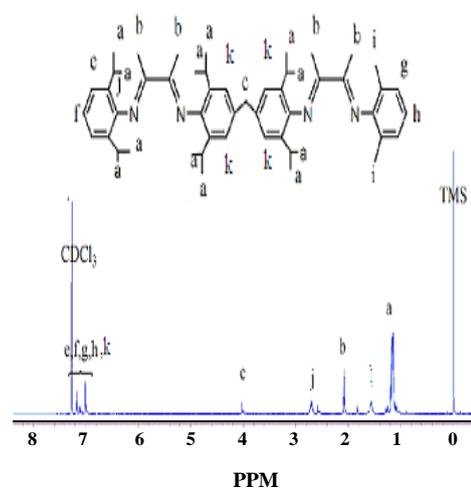

Fig. 4: ^{1}HNMR spectrum of M$_3$N$_4$ ligand.

RESULTS AND DISCUSSION

Ligand synthesis

As shown in Fig. 5, symmetric ligands M_1N_4 and M_2N_4 were conveniently synthesized by condensation reaction of 4,4′-methylene-bis(2,6-diisopropylaniline) with 3-((2,6 –diisopropyl -phenyl)imino) 2-butanone and 3-((2,6-dimethylphenyl) imino) $_2$-butanone using p-toluenesulfonic acid monohydrate as a catalyst, respectively, and their yields were more than 80%. On the contrary, the synthesis process of asymmetric ligand M_3N_4 was relatively cumbersome and it was achieved through two steps of condensation reaction and the yield was relatively low(50%) (Fig.6). The crude products were purified via column chromatography and characterized by ^1H NMR, the results indicated that the target products were synthesized successfully (Fig.4) [33,34].

Catalyst Activity

Catalytst activity is an important parameter to evaluate the merits of the catalytic polymerization performance. The nickel catalysts were obtained from an in situ reaction of the ligands with (DME)NiBr$_2$ and directly used for ethylene polymerization and the results were listed in Table 1. All the catalysts were typically activated with MAO and displayed good activity at room temperature under 1atm ethylene pressure. Moreover, the activity of each catalyst increased significantly with increasing the co-catalyst amount. For example, the activity of $M_1N_4Ni_2$ with 500 equiv MAO to catalyst toward ethylene polymerization reached to 1.06×0^6 g/mol·h, while increasing MAO to 2000 equiv, the activity was up to 1.68×0^6 g/mol·h. Among three catalysts, $M_2N_4Ni_2$/MAO exhibited highest activity under the same conditions, which suggested that low resistance of N-aryl substituent was more conducive to the ethylene insertion to produce polyethylene, the results were very consistent with the reports of the relevant literature [12]. It is known that the rotation of N-aryl bonds and the C-H activation of α-diimine nickel complexes are the main factors resulting in reducing catalytst activity. We considered that the steric bulk of binuclear α-diimine nickel(II) complexes would greatly slow down rates of N-aryl bond rotaions and C−H activation, therefore, binuclear α-diimine nickel(II) complexes exhibited high catalytst activity [16].

Molecular weight and molecular weight distribution

To further investigation of the polymerization properties of symmetric and asymmetric catalysts, the molecular weight distribution of polyethylene prepared by $M_1N_4Ni_2$, $M_2N_4Ni_2$, and $M_3N_4Ni_2$ was also enumerated in Table 1. By contrast, $M_1N_4Ni_2$ produced the highest molecular weight PE (M_n=278000 g/mol) with 500 equiv MAO at 1atm ethylene gas and room temperature, while $M_2N_4Ni_2$ obtained relatively low molecular weight PE(M_n=68000g/mol) under equivalent conditions, these observations were attributed to the catalyst metal electronic nature, which were very consistent with the reports in the related literature[12]. In addition, the polymers produced by $M_1N_4Ni_2$ and $M_2N_4Ni_2$ displayed relatively narrow weight distribution, for example, the weight distribution of the resultant polymer produced by $M_1N_4Ni_2$ with 500 equiv MAO was as low as 1.75. In contrast, with 500 equiv MAO produced the polyethylene with broad weight distribution (PDI=3.04) (as shown in Fig. 7). Unlike symmetric catalysts ($M_1N_4Ni_2$ and $M_2N_4Ni_2$) with single activity toward ethylene polymerization, asymmetric catalyst($M_3N_4Ni_2$) had two different active centers and each center operated independently in polymerization process, so the resultant polyethylenen was similar to the mixture of two polyethylenes produced by $M_1N_4Ni_2$ and $M_2N_4Ni_2$ at corresponding conditions respectively. Therefore, the independent catalytic action of two active centers readily led to relatively broad molecular weight distribution of resultant polymer.

Microstructure

^{13}C NMR measurements were adopted to investigate the branching structures of resultant polyethylene and short branches such as methyl, ethyl, butyl, to amyl, and the longer branches were identified approximatively by the unique carbon resonances (as shown as Fig. 8.), which allowed the calculation of the density of each branching type per 1000 carbons in polymers. As shown in Table 2, all the catalysts produced hyperbranched polyethylenes owed to the possible chain walking mechanism. Among branches were predominately methyl and the methyl percentages of resultant polymer produced by the symmetric and asymmetric catalysts activated respectively with 1000 equiv MAO were more than 65%. Moreover, $M_1N_4Ni_2$/MAO obtained the polymer with

Table 1: Conditions and results of ethylene polymerization[a].

Run	Cat.	Ni/Al (mol/mol/)	Acitivity (10^6g/mol·h)	M_n^b (g/mol)	PDI[b]
1	$M_1N_4Ni_2$	1/2000	1.68	219400	2.05
2	$M_1N_4Ni_2$	1/1000	1.47	258000	1.89
3	$M_1N_4Ni_2$	1/500	1.06	278000	1.75
4	$M_2N_4Ni_2$	1/2000	1.86	48600	1.95
5	$M_2N_4Ni_2$	1/1000	1.74	59500	1.82
6	$M_2N_4Ni_2$	1/500	1.45	68000	1.74
7	$M_3N_4Ni_2$	1/2000	1.72	143200	3.20
8	$M_3N_4Ni_2$	1/1000	1.58	154500	3.15
9	$M_3N_4Ni_2$	1/500	1.32	168000	3.04

[a]*Polymerization conditions: temperature time 30min；50 mL toluene solvent；room temperature；1atm ethylene gas；
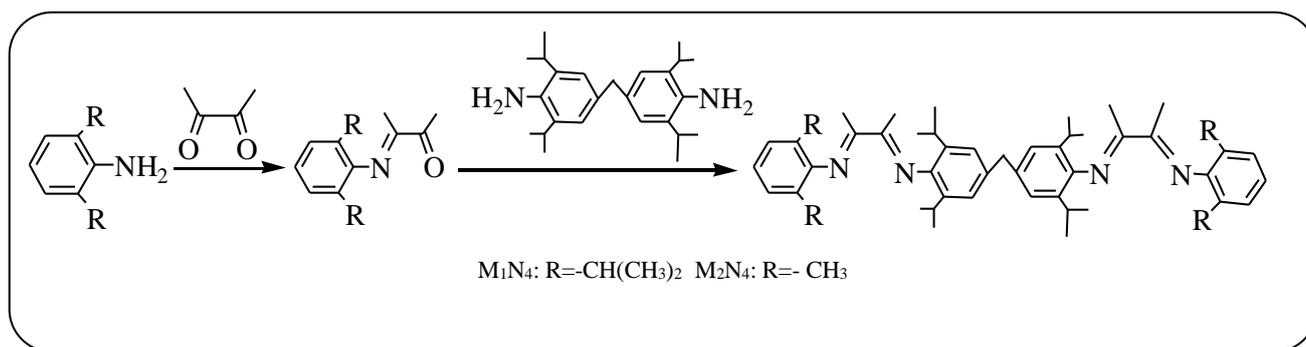MAO as cocatalyst.* [b] *Determined by GPC at 150ºC versus polystyrene standard.*

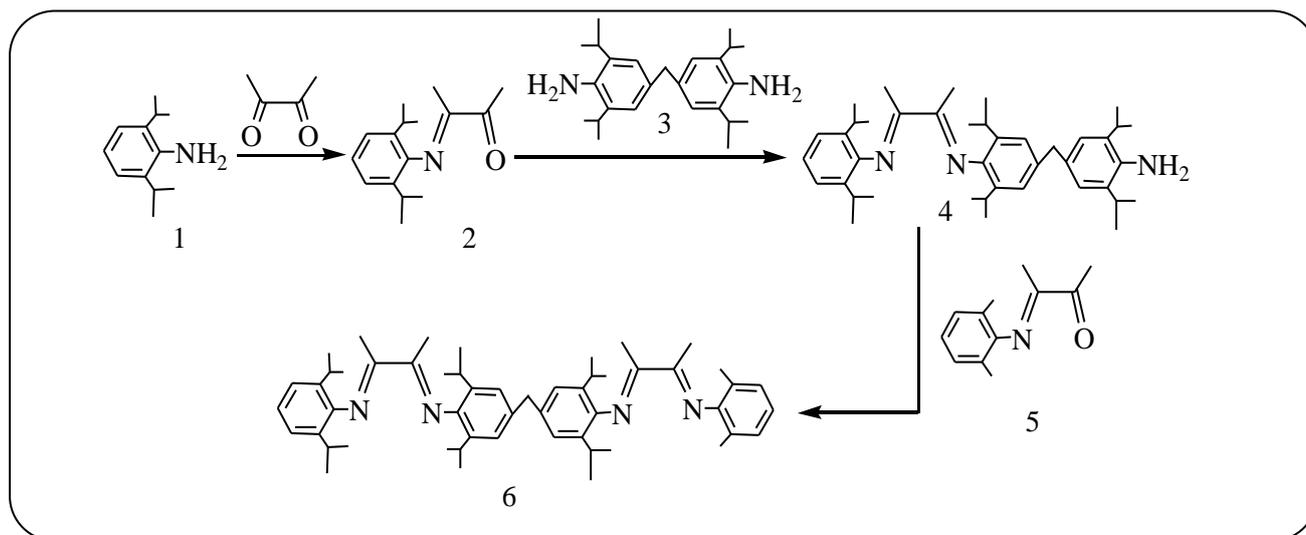*Fig. 5: Synthesis route of symmetric ligands.*

Fig. 6: Synthesis route of Asymmetric ligand (M₃N₄).

Table 2: Branching distribution determined by ^{13}C NMR spectra of polyethylenes produced using different catalyst[a].

Run	Methyl	Ethyl	propyl	Butyl	Amyl	Long branch	Percentage of Methyl[b]	Total branch[c]
2	88.0	7.5	7.0	6.8	9.4	14.0	66.3%	132.7
5	57.4	4.7	3.4	3.8	4.5	8.5	69.7%	82.3
8	74.0	6.9	6.0	5.4	6.6	10.8	67.5%	109.7

Elution time (min)

Elution time (min)
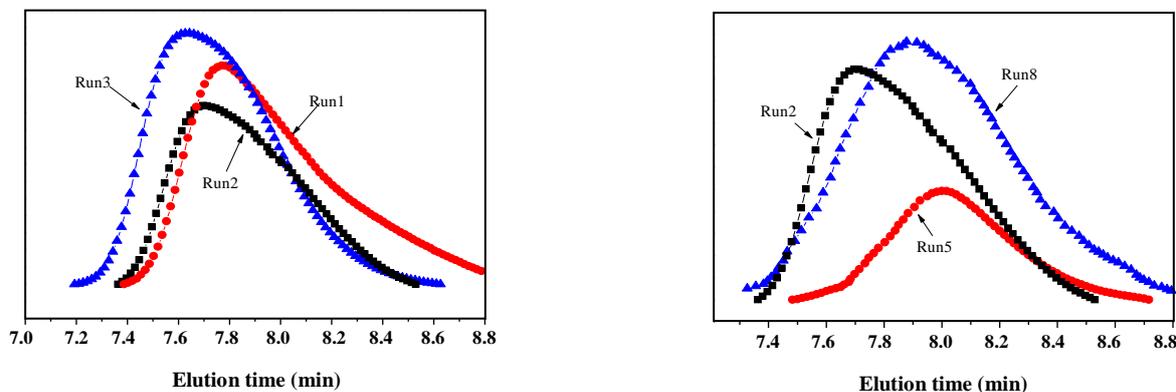
Fig. 7: Molecular weight distribution of resultant polyethylene produced with different catalysts.
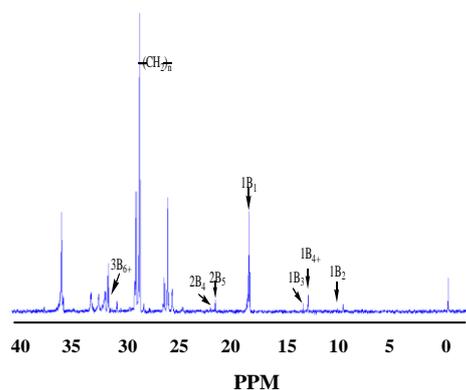
Fig. 8: ^{13}C NMR (o-C$_6$D$_4$Cl$_2$, 300 MHz, 120 °C) of branched polyethylene (Run2).

highest branching density owing to fast chain walking. The branching density of resultant polymer produced by asymmetric catalyst fell somewhere between that of polymers prepared by two symmetric catalysts, which showed that asymmetric catalyst produced a mixture once again [31-32].

CONCLUSIONS

In summary, the synthesis, characterization, and ethylene polymerization behaviors of novel symmetric and asymmetric catalysts were reported at length. All the catalysts were typically activated with MAO and displayed good activity at room temperature under 1atm ethylene pressure. The symmetric catalyst containing isopropyl on ligand activated with 500 equiv MAO produced high molecular weight polyethylene (M_n=27800g/mol) with a PDI=1.75, while the symmetric catalyst containing methyl on ligand produced relatively low molecular weight polyethylene (M_n=68000g/mol) with a PDI=1.74. By contrast, the molecular weight, branching density of resultant polymer produced by asymmetric catalyst fell roughly somewhere between that of polymers prepared by two symmetric catalysts under the same conditions, which suggested that he polymer produced by asymmetric catalyst was a mixture considering its broad molecular weight distribution.

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