Macrocyclic Binuclear *α*-Diimine Nickel Catalysts for Ethylene Polymerization

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Polyolefins are globally important plastics. Molecular weight and molecular weight distribution are two key parameters for determining the properties of polyolefin materials. In this contribution, we develop a strategy for combining the macrocyclic framework and the binuclear effect into the benchmark *α*-diimine late transition metal catalysts, and thus macrocyclic binuclear *α*-diimine nickel catalysts (**Ni₂-Me** and **Ni₂-*i*Pr**) are prepared. Compared to the classical Brookhart's acyclic mononuclear *α*-diimine nickel analogues (**Ni₁-Me** and **Ni₁-*i*Pr**), these nickel catalysts exhibit enhanced thermostability (up to 110 °C) and produce polyethylenes with higher molecular weights (up to 7 times) and lower branching densities (as low as 9 branches/1000C) in methylaluminoxane (MAO) activated ethylene polymerization. This translates into the ability of the catalyst to afford more linear high molecular weight polyethylenes. In particular, bimodal polyethylenes with broad molecular weight distributions (M_w/M_n = 8.08—14.66) are generated by the sole catalyst. This work affords diverse polyethylenes.

Keywords Polyolefin; Nickel catalyst; Diimine ligand; Macrocyclic binuclear strategy; Bimodal polyethylene

1 Introduction

Polyolefins, such as polyethylene and polypropylene, are the largest-scale synthetic polymers and are ubiquitous in modern society[1−4]. Catalyst is key for the synthesis of polyolefins, and Brookhart's *α*-diimine nickel [Ni(II)] and palladium [Pd(II)] catalysts represent a milestone in the coordination-insertion ethylene (co)polymerization (Scheme 1, **I**), opening a new era for late transition metal catalysts[5,6]. Over the past thirty years, significant efforts have been made to the advance of *α*-diimine Ni(II)/Pd(II) catalysts for improving the thermal stability of catalysts and the corresponding catalytic properties, such as polymer molecular weight and branching density[7−10]. One of the effective strategies for the catalyst design is to block the axial sites of the active metal species by increasing the steric hindrance with bulky *N*-aryl substituents, which can suppress

chain transfer reactions and improve the thermal stability of catalysts in ethylene polymerization. This strategy involving ligand electronics and sterics has been extensively used by the polyolefin community[11−37].

In contrast, the strategy on the use of macrocyclic ligand in *α*-diimine Ni(II)/Pd(II) catalysts has attracted much less attention because of the difficult synthesis. In general, the associative chain transfer mostly occurs in ethylene polymerization, which can be suppressed by shielding the axial sites. One envisions installing a linkage for bridging the *N*-aryl substituents of both sides in the *α*-diimine ligand, which not only prohibits the free rotation of the *N*-aryl groups but also blocks the apical sites *via* the linkage. This is the so-called (macro-)cyclic *α*-diimine ligand. As a pioneer, Guan *et al*.[38−40] synthesized the cyclophane-based *α*-diimine Ni(II)/Pd(II) catalysts by multi-step reactions, which showed significantly higher thermal stability and gave higher polymer molecular weight at an elevated temperature relative to the acyclic analogues (Scheme 1, **II**). It should be noted that a too flexible bridge is unfavored for the catalyst, which is reflected by the alkyl-bridged macrocyclic *α*-diimine Ni(II)/Pd(II) catalysts that are almost inactive for ethylene polymerization (Scheme 1, **III**)[41]. By using the cyclic strategy, Takeuchi *et al*.[42] upgraded the macrocyclic *α*-diimine ligand to binuclear Pd(II) catalysts (Scheme 1, **IV**). The cooperation of the two Pd(II) active species, which are fixed in the rigid macrocyclic ligand, has a significant binuclear effect on the copolymerization of ethylene and acrylates, producing branched ethylene-acrylate copolymers with the acrylate unit mostly incorporated into the main chain. This differed from that produced by the acyclic mononuclear Pd(II) catalyst. Chen *et al*.[43,44] prepared a series of acyclic binuclear *α*-diimine Ni(II)/Pd(II) catalysts bearing rigid naphthalene, biphenylene, or xanthene linkages *via* an unsymmetrical strategy (Scheme 1, **V**), generating polyethylenes with higher molecular weights.

Based on the above-mentioned pioneering progresses, we envision that the combination of macrocyclic strategy[45−50] and binuclear effect[51−54] can generate a new kind of *α*-diimine Ni(II) catalysts, which concurrently possess rational bulky substituents close to the metal center and rigid anthracene bridges (Scheme 1, **VI**). The rigid macrocyclic structure

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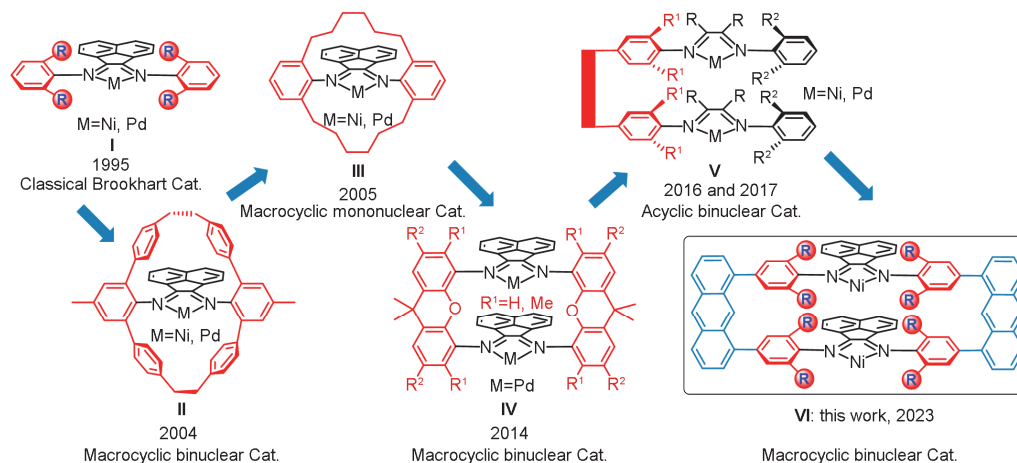
Scheme 1 *α*-Diimine Ni(II) and Pd(II) catalysts bearing acyclic/cyclic mono-/bi-nuclear structures

effectively blocks the axial direction of nickel metal centers and brings two nickel metal centers closer at the same time, which would offer the catalyst a promising performance in ethylene polymerization. Herein, we report these macrocyclic binuclear *α*-diimine Ni(II) catalysts have enhanced thermostability and afford polyethylenes with higher molecular weights and lower branching densities. In particular, bimodal polyethylenes are produced by one catalyst alone. This obviously differs from the Brookhart's acyclic mononuclear *α*-diimine Ni(II) catalysts.

2 Experimental

2.1 General Methods

All syntheses involving air- and moisture-sensitive compounds were carried out using standard Schlenk-type glassware (or in a glove box) under an atmosphere of nitrogen. All solvents were purified from the MBraun SPS system. NMR spectra for the ligands, complexes, and polymers were recorded on a Bruker AV400 (^{1}H: 400 MHz, ^{13}C: 100 MHz) or a Bruker AV500 (^{1}H: 500 MHz, ^{13}C: 125 MHz). The molecular weights (M_n) and molecular weight distributions (M_w/M_n) of polyethylenes were measured through gel permeation chromatography (GPC) on a PL-GPC 220-type high-temperature chromatograph equipped with three PL-gel 10 μm Mixed-B LS type columns at 150 °C. The polymer sample was dissolved in 1,2,4-trichlorobenzene as an organic solvent on a 160 °C hot bench for 6—10 h, and 0.05% (mass fraction) BHT (2,6-di-*tert*-butyl-4-methylphenol) was added as an inhibitor to prevent free radical reaction. Melting points (T_m) of polyethylenes were measured through DSC analyses, which were carried out on a Mettler TOPEM TM DSC instrument under the nitrogen atmosphere at heating and cooling rates of 10 °C/min (temperature range: 20—160 °C). Elemental analysis was performed at the National Analytical

Research Centre of Changchun Institute of Applied Chemistry, CAS. Mass spectra of compounds were recorded on an Acquity UPLC & Quattro Premier.

The synthesis of *α*-diimine ligands and nickel catalysts can be found in the Electronic Supplementary Material of this paper.

2.2 General Procedure for Ethylene Polymerization

In a typical experiment, a 350 mL glass pressure reactor connected with a high-pressure gas line was firstly dried at 90 °C under vacuum for at least 1 h. The reactor was then adjusted to the desired polymerization temperature, 98 mL of toluene (hexane) and methylaluminoxane (MAO) co-catalyst was added to the reactor under the N$_2$ atmosphere, and then the desired amount of nickel catalyst in 2 mL of CH$_2$Cl$_2$ was injected into the polymerization system *via* syringe. With a rapid stirring, the reactor was pressurized and kept constant at 8 bar (1 bar = 0.1 MPa) of ethylene. After a specific time, the pressure reactor was vented and the polymerization was quenched *via* the addition of 100 mL of acidic EtOH (10% HCl in EtOH) to the reactor and dried in a vacuum oven at 50 °C to a constant mass for at least 48 h. The MAO (from Albemarle Corporation, USA) used in this polymerization is a toluene solution with a concentration of 1.5 mol/L.

3 Results and Discussion

3.1 Design and Synthesis of Macrocyclic *α*-Diimine Ligands and Binuclear Ni(II) Catalysts

In olefin polymerization catalyzed by the *α*-diimine Ni(II) complexes, catalytic activities and polymer properties are strongly influenced by the ligand steric effect at the axial positions[11,16,20,26—27]. These properties include polymer

molecular weight, branching density, and polydispersity index (PDI). In this work, we design new α-diimine ligands with the macrocyclic structure, where the installation of 2,6-di-substituents (R=Me, ^{i}Pr) provides a sterically bulky environment around the center metal for preventing the deactivation of the catalyst. Furthermore, the use of the rigid bridge (anthracenyl group) not only helps inhibit the rotation of the *N*-aryl group but also enables the ligand to support the binuclear Ni(II) catalyst in a macrocyclic environment. As a result, the strategy differs from the pioneering approaches and should enable the macrocyclic binuclear Ni(II) catalysts to show distinct catalytic performances relative to their mononuclear analogues.

Macrocyclic binuclear α-diimine ligands were synthesized *via* Suzuki coupling reactions and subsequent condensation reactions *via* four steps (Scheme 2). Firstly, 1,8-dichloroanthracene was obtained by reducing 1,8-dichloroanthraquinone (8 g, 97%, Energy Chemical) with a zinc powder (32 g, A. R., XiLONG SCIENTIFIC, Shantou, China) in aqueous ammonia (200 mL, 25%, XiLONG SCIENTIFIC) without column chromatography (yield: 70%—78%)[18]. Then, 1,8-bis(neopentyl glycolatoboryl)anthracene was prepared by reacting 1,8-dichloroanthracene (4 g) with 2 equiv. of bis(neopentylglycolato)diboron (9.2 g, 98%, Energy Chemical) using Pd$_2$(dba)$_3$ (0.3 g, 99%, J&K Scientific) and

Xphos [0.6 g, 98% (NMR), Energy Chemical] as catalysts[55]. Finally, Suzuki coupling of the bis(neopentylglycolato)diboron with 2 equiv. of bromo-substituted aniline afforded the desired bisaniline (**3**: **NH₂-Me, NH₂-iPr**) in a *ca*. 58% yield. Macrocyclic α-diimine ligands **4** (**L-Me** and **L-iPr**) were obtained by condensing bisaniline with 1 equiv. of acenaphthenequinone in ethanol using 5% (molar ratio) of *p*-toluenesulfonic acid under N₂[42]. The product was pure enough for the next reaction and did not require column chromatography for further purification. The ligands were characterized by ^{1}H, ^{13}C NMR spectroscopy, MALDI-TOF, and elemental analysis. Macrocyclic binuclear α-diimine Ni(II) catalysts **Ni₂-Me** and **Ni₂-iPr** were finally prepared by reacting the ligands with 2 equiv. of NiBr₂(DME) (DME=ethylene glycol dimethyl ether) in dry THF for three days (yield: 72%—74%). More synthesis and post-processing details can be seen in the supporting information. These Ni(II) complexes were fully characterized by elemental analysis and MALDI-TOF mass spectrometry. Due to the poor solubility of both ligands and catalysts, no single crystal suitable for X-ray diffraction analysis was obtained despite several attempts. Besides, mononuclear Ni(II) complexes (**Ni₁-Me** and **Ni₁-iPr**) were also synthesized for comparison according to the literature methods (Scheme 2)[56].
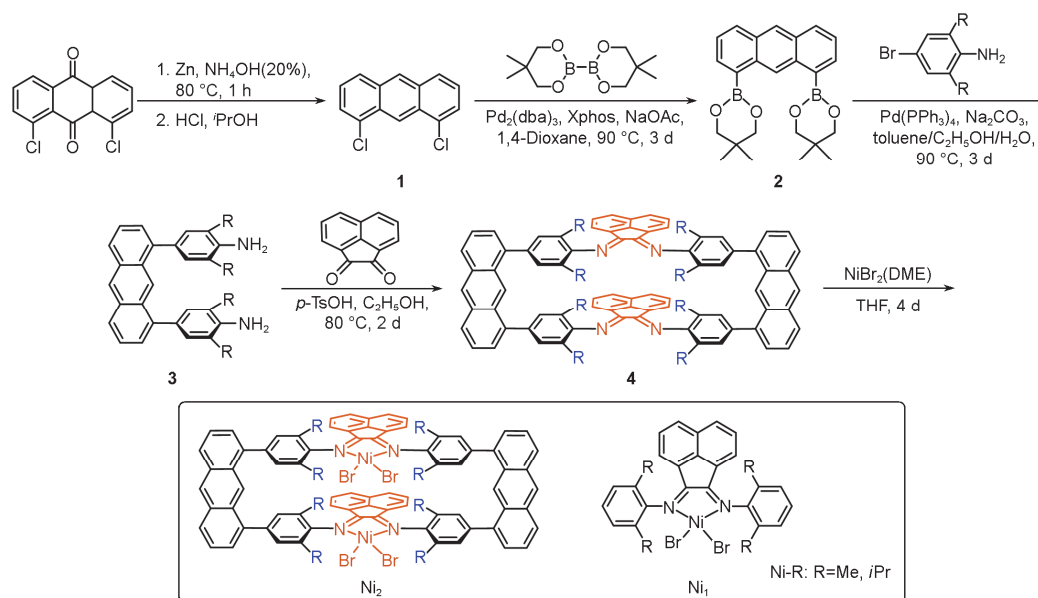
**Scheme 2 Synthesis of macrocyclic α-diimine ligands and the corresponding binuclear Ni(II) catalysts**

3.2 Ethylene Polymerization with the Ni(II) Catalysts

All new macrocyclic binuclear Ni(II) catalysts showed different behaviors from their mononuclear Ni(II) analogues in ethylene polymerization when activated with MAO in

toluene at a ratio of 500:1 under 8 bar of ethylene pressure. Binuclear Ni(II) complexes **Ni₂-Me** and **Ni₂-iPr** exhibited better thermostability than their mononuclear Ni(II) analogues **Ni₁-Me** and **Ni₁-iPr**, respectively, and produced polymers with both higher molecular weight, and lower branching densities (Fig.1 and Fig.2).

The highest catalytic activity of **Ni₂-Me** could reach 1.6×10^6 $g \cdot mol^{-1} \cdot h^{-1}$, generating polyethylene with a M_w of 46.4×10^4, when the polymerization was carried out at 30 °C (Table 1, entry 5). Moreover, the molecular weight of polymers prepared by **Ni₂-Me** was significantly higher than that by **Ni₁-Me** in the wide temperature range of 30 °C to 90 °C (Table 1, entries 1—4 *vs.* 5—8). At 50 °C, the molecular weight of the polymer generated by **Ni₂-Me** ($M_w=30.5 \times 10^4$) was almost 6 times higher than that generated by **Ni₁-Me** ($M_w=5.2 \times 10^4$), and the polymer branching density was lower by 47% (Table 1,

entries 2 *vs.* 6). Under identical polymerization conditions, the catalytic activity of all Ni(II) catalysts decreased with rising polymerization temperature, which could be attributed to the slow deactivation of the catalyst and the lower solubility of ethylene at a higher temperature. At 90 °C, **Ni₁-Me** completely deactivated without the formation of any polymer; however, **Ni₂-Me** still maintained activity of 1.8×10^5 $g \cdot mol^{-1} \cdot h^{-1}$, and the molecular weight of polymer ($M_w=9.7 \times 10^4$) obtained at 90 °C by **Ni₂-Me** was even slightly higher than that generated by **Ni₁-Me** ($M_w=9.5 \times 10^4$) at 30 °C (Table 1, entries 4 *vs.* 8),
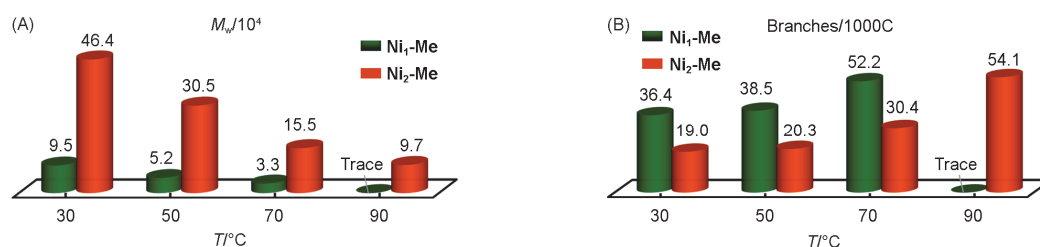
Fig.1 Comparisons of molecular weight (A) and branching density (B) of polyethylenes generated by Ni₁-Me and Ni₂-Me catalysts at different temperatures
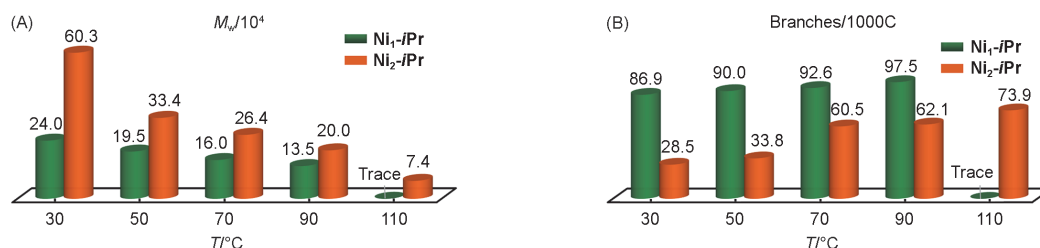
Fig.2 Comparisons of molecular weight (A) and branching density (B) of polyethylenes generated by Ni₁-*i*Pr and Ni₂-*i*Pr catalysts at different temperatures

Table 1 Ethylene polymerization using Ni(II) catalysts[a]

Entry	Cat.	$T/°C$	Yield/g	Act.[b]	M_w[c]	M_w/M_n[c]	M_p[c]	brs[d]	T_m[e]/°C
1	**Ni₁-Me**	30	4.57	4.6×10^6	9.5×10^4	2.77	5.8×10^4	36.4	116.7
2	**Ni₁-Me**	50	3.38	3.4×10^6	5.2×10^4	2.11	3.9×10^4	38.5	106.2
3	**Ni₁-Me**	70	1.46	1.5×10^6	3.3×10^4	2.02	2.6×10^4	52.2	88.3
4	**Ni₁-Me**	90	Trace	——	——	——	——	——	——
5	**Ni₂-Me**	30	0.78	1.6×10^6	46.4×10^4	2.21	42.8×10^4	19.0	125.0
6	**Ni₂-Me**	50	0.57	1.1×10^6	30.5×10^4	2.14	21.1×10^4	20.3	121.2
7	**Ni₂-Me**	70	0.12	0.24×10^6	15.5×10^4	2.48	9.2×10^4	30.4	116.3
8	**Ni₂-Me**	90	0.09	0.18×10^6	9.7×10^4	2.81	5.5×10^4	54.1	96.7
9	**Ni₁-*i*Pr**	30	7.93	4.6×10^6	24.0×10^4	1.83	19.2×10^4	86.9	——
10	**Ni₁-*i*Pr**	50	5.61	3.4×10^6	19.5×10^4	1.89	15.5×10^4	90.0	——
11	**Ni₁-*i*Pr**	70	4.63	1.5×10^6	16.0×10^4	1.98	13.8×10^4	92.6	——
12	**Ni₁-*i*Pr**	90	2.79	4.6×10^6	13.5×10^4	1.89	10.9×10^4	97.5	——
13	**Ni₁-*i*Pr**	110	Trace	——	——	——	——	——	——
14	**Ni₂-*i*Pr**	30	0.47	0.94×10^6	60.3×10^4	11.95	$52.9 \times 10^4/2.3 \times 10^4$	28.5	109.3
15	**Ni₂-*i*Pr**	50	0.38	0.76×10^6	33.4×10^4	8.08	$39.9 \times 10^4/1.3 \times 10^4$	33.8	112.3
16	**Ni₂-*i*Pr**	70	0.36	0.72×10^6	26.4×10^4	11.31	$21.1 \times 10^4/0.7 \times 10^4$	60.5	102.2/125.2
17	**Ni₂-*i*Pr**	90	0.35	0.70×10^6	20.0×10^4	14.66	$22.6 \times 10^4/0.7 \times 10^4$	62.1	108.9
18[f]	**Ni₂-*i*Pr**	110	0.16	0.06×10^6	7.4×10^4	9.75	$8.4 \times 10^4/0.8 \times 10^4$	73.9	115.5/123.0
19[g]	**Ni₁-Me**	30	12.03	12.0×10^6	4.8×10^4	4.88	1.6×10^4	52.8	108.3
20[g]	**Ni₂-Me**	30	2.58	5.2×10^6	33.5×10^4	3.86	20.5×10^4	9.0	127.8

*a*. Reaction conditions: Ni₁ catalyst (2 μmol), Ni₂ catalyst (1 μmol), MAO (500 equiv.), toluene/CH₂Cl₂ (98 mL/2 mL), polymerization time (30 min), polymerization pressure (8 bar), all entries are based on at least two runs, unless noted otherwise; *b*. activity is in the unit of $g \cdot mol^{-1} \cdot h^{-1}$; *c*. determined by GPC in 1,2,4-trichlorobenzene at 150 °C using a light scattering detector; *d*. brs=number of branches per 1000C, as determined by ¹H NMR spectroscopy; *e*. determined by DSC (second heating); *f*. Ni₂ catalyst (5 μmol); *g*. *n*-hexane/CH₂Cl₂ (98 mL/2 mL).

indicating the enhanced thermostability and the suppression of chain transfer enabled by the macrocyclic structure of **Ni₂-Me**.

When the solvent changed from toluene to industrially preferred aliphatic hydrocarbon hexane, polymer molecular weight, and branching density showed the same trend, and the activity of **Ni₂-Me** was as high as 5.2×10^6 g·mol⁻¹·h⁻¹. At 30 °C, the molecular weight of the polymer generated by **Ni₂-Me** ($M_w=33.5\times10^4$) was 7 times higher than that of the polyethylene produced by **Ni₁-Me** ($M_w=4.8\times10^4$), and the polymer branching density decreased by 83% (Table 1, entries 19 *vs*. 20).

The effect of replacing the methyl substituent with isopropyl at the 2,6-position of *N*-aryl group on ethylene polymerization was investigated using **Ni₂-iPr** and **Ni₂-Me**. Polyethylenes produced by **Ni₂-iPr** had a higher weight-average molecular weight (M_w), peak molecular weight (M_P), and lower branching density than those produced by **Ni₂-Me** (Table 1, entries 5—8 and 14—18). Moreover, **Ni₂-iPr** exhibited enhanced thermostability than **Ni₂-Me**, as evidenced by its higher polymerization temperature of 110 °C (Table 1, entry 18). The time-dependent polyethylene yield at 70 °C showed that **Ni₂-iPr** maintained catalytic activity for up to 120 min (Fig.3). This result demonstrated the excellent thermostability of **Ni₂-iPr** and its potential for producing high molecular weight polyethylene.

A distinctive feature of **Ni₂-iPr** compared with the classical Brookhart's catalyst **Ni₁-iPr** was its ability to produce polymers with a bimodal molecular weight distribution (Table 1, entries 14—18), which could facilitate processing[57,58]. This suggests that two different MAO-activated nickel species were present during ethylene polymerization, with one of the active species generating high-molecular-weight polyethylene while the other producing low-molecular-weight polyethylene (Fig.4)[42]. The axial site substituents of the nickel center were crucial for polymerization activity, and we hypothesized that **Ni₂-iPr** existed as a mixture of *syn* and *anti*-isomers in terms of the backbone structure relative to the metal center due to the steric hindrance of isopropyl groups (Fig.5)[28]. One that could better shield the ethylene monomer had a more hindered axial environment, leading to slower chain transfer. As a result, high-molecular-weight polyethylene was formed. On the contrary, another preferred chain transfer and formed the low-molecular-weight polyethylene. Compared with **Ni₂-Me**, the key feature of **Ni₂-iPr** is that bulkier *ortho*-position substituents (Me *vs*. *i*Pr) suppress the rotation of acenaphthequinone and inhibit the interconversion of two isomers, resulting in the stable existence of both active species at the same time. These findings indicate that the new macrocyclic binuclear strategy could achieve different polymerization outcomes by tuning the catalyst structure from design.
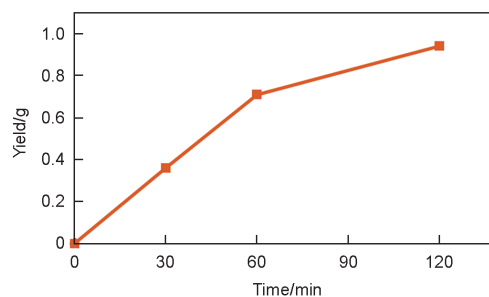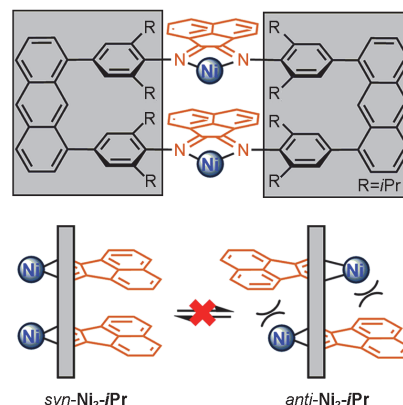

Fig.3 Plot of yield of polyethylene *versus* time of Ni₂-*iPr*

Conditions: **Ni₂-*iPr***: 1 μmol, ethylene: 8 MPa, CH₂Cl₂: 2 mL, toluene: 98 mL, 70 °C.
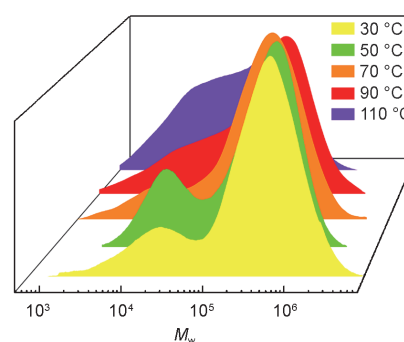
Fig.4 Molecular-weight distributions as functions of temperature for Ni₂-*iPr*

Fig.5 Schematic diagram of *syn*-Ni₂-*iPr* and *anti*-Ni₂-*iPr*

4 Conclusions

In summary, we have developed a new type of macrocyclic binuclear *α*-diimine nickel catalysts for ethylene polymerization by combining the design of a cyclic structure and the binuclear strategy. These catalysts exhibit advantages over their acyclic mononuclear counterparts in terms of the enhancement of molecular weight, tunable molecular weight distribution, lower branching density, and the improvement of the thermostability of the catalyst itself. This indicates the effectiveness of these macrocyclic binuclear catalysts. Notably, the polyethylene polydispersity can be facilely tuned from monomodal to bimodal by simply altering the

ortho-substituents of the *N*-aryl group. This enables the production of both linear low density polyethylene (LLDPE) analogue and high-density polyethylene (HDPE) analogue and also bimodal polyethylene, which are highly desired in the industry. This macrocyclic binuclear strategy provides an alternative pathway to manipulate polymer properties and may open up new possibilities for developing advanced olefin polymerization catalysts bearing the unique macrocyclic structure.

Conflicts of Interest

The authors declare no conflicts of interest.

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