

Synthesis of Branched Polyethylene via Bulky α -Diimine Nickel(II)-Catalyzed Ethylene Chain-Walking Polymerization

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Abstract

The catalysis of olefin polymerization through the chain-walking process is a subject of great interest. In this contribution, the successful synthesis of a Brookhart-type unsymmetrical α -diimine nickel catalyst **Ni**, which contains both dibenzhydryl and phenyl groups, was determined by X-ray crystallography. The compound has a pseudo-tetrahedral geometry at the Ni center, showing pseudo-C₂-symmetry. Upon activation with modified methylaluminoxane (MMAO), **Ni**1 exhibits high catalytic activity up to 1.02×10^7 g PE (mol Ni h)⁻¹ toward ethylene polymerization, enabling the synthesis of high molecular weight branched polyethylene. The molecular weights and branching densities could be tuned over a very wide range. The polymerization results indicated the possibility of precise microstructure control, depending on the polymerization temperature. The branching densities were decreased with increasing the polymerization temperature.

Keywords

Ethylene Polymerization, α -Diimine Ni(II) Complex, Chain-Walking Polymerization, Branched Polyethylene

1. Introduction

In 1995, a significant discovery was made by Brookhart and his colleagues [1], demonstrating the high activity of α -diimine palladium and nickel catalysts in ethylene polymerization [2], as well as their capability to generate polymers with high molecular weight. This particular type of α -diimine catalyst has been widely recognized as the “Brookhart catalyst” and has attracted significant attention over the past two decades [3]-[8]. Chain-walking polymerization can give po-

lyolefins with unique structures which cannot be obtained by common vinyl polymerization [9] [10]. The highly branched polyethylene, characterized by a significant presence of methyl and alkyl branches [11] [12] [13], exhibits an amorphous nature, whereas the chain-straightened polyethylene with its distinctive slow chain-walking mechanism demonstrates semi-crystalline behavior. Furthermore, the Brookhart catalyst demonstrated exceptional efficacy in facilitating the copolymerization of ethylene, propylene, and methyl acrylate, thus representing a significant breakthrough in addressing challenges associated with polar monomers [14] [15] [16] [17] [18].

We have previously reported that a series of bulky nickel catalysts with systematically varied ligand sterics for ethylene polymerization [19] [20] [21], the molecular weights and branching densities could be tuned over a very wide range [22] [23] [24]. The present study focuses on the synthesis of an unsymmetrical α -diimine nickel complex featuring dibenzhydryl and phenyl groups, as well as the investigation into how ligand structure and polymerization conditions influence ethylene polymerization.

2. Experimental Section

2.1. General Considerations

All manipulations were performed under nitrogen gas using standard Schlenk techniques. Research grade ethylene and propylene were purified by passing it through a deoxygenation and a dry columns. Methylene chloride and *o*-dichlorobenzene were pre-dried with 4 Å molecular sieves and distilled from CaH₂ under dry nitrogen. Toluene, hexane, diethyl ether and 1,2-dimethoxyethane (DME) were distilled from sodium/benzophenone under nitrogen atmosphere and distilled before use. MMAO were donated by Tosoh-Finechem. Complex **Ni^I** [25] was prepared according to reported procedures. Other chemicals were commercially obtained and purified with common procedures.

¹H and ¹³C NMR spectra were recorded with a Bruker Ascend 400 spectrometer at ambient temperature unless otherwise stated. The chemical shifts of the ¹H and ¹³C NMR spectra were referenced to tetramethylsilane (TMS). Elemental analysis was performed by the Analytical Center of the Changzhou University. X-ray diffraction data were collected at 298(2) K on a Bruker Smart CCD area detector with graphite-monochromated MoK_α radiation ($\lambda = 0.71073$ Å). Gel permeation chromatography (GPC) was carried out at 150 °C by using a PL-GPC 220 high-temperature gel permeation chromatography system. 1,2,4-Trichlorobenzene (TCB) was used as the solvent at a flow rate of 1.0 mL min⁻¹, and the system was calibrated by using a polystyrene standard and are corrected for linear polyethylene by universal calibration by using the Mark–Houwink parameters of Rudin: $K = 1.75 \times 10^{-2}$ cm³ g⁻¹ and $R = 0.67$ for polystyrene and $K = 5.90 \times 10^{-2}$ cm³ g⁻¹ and $R = 0.69$ for polyethylene.

2.2. Synthesis and Characterizations

Synthesis of (2,4-dibenzhydryl-6-phenylphenylimino)-butanone **L^I**

A solution of 2,6-bis(diphenylmethyl)-4-phenylaniline (20 mmol) [26], 2,3-butadione (100 mmol) and Formic acid (1mL) in methyl alcohol (80 mL) was stirred at 60 °C for 12 h, until there was one main point on the TLC plate. The solvent was partially evaporated under reduced pressure until the formation of a light yellow solid (9.10 g, 80%). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.24 - 6.98 (m, 24H), 6.94 - 6.86 (m, 2H), 6.73 (t, *J* = 7.6 Hz, 1H), 5.45 (d, 2H, -CHPh₂), 2.43 (s, 3H, -CH₃), 0.72 (s, 3H, -CH₃).

Synthesis of [*N*-(2,4-dibenzhydryl-6-phenylphenyl)-*N'*-(2,6-dimethylphenyl)]-2,3-butadiene **L**

A mixture of **L1'** (5.69 g, 10 mmol), aniline (1.86 g, 10 mmol), and a catalytic amount of *p*-toluenesulfonic acid in 150 mL toluene was refluxed for 24 h. The solution was evaporated at reduced pressure, and the remaining solution was diluted in methanol (300 mL). The yellow solid was isolated by filtration, followed by recrystallization from dichloromethane and methanol (5.50g, 95%). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.27 (t, *J* = 7.6 Hz, 4H), 7.24 - 7.04 (m, 20H), 7.02 - 6.96 (m, 4H), 6.87 (t, *J* = 7.6 Hz, 1H), 6.74 (t, *J* = 7.6 Hz, 1H), 5.56 (s, 2H, -CHPh₂), 5.48 (s, 2H, -CHPh₂), 1.92 (s, 6H, -CH₃), 1.70 (s, 3H, -CH₃), 0.93 (s, 3H, -CH₃). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 168.77 (C=N), 167.34 (C=N), 130.09, 129.71, 129.56, 129.37, 128.38, 128.15, 127.98, 127.75, 126.55, 126.23, 124.53, 123.12, 56.54 (-CHPh₂), 52.83 (-CHPh₂), 17.91 (-CH₃), 17.53 (-CH₃), 16.19 (-CH₃), 15.75 (-CH₃). Anal. Calcd. for C₅₀H₄₄N₂ (672.92): C, 89.25; H, 6.59; N, 4.16. Found: C, 89.29; H, 6.63; N, 4.10. FT-IR (KBr): 1649 cm⁻¹ (ν_{C=N}).

Synthesis of {[*N*-(2,4-dibenzhydryl-6-phenylphenyl)-*N'*-(2,6-dimethylphenyl)]-2,3-butadiene}dibromonickel **Ni**

A mixture of the ligand **L** (1 mmol), (DME)NiBr₂ (308 mg, 1 mmol) in CH₂Cl₂ (20 mL) was stirred for 2 hours at room temperature, Then concentrate the solvent, add ether to precipitate the solid catalyst, filter and clear with ether for three to five times, and vacuum dry the solid to obtain the catalyst **Ni** (93%, 5.50 g). Anal. Calcd. for C₅₀H₄₄Br₂N₂Ni (891.42): C, 67.37; H, 4.98; N, 3.14. Found: C, 67.41; H, 4.93; N, 3.17. FT-IR (KBr): 1643 cm⁻¹ (ν_{C=N}).

2.3. X-Ray Structure Determination

Single crystal of ligand for X-ray analysis were obtained by dissolving the nickel complex in CH₂Cl₂, followed by slow layering of the resulting solution with at room temperature. Data collections were performed at 150 K on a Bruker SMART APEX diffractometer with a CCD area detector, using graphite monochromated MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). The determination of crystal class and unit cell parameters was carried out by the SMART program package. The raw frame data were processed using SAINT and SADABS to yield the reflection data file. The structures were solved by using the SHELXTL program. Refinement was performed on *F*² anisotropically for all non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters.

2.4. Ethylene Polymerization

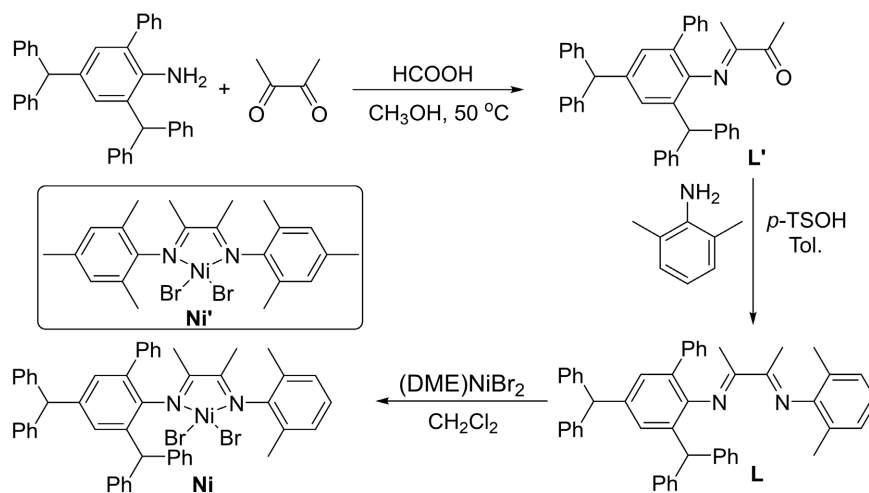
Ethylene polymerization was performed in a 100-mL glass reactor equipped with a magnetic stirrer. After drying the reactor under N₂ atmosphere, toluene was added to the reactor. The solvent was then saturated with a prescribed ethylene pressure. The co-catalyst (MMAO) was added in Al/Ni molar ratios to the reactor via a syringe, the solution was thermostated to the desired temperature and allowed to equilibrate for 10 min. Then, the catalyst solution in toluene was added to the reactor. The polymerization, conducted under 1.2 atm of ethylene pressure, was terminated with 200 mL of a 3% HCl-MeOH solution. The polymers obtained were adequately washed with methanol and dried under vacuum at 50 °C for 6 h.

Analysis of the polyethylene branching by ¹H NMR spectroscopy [27]: branching density, branches/1000C = (CH₃/3)/[(CH + CH₂ + CH₃)/2] × 1000. CH₃ (alkyl methyl, alk-CH₃, m, 0.70 - 0.95 ppm), CH₂ and CH (alk-CH and alk-CH₂, m, ca. 1.00 - 1.45 ppm) refer to the intensities of the methyl, methylene and methine resonances in ¹H NMR spectra.

3. Results and Discussion

3.1. Synthesis and Characterization of the Nickel Complex

The monoimine ligand **L'** (2,4-dibenzhydryl-6-phenylphenylimino)-butanone was prepared from the reaction of 2,4-bis(diphenylmethyl)-6-methylaniline [26] with 5 equiv of 2,3-butanedione at 80% yield on multigram scale (**Scheme 1**). Subsequently, the reaction with 1 equiv of the corresponding aniline led to the formation of the α -diimine ligand **L** at 95% yields. The reaction of ligand **L** with 1.1 equiv of (DME)NiBr₂ in CH₂Cl₂ afforded the desired nickel complex **Ni** at 93% yield (**Scheme 1**). Compounds were characterized by ¹H and ¹³C NMR spectroscopies, and elemental analysis. In addition, the classic catalyst **Ni'** [25] was also used for comparison in this study.



Scheme 1. Synthesis of α -diimine ligand **L** and its nickel complex **Ni**.

3.2. X-Ray Crystallographic Studies

Furthermore, to confirm the molecular structure of catalyst the single crystal of **Ni1** was also grown by slow diffusion of *n*-hexane in dichloromethane, and their molecular structures were confirmed by single-crystal X-ray diffraction analysis (**Figure 1**). X-ray diffraction data of single crystal was collected at 100 K on a Bruker Smart CCD area detector with graphite monochromated MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). Selected bond lengths (\AA) and angles ($^\circ$) for **Ni** are listed in **Table 1**. Crystal data, data collection and refinement parameters are listed in **Table 2**.

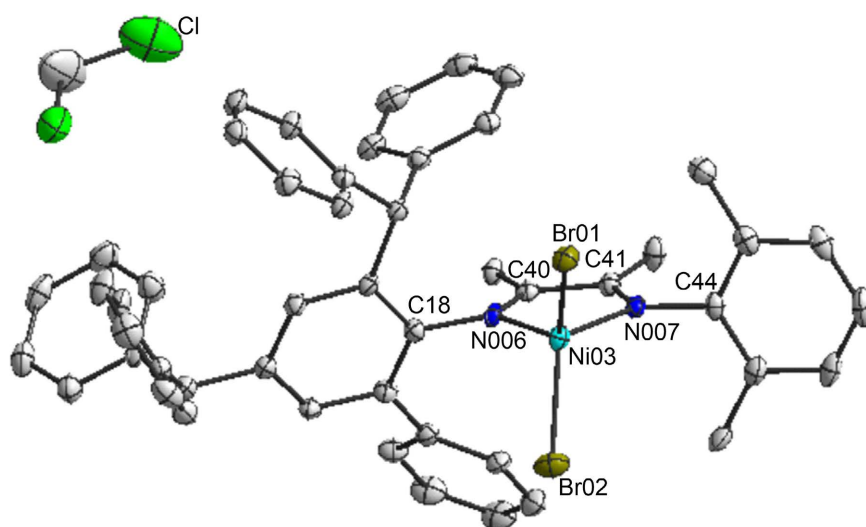


Figure 1. Molecular structure of **Ni1** at 30% probability ellipsoids (CCDC 2339033). Hydrogen atoms were omitted for clarity.

Table 1. Bond lengths (\AA) and angles ($^\circ$) for **Ni**.

| | | | |
|----------------|-------------|---------------|------------|
| Br01—Ni03 | 2.3573 (10) | Cl1—C52 | 1.730 (15) |
| Br02—Ni03 | 2.3317 (11) | N006—C18 | 1.455 (7) |
| Ni03—N006 | 2.009 (5) | N006—C40 | 1.291 (7) |
| Ni03—N007 | 1.996 (5) | N007—C44 | 1.445 (7) |
| Cl00—C52 | 1.664 (15) | N007—C41 | 1.291 (7) |
| Br02—Ni03—Br01 | 117.60 (4) | C44—N007—Ni03 | 124.2 (4) |
| N006—Ni03—Br01 | 122.19 (14) | C41—N007—Ni03 | 114.5 (4) |
| N006—Ni03—Br02 | 107.21 (13) | C41—N007—C44 | 121.3 (5) |
| N007—Ni03—Br01 | 109.04 (13) | C19—C18—N006 | 117.5 (5) |
| N007—Ni03—Br02 | 114.86 (14) | C17—C18—N006 | 120.7 (5) |
| N007—Ni03—N006 | 80.50 (19) | C17—C18—C19 | 121.7 (5) |
| C18—N006—Ni03 | 122.9 (4) | C45—C44—N007 | 118.5 (5) |
| C40—N006—Ni03 | 115.0 (4) | C50—C44—N007 | 118.7 (6) |
| C40—N006—C18 | 121.9 (5) | C44—N007—Ni03 | 124.2 (4) |

Table 2. Crystal data and structure refinement for **Ni**.

| Identification code | Ni1 |
|-------------------------------------|---|
| CCDC | 2339033 |
| Empirical formula | C ₅₀ H ₄₄ Br ₂ N ₂ Ni·CH ₂ Cl ₂ |
| Formula weight | 976.33 |
| Temperature/K | 150 |
| Crystal system | Monoclinic |
| Space group | P2(1)/n |
| a/Å | 9.1499(19) |
| b/Å | 35.806(7) |
| c/Å | 13.852(3) |
| α/° | 90 |
| β/° | 99.890(7) |
| γ/° | 90 |
| Volume/Å ³ | 4470.8(15) |
| Z | 4 |
| ρ _{calc} g/cm ³ | 1.451 |
| μ/mm ⁻¹ | 2.378 |
| F(000) | 1992.0 |
| Crystal size/mm ³ | 0.07 × 0.05 × 0.04 |
| Radiation | MoKα (λ = 0.71073) |
| 2θ range for data collection/° | 3.752 to 52.96 |
| Index ranges | -11 ≤ h ≤ 11, -44 ≤ k ≤ 44, -14 ≤ l ≤ 17 |
| Reflections collected | 28200 |
| Independent reflections | 9008 [Rint = 0.1014, Rsigma = 0.1019] |
| Data/restraints/parameters | 9008/521/527 |
| Goodness-of-fit on F ² | 1.028 |
| Final R indexes [I ≥ 2σ(I)] | R1 = 0.0702, wR2 = 0.1603 |
| Final R indexes [all data] | R1 = 0.1194, wR2 = 0.1860 |

Ni-CH₂Cl₂ has a *pseudo*-tetrahedral geometry at the Ni center, showing *pseudo*-C₂-symmetry. The crystals exhibit an asymmetrical α -diimine structure and encapsulate a CH₂Cl₂ molecule. Bond lengths and angles are within the expected range for α -diimine, for example, the bond length of N006-C40 [1.291(7) Å] and N007-C41 [1.291(7) Å] have typical imine double bonds character. Its structure is similar to those reported in the literature for a [NiBr₂(α -diimine)] compound characterized by X-ray diffraction, {bis[*N,N*-(2,4,6-trimethylphenyl)imino]acenaphthene}dibromonickel **Ni'** [25]. In fact, the Ni–N bond distances in complex **Ni** (2.005 and 1.996 Å) are similar to those determined for **Ni'** (2.021 Å), and the Ni–Br bond distances in com-

plexes **Ni** and **Ni'** are almost identical (2.3573 and 2.3317 Å for **Ni'** vs. 2.323 Å for **Ni**). In addition, the N-Ni-Br angles (112.96° for complex **C1**) are also approximate to those for complex **C7** (114.4°). Specifically, the Br01-Ni03-Br02 angle in **Ni** is more open and measures 117.60(4)°, while the bite angles of N007-Ni03-N006 are 80.50(19)°. This asymmetrical dibenzhydryl and phenyl substituted α -diimine ligand may induce a coordination effect in olefin polymerization [9].

3.3. Ethylene Polymerization Studies

Polymerization of ethylene with **Ni** activated by MMAO were carried out at various polymerization temperatures and the [Al]/[Ni] ratio for 10 min under 6 atm of ethylene, and the results are listed in **Table 3**. At room temperature, the influence of the [Al]/[Ni] with MMAO was investigated by increasing the [Al]/[Ni] molar ratio from 200 to 800 (entries 1 - 3, **Table 1**). The highest activity of 6.45×10^6 g PE/(mol Ni h) and the highest molecular weight of the polymers were achieved with the [Al]/[Ni] ratio of 500 (entry 3, **Table 1**).

Table 3. Effect of catalyst and temperature on ethylene polymerization^a.

| Entry | Precat. | [Al]/[Ni] | Temp (°C) | Yield (g) | Activity ^b | M_n^c ($\times 10^4$) | M_w/M_n^c | B^d |
|-------|------------|-----------|-----------|-----------|-----------------------|---------------------------|-------------|-------|
| 1 | Ni | 200 | RT | 2.41 | 5.16 | 35.1 | 2.13 | - |
| 2 | Ni | 500 | RT | 3.01 | 6.45 | 38.6 | 2.27 | - |
| 3 | Ni | 800 | RT | 2.83 | 6.06 | 37.5 | 2.64 | - |
| 4 | Ni | 500 | 0 | 2.77 | 5.94 | 20.3 | 1.97 | 39 |
| 5 | Ni | 500 | 25 | 3.85 | 8.25 | 51.7 | 2.27 | 46 |
| 6 | Ni | 500 | 50 | 4.74 | 10.16 | 48.9 | 2.39 | 59 |
| 7 | Ni | 500 | 75 | 3.58 | 7.67 | 37.1 | 2.55 | 68 |
| 8 | Ni | 500 | 100 | 2.15 | 4.61 | 23.0 | 2.69 | 76 |
| 9 | Ni' | 500 | 50 | 0.78 | 1.67 | 9.4 | 2.47 | 81 |

^aPolymerization conditions: **Ni** = 2.8 μ mol in CH₂Cl₂ (2 mL); cocatalyst MMAO; solvent = toluene (30 mL); 6 atm of ethylene; time = 10 min. ^b 10^6 g of PE (mol of Ni)⁻¹ h⁻¹. ^c M_n and M_w/M_n determined by GPC, 10^4 g mol⁻¹. ^dBranching numbers per 1000C were determined by ¹H NMR.

The influence of the polymerization temperature was studied by varying the temperature from 0 °C to 100 °C (entries 4 - 8, **Table 1**). The maximum catalytic activities of complex **Ni1** was observed at 50 °C (entry 6, **Table 1**), and the polymerization at 100 °C still gave high catalytic activities on the level of 10^6 g of PE/(mol Ni h) (entry 8, **Table 1**).

The molecular weights of the polymers were also investigated at various polymerization temperatures from 0 °C to 100 °C (entries 4 - 8, **Table 1**). The polymer obtained by **Ni** exhibited its highest molecular weight at 25 °C (entry 5, **Table 1**). Subsequent temperature increases resulted in a decrease in the mole-

cular weight accompanied by broadening of the molecular weight distribution. The observation implies that rapid chain transfer occurs at elevated temperatures [9].

Steric effect of *ortho*-position in anilinic moiety can be evaluated by comparing **Ni** and **Ni'** (entries 6 and 9, **Table 1**). **Ni1**-MMAO exhibited higher activity and much higher thermal stability than the corresponding methyl substituted **Ni'** (entries 6 vs 9, **Table 1**), which can be attributed to the steric effect caused by the presence of dibenzhydryl and phenyl groups in the *ortho*-position [9]. The significantly higher molecular weight of 4.89×10^5 g mol⁻¹ obtained by **Ni** (**Figure 2**), as compared to that from **Ni'**, suggests that the presence of bulky dibenzhydryl and phenyl *ortho*-substituents on the ligand's aryl rings greatly enhances the rate of chain propagation, effectively suppressing chain-transfer reactions [28].

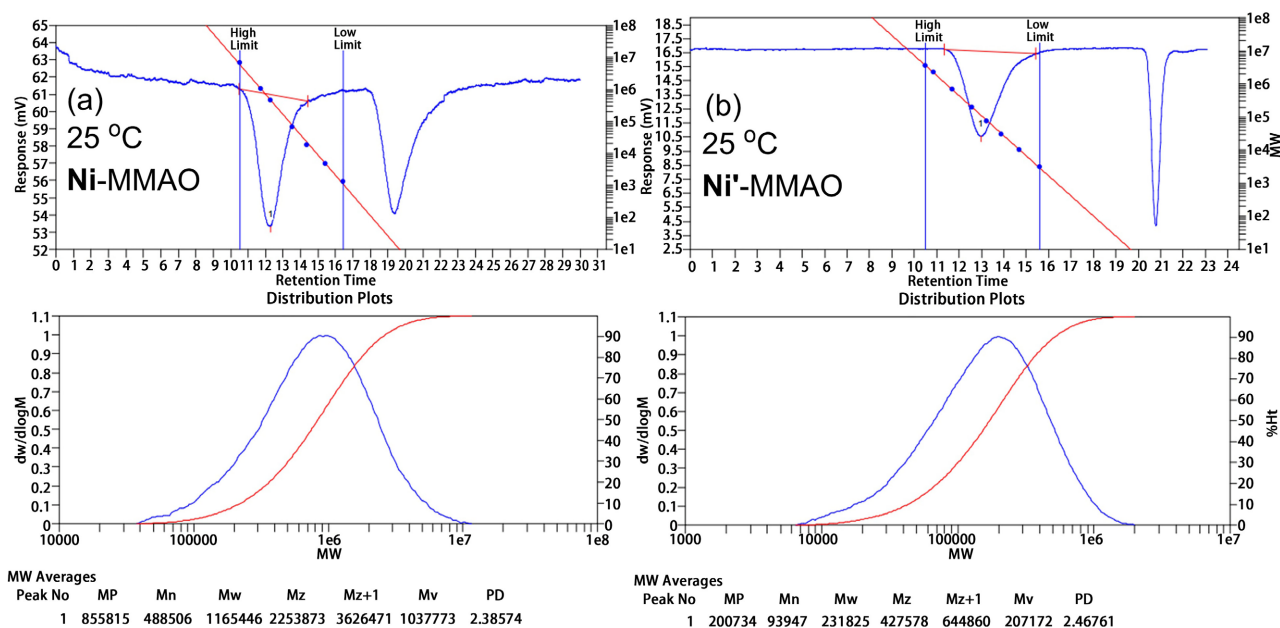


Figure 2. GPC traces for the PEs obtained with **Ni1**-MMAO and **Ni'**-MMAO at 25°C (entries 6 and 9, **Table 1**).

The branching densities of the polyethylenes obtained were determined using ¹H NMR spectroscopy [29] [30] [31]. The branching densities of 39 - 76 branches per 1000C were increased with polymerization temperature from 0°C to 100°C (entries 4 - 8, **Table 1**). In addition, the branching densities were reduced by increasing the steric bulk of the *ortho*-substituents on the α -diimine ligand, as evidenced by a comparison between **Ni** and **Ni'** at 50°C (entries 6 vs 9, **Table 1**). The observed disparity in microstructure and lower degree of branching density for the sterically bulkier catalysts may be attributed to a relatively higher propensity for ethylene insertion into primary metal alkyl species compared to secondary metal alkyl species [9].

The branching structures analysis based on ¹³C NMR [20] showed that 56 methyl, 5 ethyl, 3 *n*-propyl, 2 *n*-butyl, 1 *sec*-butyl and 10 longer chains (>C4 branches)

exist for the polyethylene produced by complex **Ni** at 100 °C (**Figure 3(i)**, entry 8, **Table 1**). In contrast, only 39 methyl branches were observed for **Ni** at 0 °C (**Figure 3(ii)**, entry 4, **Table 1**).

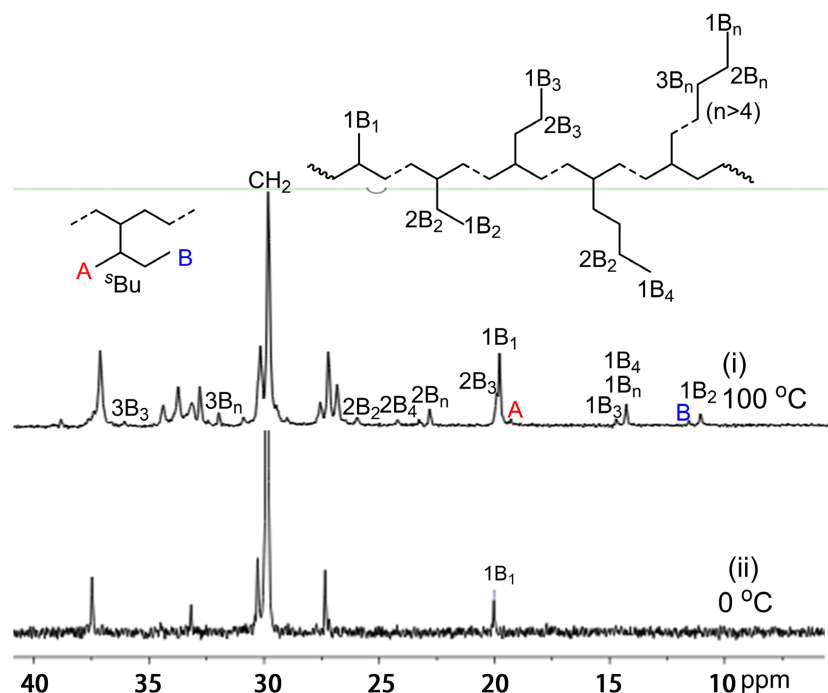


Figure 3. ^{13}C NMR spectrum of polyethylenes obtained by complex **Ni** at 0 °C (ii) and 100 °C (i) (A and B refer to methyl carbon of *sec*-butyl branches, entries 4 and 8, **Table 1**).

4. Conclusion

In conclusion, an unsymmetrical α -diimine nickel catalyst **Ni** bearing dibenzhydryl and phenyl groups was prepared and investigated in ethylene polymerization. The catalytic activity of **Ni** activated by MMAO is significantly enhanced compared to the classic nickel catalyst **Ni'** with methyl substitution, thereby facilitating the production of high molecular weight branched polyethylene. Moreover, the branching densities and molecular weights can be finely adjusted over a wide range. The branching densities decrease as the polymerization temperature increases. The chain-walking polymerization mechanism is responsible for the formation of major types of branches (methyl, ethyl, propyl, butyl, and longer chains) in the resulting polyethylenes.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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