Thermostable α-Diimine Nickel Complexes with Substituents on Acenaphthequinone-backbone for Ethylene Polymerization

Rui-Fang Zhang, Yan-Hui Hou, Xu-Ling Wei, Ding-Ding Zhao, Mi-Mi Cui, Fei-Fan Zhai, Xiang-Liu Li, Bin-Yuan Liu, and Min Yang

Hebei Key Laboratory of Functional Polymers, Tianjin Key Laboratory of Chemical Process Safety, Institute of Polymer Science and Engineering, Hebei University of Technology, Tianjin 300130, China
State Key Laboratory of Separation Membranes and Membrane Processes, School of Material Science and Engineering, Tiangong University, Tianjin 300160, China
Lanzhou Petrochemical Research Center, Petrochemical Research Institute of CNPC, Lanzhou 730060, China

Abstract In order to promote the thermostability of α-diimine nickel complex by ligand backbone structure, a series of α-diimine nickel complexes with substituents on acenaphthequinone backbone were synthesized and used as catalysts for ethylene polymerization. When the hydroxyethyl phenoxyl group was introduced to the acenaphthequinone-backbone, the thermal stability and activity of the catalyst could be significantly improved. The catalytic activity of complex C2 [5-(4-(2-hydroxyethyl)phenoxyl)-N,N-bis(2,6-diisopropyl)acenaphthylene-1,2-diimine]nickel(I) dibromide with isopropyl substituents on N-aryl reached 8.2 × 10³ g/(mol-h) at 70 °C and 2 MPa. The activity of [5-(4-(2-hydroxyethyl)phenoxyl)-N,N-bis(2,6-dibenzhydryl)-4-methylenylphenylacenaphthylene-1,2-diimine]nickel(II) dibromide (C3) still maintained at 6.7 × 10³ g/(mol-h) at 120 °C. Compared with C3 containing bulky dibenzhydryl substituents, the activity of C2 was sensitive to the change of the polymerization pressure. However, the polyethylenes obtained from complex C3 had lower branching density. Meanwhile, the molecular weight could reach 971 kg/mol, which is almost 5 times as much as that of the polyethylene obtained from complex C2.

Keywords α-Diimine nickel; Ethylene polymerization; Thermostability; Ligand backbone structure

INTRODUCTION

Since Brookhart’s seminal discovery on nickel and palladium complexes bearing α-diimine ligands,[1,2] there has been tremendous interest in exploring new α-diimine ligands. These catalysts are capable of producing polymers with various types of branches, and have good tolerance to many polar comonomers.[3–9] Despite their unique properties, Brookhart-type α-diimine catalysts suffer from poor thermal stability, which has greatly limited their potential industrial application. Driven by the desire for enhanced thermal stability, higher activity and polymer molecular weight, tremendous efforts have been made on typical α-diimine nickel/palladium complexes, which involve modifying N-aryl substituents and ligand backbone structures.[10–19] For example, Guan and co-workers developed α-diimine ligands bearing different substituents, and designed novel cyclic α-diimine complexes, which showed high activity and thermal stability for ethylene polymerization.[20,21] It is worth mentioning that the bulky substituents on N-aryl can significantly enhance the catalytic properties of the corresponding precatalysts. More recently, the investigation of benzhydryl-derived ligand frameworks aroused high discussion interests.[22–26] Sun’s group developed a series of unsymmetrical diimine complexes bearing the dibenzhydryl substituent, which are better for inducing high thermal stability.[22,23] Long’s group reported the synthesis of a series of sterically demanding α-diimine nickel(II) complexes by the use of 2,6-bis(diphenyl-methyl)-4-methylaniline.[24,25] Moreover, Chen’s group reported a series of dibenzhydryl-based α-diimine complexes bearing a range of electron-donating and electron-withdrawing substituents and investigated the electronic effects on the ethylene polymerization.[26] All of the complexes show highly catalytic activity in ethylene polymerization and the excellent thermal stability of these catalysts makes them suitable for use in industrial polymerization temperature (70–100 °C).

For the modification of ligand backbone structure, some groups provided advanced strategies by increasing the steric bulk of the α-diimine ligand backbone for enhancing the...
thermal stability of catalysts. Gao’s group reported catalysts containing a camphyl backbone and dienzenobarrelene-derived α-dimine nickel catalysts for ethylene polymerization to promote the thermooxidative stability of nickel catalyst by the ligand backbone. Sun’s group explored the ethylene polymerization performance of the nickel dihalides (X = Cl, Br) bearing 4,5-bis arylimino)pyrenylidene N\N-ligands. Coates’ group has investigated the ethylene polymerization behavior by a dienzenobarrelene-derived α-dimine nickel complex.

Comparing with modifications of the N-aryl substituents, there have been few works related to the modifications of theacenaphthquinone backbone structures for improving thermal stability of the catalyst. So, three α-dimine nickel catalysts with substituents on acenaphthquinone backbone (C1−C3) were synthesized in this work. In order to investigate the effect of substituents on theacenaphthquinone backbone, C1−C3 were compared with Brookhart-type catalyst C concerning the effect of the nickel α-dimine complex structure on the thermal stability and catalytic performances in ethylene polymerization. Meanwhile, the effects of the polymerization pressure and temperature on catalyst activity, branching degree, and molecular weight and distribution of polymers were also investigated.

**EXPERIMENTAL**

**General Considerations**

All manipulations of the air- and/or moisture-sensitive materials were carried out under a dry argon atmosphere using standard Schlenk techniques. Toluene and hexane were dried through an activated molecular sieve (4Å) and then refluxed and distilled over sodium diphenylketyl complex prior to use. Dichloromethane was distilled from calcium hydride. Methylaluminoxane (MAO, 1.5 mol/L in toluene) and diethylaluminum chloride (1.0 mol/L in toluene) were purchased from Air Products & Chemicals (Tianjin) Co., Ltd. and used as received. All other chemicals were obtained commercially and used as received.

Fourier transform infrared (FTIR) spectra were recorded on a Bruker Tensor-27 spectrometer using the pressed KBr pellets. Elemental analysis was carried out using a Flash EA 1112 microanalyzer. NMR spectra of ligands and complexes were recorded on a Bruker DMX 400 MHz instrument at ambient temperature in deuterated chloroform using TMS as an internal standard; δ values were given in ppm and J values in Hz. MS elemental analyses were performed on a Vario EL microanalyzer. Molecular weights and molecular weight distribution of polyethylene were determined by a PL-GPC 220 at 150 °C, with 1,2,4-trichlorobenzene as the solvent. 13C-NMR spectra of polyethylene were also recorded on a Bruker DMX 400 MHz instrument at 120 °C in deuterated 1,2-dichlorobenzene with TMS as an internal standard. The melting temperatures (Tm) and the fusion enthalpy (ΔHf) of the polymers were determined by differential scanning calorimetry (DSC) with a DSC-Diamond (Perkin-Elmer Co.) operating at a heating rate of 10 °C/min from 0 °C to 150 °C under nitrogen atmosphere, and Tm was determined in the second scan. The crystallinity (Xc, %) was calculated from the heat of fusion, (ΔHf/ΔHf0) × 100%, where ΔHf0 is the heat of fusion of folded-chain polyethylene (289.0 J/g).[21]

### Synthesis of Complexes

#### Synthesis of complexes C1, C1, and C’

According to the reported procedures, the complexes C1[22] and C’ were synthesized.[23]

#### Synthesis of Complexes C2 and C3

5-(4-(2-Hydroxyethyl)phenoxy)acenaphthylen-1,2-dione. Bromoacenaphthylen-1,2-dione (50 mmol) and K2CO3 (150 mmol) were stirred in dimethylformamide (50 mL, treated with a desiccant) and 2-(4-hydroxy-phenylethanol (100 mmol) was added to the mixture slowly. The solution was refluxed at 60 °C until the reaction was detected to be complete. The crude product was purified by column chromatography on silica gel to afford a yellow powder in 94% yield. 1H-NMR (400 MHz, CDCl3, δ, ppm): 8.62 (d, J = 8.4 Hz, 1H), 8.16 (d, J = 7.0 Hz, 1H), 8.05 (d, J = 7.8 Hz, 1H), 7.89 (t, J = 7.8 Hz, 1H), 7.40 (d, J = 8.3 Hz, 2H), 7.20 (d, J = 8.3 Hz, 2H), 7.02 (d, J = 7.9 Hz, 1H), 3.97 (t, J = 6.4 Hz, 2H), 2.98 (t, J = 6.4 Hz, 2H), MS (ESI): m/z 319 (M+H+).

5-(4-(2-Hydroxyethyl)phenoxy)-N,N-bis(2,6-diisopropyl)acenaphthylen-1,2-dione (L2). A mixture of 5-(4-(2-hydroxyethyl)phenoxy)acenaphthylen-1,2-dione (8 mmol), 2,6-diisopropylphenolamine (19 mmol), and p-toluene-sulfonic acid in toluene (150 mL) was refluxed until the reaction was complete. And in this process, we should pay attention to removing the moisture generated during the reaction. The wine-red solution was evaporated at reduced pressure and yellow solid L2 was obtained in 87% yield. FTIR (ν, cm−1): 3405, 3058, 2965, 2921, 2373, 2373, 1637, 1644 (C=N), 1580, 1581, 1512, 1426, 1384, 1353, 1352, 1217, 1169, 1166, 1129, 1100, 1072, 934, 883, 825, 783, 753. Elemental Anal. Calcd. for C41H42N2O2 (%): C, 82.98; H, 7.60; N, 4.40. Found: C, 82.36; H, 7.78; N, 4.46. 1H-NMR (400 MHz, CDCl3, δ, ppm): 8.23 (d, J = 8.4 Hz, 1H), 7.39 (t, J = 7.8 Hz, 1H), 7.32−7.16 (m, 16H), 7.06 (d, J = 8.4 Hz, 2H), 6.67 (d, J = 7.1 Hz, 1H), 6.55 (d, J = 8.1 Hz, 1H), 6.46 (d, J = 8.1 Hz, 1H), 3.90 (t, J = 6.5 Hz, 2H), 3.09−3.02 (m, 4H), 2.90 (t, J = 6.5 Hz, 2H), 1.27−1.24 (m, 12H), 1.02−0.98 (m, 12H), 13C-NMR (400 MHz, CDCl3, δ, ppm): 161.48, 160.23, 156.60, 153.48, 147.53, 147.38, 146.72, 146.10, 142.74, 135.78, 135.62, 135.37, 130.67, 129.83, 129.00, 128.93, 128.61, 127.37, 124.66, 124.37, 124.22, 124.17, 123.88, 123.79, 123.50, 120.72, 63.42, 38.46, 28.70, 28.62, 28.55, 28.39, 23.61, 23.57, 23.47, 23.44, 23.14, 23.11, MS (ESI): m/z 638 (M+H+).

5-(4-(2-Hydroxyethyl)phenoxy)-N,N-bis(2,6-dibenzyldihydrazoyl)-4-methylphenylacenaphthylen-1,2-diene (L3). Using the same synthetic process of L2, L3 was obtained as orange powder in 85% yield. FTIR (ν, cm−1): 3423, 3058, 2026, 2924, 1662 (C=N), 1598 (C=N), 1506, 1444, 1430, 1336, 1238, 1211, 1176, 1106, 1076, 1051, 1031, 1005, 860, 821, 763, 736, 700, 607, 571, 551, 457, 421. Elemental Anal. Calcd. for C60H43N2O2 (1160.53) (%): C, 88.93; H, 5.90; N, 2.41. Found: C, 88.73; H, 6.01; N, 2.48. 1H-NMR (400 MHz, CDCl3, δ, ppm): 7.73 (d, J = 8.4 Hz, 1H), 7.30 (d, J = 8.9 Hz, 2H), 7.14−6.65 (m, 47H), 6.20−6.13 (m, 2H), 5.97 (d, J = 7.9 Hz, 1H), 5.71 (s, 4H), 3.92 (t, J = 6.5 Hz, 2H), 2.92 (t, J = 6.5 Hz, 2H), 2.29 (s, 3H), 2.23 (s, 3H). 13C-NMR (400 MHz, CDCl3, δ, ppm): 163.90, 162.71, 155.10, 154.55,
Ethylene Polymerization

Different polyethylene samples were synthesized by using different α-diimine nickel (II) complexes (Scheme 1). The polymerization was carried out in a 100 mL reactor with stirring bar and temperature and pressure controller. It should be noted that the reactor was dried under vacuum at 100 °C for 30 min and cooled to room temperature under an argon atmosphere, then purged with dry argon two times and ethylene once. Then, toluene and a prescribed amount of catalyst solution and cocatalyst solution were injected and the mixture was maintained at the desired temperature and ethylene pressure. The polymerization mixture was quenched by the addition of 10 vol% HCl/ethanol solution after 60 min. The obtained polymers were washed with water and ethanol, and then dried at 60 °C in vacuum oven to constant weight.

RESULTS AND DISCUSSION

Synthesis of α-Diimine Ligands and Complexes C1–C3

The complex C1 was synthesized according the literature.32 The synthetic procedures of α-diimine nickel(II) complexes C2 and C3 are shown in Scheme 2.

At first, 5-(4-(2-hydroxyethyl)phenoxy)anthraquinone was synthesized. When the anthraquinone reacted with 2,6-disopropylaniline and 2,6-dibenzhydryl-4-methylaniline, respectively, the ligands L2 and L3 were produced. The α-diimine
nickel(II) dibromide complexes were obtained by the reaction of corresponding ligands with (DME)NiBr₂ in high yields. These ligands and corresponding complexes were characterized by FTIR, ¹H-NMR, and elemental analysis.

**Ethylene Polymerization with α-Diimine Nickel Complexes**

It is well known that the α-diimine nickel complex C (shown in Scheme 1) showed a poor thermal stability. As shown in Table 1, the activity decreased rapidly as the polymerization temperature increased from 30 °C to 70 °C. In order to study the modification in backbone group for improving thermal stability of catalyst, we synthesized complex C₁, which has a phenox substituent attached to the acenaphthquinone-backbone and isopropyl substituents on N-aryl structures.

However, contrary to our original wish, the activity of complex C₁ was lower than that of complex C at 30 and 50 °C. This indicates that the benzoxo group is not good for the activity of catalyst. The same phenomenon was also found by Kim et al. in the ethylene polymerization catalyzed by pyridine-bis-imine iron catalyst with benzoxo substituent.⁴¹ The authors suggested that the electron-donating characteristic of benzoxo group resulted in a decreased coordination power with respect to ethylene monomer, thus causing a lower propagation rate. Furthermore, the decreased activity was also caused by complicated complexion between cationic active species and benzoxo group. This complexation stabilized the active species and retarded the coordination of incoming monomer, resulting in decreased catalytic activity. Similarly, for the α-diimine nickel catalyst C₁ with benzoxo group, the decrease of catalyst activity was related to the electron-donating character, as well as the complexion between cationic active species and benzoxo group. Despite all of these, the activity of C₁ was higher than that of C at 70 °C, which shows the steric hindrance of phenox substituent can improve the thermal stability of α-diimine complex to a certain extent.

Furthermore, we synthesized complex C₂, which has an additional hydroxyethyl group on the benzoxo group compared to complex C₁. However, the hydroxyethyl group made C₂ show a higher catalytic activity. At 70 °C, the activity of complex C₂ was 1.76 × 10⁶ g/(mol·h), which is higher not only than that of C₁, but also than that of C. It is suggested that the presence of hydroxy group can make up for the negative effects of benzoxo group, and improve the catalytic activity, especially at the higher polymerization temperature. One possible reason is that the hydroxy group may interact with the cocatalyst anion in the active center ion pair, which increased the distance between cation species and anion. So, the insertion of ethylene monomer was easier, and catalytic activity and thermal stability were enhanced. Another possible reason is that after the hydroxy group reacted with the cocatalyst, the formed bulkier substituent blocked the formation of complexation between cationic active species and benzoxo group. Anyhow, the hydroxy group plays an important role in improving the catalytic behaviors. Meanwhile, it can be seen that complex C₂ with AlEt₃Cl showed higher activity than with MAO in ethylene polymerization. So, the cheaper AlEt₃Cl was selected as the co-catalyst for further investigations.

For investigating the stability of complex C₂ at elevated temperature and pressure, polymerizations were conducted at different temperatures and ethylene pressures (Table 2). At 70 °C and 0.5 MPa ethylene pressure, the catalytic activity of C₂ reached 2.36 × 10⁶ g/(mol·h) (entry 2, Table 2), which suggested that C₂ had good thermal stability. As the temperature increased to 90 °C, the activity reduced by an order of magnitude, which should result from the smaller steric hindrance of isopropyl on the N-aryl. Nevertheless, although the ortho-site substituents of N-aryl structure are small steric hindrance isopropyl, the hydroxyethyl phenox group on acenaphthquinone-backbone made complex C₂ show higher catalytic activity and thermal stability than reported α-diimine catalysts with isopropyl substituents on N-aryl.

To further improve the thermal stability of the catalyst, two dibenzhydryl groups were introduced into the ortho-N-aryl substituents, and a new complex C₃ was obtained. At 70 °C, the activity of C₃ was lower than that of C₂, which indicates that the dibenzhydryl groups could inhibit the insertion of monomer and lead to the decrease of activity. However, when the temperature was improved to 90 °C, as compared to complex C₂, complex C₃ demonstrated much greater thermal stability by showing higher activity by up to an order of magnitude (2.0 × 10⁶ g/(mol·h), entry 6, Table 2). It is worth mentioning that the activity of C₃ still maintained at 6.7 × 10⁵ g/(mol·h) (entry 10, Table 2) at 120 °C. Few studies on catalytic polymerization of α-diimine nickel catalysts at such high temperatures have been reported in the literatures.

Furthermore, it is found that C₃ had higher catalytic activity than C under the same polymerization condition (entries 7 and 14, Table 2). It indicates that the hydroxy group makes the dibenzhydryl-based α-diimine complex have better activity. This is consistent with the comparison of catalytic activity between C₂ and C. These data clearly indicate that under the dual actions of large steric hindrance substituent dibenzyl and hydroxyl on the backbone, the α-diimine complex C₃ has high thermal stability and high catalytic activity at high temperature.

Employing different ethylene pressures, higher activities of complexes C₂ and C₃ were gradually observed along with increasing the ethylene pressure from 0.5 MPa to 2 MPa (entries 2, 4, and 5 for C₂, entries 7, 12, and 13 for C₃, Table 2). By comparison, it is found that the increase of C₂ activity was more notable. At 2 MPa and 70 °C, complex C₂ showed the better activity up to 8.2 × 10⁶ g/(mol·h). The significant in-

---

Table 1. Ethylene polymerizations with different complex systems. ⁴

| Cat. | T (°C) | Product (g) | Activity a | Cat. | T (°C) | Product (g) | Activity a | Cat. | T (°C) | Product (g) | Activity a |
|------|--------|-------------|------------|------|--------|-------------|------------|------|--------|-------------|------------|
| C    | 30     | 1.85        | 3.70       | C₁   | 30     | 1.24        | 2.48       | C₂   | 50     | 1.43        | 2.86       |
| C    | 50     | 1.36        | 2.72       | C₁   | 50     | 0.81        | 1.62       | C₂   | 50     | 2.31        | 4.62       |
| C    | 70     | 0.20        | 0.40       | C₁   | 70     | 0.86        | 1.76       | C₂   | 70     | 0.88        | 1.76       |

⁴ Condition: 50 mL of toluene, 5.0 μmol of catalyst, MAO as cocatalyst, n(Al)/n(Ni) = 1000, 60 min, 0.1 MPa. ⁵ Activity, × 10⁶ g/(mol·h). ⁶ AlEt₃Cl as cocatalyst.
Catalytic results of ethylene polymerization with \( \text{C}_2 \) and \( \text{C}_3 \)

Table 2

| Entry | Cat. | \( T (\degree C) \) | \( P (\text{MPa}) \) | Activity \( \times 10^{3} \) (g/\text{mol Ni} h) | \( M_n \) (kg/mol) | PDI | 
|-------|------|-----------------|-----------------|-----------------|-----------------|-----|
| 1     | \( \text{C}_2 \) | 50 0.5          | 3.42            | 172             | 2.4             |     |
| 2     | \( \text{C}_2 \) | 70 0.5          | 2.36            | 168             | 2.5             |     |
| 3     | \( \text{C}_2 \) | 90 0.5          | 0.32            | n.d.             | n.d.             |     |
| 4     | \( \text{C}_2 \) | 70 1.0          | 6.60            | 185             | 2.0             |     |
| 5     | \( \text{C}_2 \) | 70 2            | 8.20            | n.d.             | n.d.             |     |
| 6     | \( \text{C}_3 \) | 50 0.5          | 2.06            | 657             | 1.7             |     |
| 7     | \( \text{C}_3 \) | 70 0.5          | 2.10            | 696             | 2.3             |     |
| 8     | \( \text{C}_3 \) | 90 0.5          | 2.00            | n.d.             | n.d.             |     |
| 9     | \( \text{C}_3 \) | 110 0.5         | 0.80            | 360             | 2.7             |     |
| 10    | \( \text{C}_3 \) | 120 0.5         | 0.67            | n.d.             | n.d.             |     |
| 11    | \( \text{C}_3 \) | 70 0.1          | 0.24            | 212             | 1.9             |     |
| 12    | \( \text{C}_3 \) | 70 1            | 3.16            | 971             | 2.1             |     |
| 13    | \( \text{C}_3 \) | 70 2            | 4.51            | n.d.             | n.d.             |     |
| 14    | \( \text{C}_4 \) | 70 0.5          | 1.15            | n.d.             | n.d.             |     |

* Condition: 50 mL of toluene, 1.0 \( \mu \)mol of catalyst, \( \text{AlEtCl}_2 \) as cocatalyst, \( n(\text{Al})/n(\text{Ni}) = 1000, 30 \text{ min.} \)

\(^{a}\) Determined by GPC. \(^{b}\) n.d. = not determined.

Fig. 1

GPC curves of polyethylene obtained with \( \text{C}_2 \) and \( \text{C}_3 \)

The catalytic results of ethylene polymerization with \( \text{C}_2 \) and \( \text{C}_3 \)

Table 3

| Entry | Cat. | \( T (\degree C) \) | \( P (\text{MPa}) \) | \( T_m \) (°C) | \( \chi_c \) (%) | Branches (\%/1000C) | Methyl | Ethyl | Propyl | Butyl | Amyl | LCB |
|-------|------|-----------------|-----------------|-------------|-------------|-----------------|-------|-------|-------|-------|-------|-----|
| 1     | \( \text{C}_2 \) | 50 0.5          | 47              | 7.1         | 96          | 66.0            | 7.6   | 6.8   | 6.4   | 10.5  | 2.7  |
| 2     | \( \text{C}_2 \) | 70 0.5          | –               | –           | –           | 63.7            | 10.1  | 5.6   | 5.6   | 5.1   | 9.4  |
| 3     | \( \text{C}_3 \) | 50 0.5          | 76              | 15.0        | 48          | 71.5            | 1.6   | 1.3   | 2.0   | 1.0   | 22.6 |
| 4     | \( \text{C}_3 \) | 70 0.5          | 60              | 12.6        | 61          | 66.0            | 2.7   | 3.7   | 2.2   | 2.4   | 23.0 |
| 5     | \( \text{C}_3 \) | 90 0.5          | 57              | 10.9        | 66          | 55.6            | 3.6   | 4.1   | 2.7   | 3.5   | 30.5 |
| 6     | \( \text{C}_3 \) | 110 0.5         | 51              | 9.8         | 75          | 54.6            | 3.8   | 5.1   | 1.7   | 12.2  | 37.6 |
| 7     | \( \text{C}_3 \) | 70 0.1          | 61              | 13.4        | 63          | 57.3            | 3.4   | 7.4   | 2.1   | 1.0   | 28.8 |
| 8     | \( \text{C}_3 \) | 70 1            | 69              | 14.6        | 51          | 64.3            | 3.5   | 3.0   | 2.2   | 1.5   | 25.5 |
| 9     | \( \text{C}_3 \) | 70 2            | 64              | 12.3        | 50          | 70.7            | 2.0   | 2.2   | 1.8   | 1.9   | 21.4 |

* Determined by DSC. \(^{b}\) Measured by \(^{13}\)C-NMR spectroscopy; \(^{c}\) –: no signal; \(^{d}\) LCB: long chain branching (≥2 C).
the temperature increased from 50 °C to 70 °C, the branching density of polyethylene produced using complex C2 increased from 96/1000C to 114/1000C, and the melting point changed from 47 °C to no melting point (entries 1 and 2, Table 3).

As shown in Fig. 2 and Table 3, being interpreted according to the literature, the polyethylene obtained by C2 at 70 °C and 0.5 MPa possessed 114/1000C branches, including methyl (63.7%), ethyl (10.1%), propyl (5.1%), butyl (6.6%), amyl (5.1%), and LCB (9.4%), while the polyethylene obtained by C3 under the same polymerization condition had 61 branches/1000C, containing 66.0% methyl, 2.7% ethyl, 3.7% propyl, 2.2% butyl, 2.4% amyl, and 23.0% LCB. The reducing branching density could be reasonably attributed to the slow chain walking suppressed by ortho bulky substituents. However, beside the methyl chains, the polyethylenes containing high content of LCB were also obtained by C3. Similar observations have been found by Gao et al., when they used α-dimine nickel catalysts with bulky aryl on aniline moieties to synthesize polyethylenes. They proposed a different “chain walking” mechanism to interpret the phenomenon. As described in the mechanistic model, the long branching chains were formed by ethylene insertion into the primary Ni-alkyl species originating from nickel migration to methyl terminal of the growing chain because of restricted ethylene insertion into secondary Ni-alkyl species with an α-ethyl or a bulkier alkyl group. For branched chain distributions of polyethylenes obtained from the complex C3, another interesting phenomenon is that the proportion of short branch chains decreased and meanwhile the proportion of LCB increased with the increase of reaction temperature, implying that the nickel migration to methyl terminal of the growing chain, as the different “chain walking” mechanism proposed by Gao, became very easy. For the polyethylenes obtained from the complex C3, the increases in pressure and monomer concentration were favorable for the linear growth reaction of the chain, which reduced the degree of polymer branching. If the pressure was too high, e.g., 2 MPa, there was no significant change in the branching density. Although the polymers in entries 8 and 9 had similar branching densities, the polymer in entry 8 had a slightly higher melting point than that in entry 9.

![Fig. 2](https://doi.org/10.1007/s10118-020-2430-x)
substituted ligands. cationic linear polymer properties. Preparation of polymerization by sterically and electronically modulated Ni(II) catalysts for high temperature ethylene polymerization. J. Am. Chem. Soc. 2013, 135, 16316–16319.

Rhinehart, J. L.; Mitchell, N. E.; Long, B. K. Enhancing α-diihmine catalysts for high-temperature ethylene polymerization. ACS Catal. 2014, 4, 2501–2504.

Guo, L. H.; Dai, S. Y.; Sui, X. L.; Chen, C. L. Palladium and nickel catalyzed chain walking olefin polymerization and copolymerization. ACS Catal. 2016, 6, 428–441.

Liu, F. S.; Hu, H. B.; Xu, Y.; Guo, L. H.; Zai, S. B.; Song, K. M.; Gao, H. Y.; Zhang; L.; Zhu, F. M.; Wu, Q. Thermostable α-diihmine nickel(II) catalyst for ethylene polymerization: effects of the substituted backbone structure on catalytic properties and branching structure of polyethylene. Macromolecules 2009, 42, 7789–7796.

Zhong, L.; Li, G. L.; Liang G. D.; Gao, H. Y.; Wu, Q. Enhancing thermal stability and living fashion in α-diihmine–nickel–catalyzed (co)polymerization of ethylene and poly monofer by increasing the steric bulk of ligand backbone. Macromolecules 2017, 50, 2675–2682.

Song, K.; Yang, W.; Li, B.; Liu, Q.; Redshaw, C.; Li, Y. S.; Sun, W. H. Nickel(II) complexes bearing 4, 5-bis(arylmino)pyrenylidenes: synthesis, characterization, and ethylene polymerization behaviour. Dalton Trans. 2013, 42, 9166–9175.

Long, B. K.; Eagan, J. M.; Mulzer, M.; Coates, G. W. Semi-crystalline polar polyethylene: ester-functionalized linear polyolefins enabled by a functional-group-tolerant, cationic nickel catalyst. Angew. Chem. Int. Ed. 2015, 55, 7106–7110.

Clas, S. D.; Heyding, R. D.; McFadding, D. C.; Russell, K. E.; Scammell-Bullock, M. V.; Kelusky, E. C.; St-Cyr, D. Crystallinities of copolymers of ethylene and 1-alkenes. J. Polym. Sci., Polym. Chem. Ed. 1986, 26, 1271–1286.

Zhai, F. F. Synthesis and olefin polymerization behavior of new-type late transition metal α-diihmine catalysts. Thesis, Tianjin University of Technology, Tianjin, 2015, p.18.

Kim, I.; Han, B. H.; Kim, J. S.; Ha, C. S. Allyloxy- and benzoyl-substituted pyridine-bis-imine iron(II) and cobalt(II) complexes for ethylene polymerization. Macromol. Res. 2005, 13, 2–7.

Galland, G. B.; Souza, R. F. D.; Mauler, R. S.; Nunes, F. F. 13C NMR determination of the composition of linear low-density polyethylene obtained with[η3-Methylal-nickel-diimine]PF6 complex. Macromolecules 1999, 32, 1620–1625.

Pei, L. X.; Liu, F. S.; Xiao, H.; Gao, J.; Zhong, L.; Gao, H. Y.; Wu, Q. Synthesis of polyethylenes with controlled branching with α-diihmine nickel catalysts and revisiting formation of long-chain branching. ACS Catal. 2018, 8, 1104–1113.