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Journal Name

ARTICLE

Synthesis, characterization, and ethylene polymerization of 1-[2,4-bis(bis(4-fluorophenyl)methyl)naphthylimino]-2-aryliminoacenaphthynickel bromides: Influences of polymerization parameters on polyethylenes

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A series of 1-[2,4-bis(bis(4-fluorophenyl) methyl)naphthylimino]-2-aryliminoacenaphthylene derivatives (**L1–L5**) was prepared and used to react with (DME)NiBr₂ for forming the title complexes (**C1–C5**). The organic compounds were characterized by ¹H/¹³C NMR measurement, FT-IR spectra and elemental analysis, meanwhile the nickel complexes were analyzed by FT-IR spectra and elemental analysis as well as the single-crystal X-ray diffraction of the representative complex **C1**, which indicated a distorted tetrahedral geometry around nickel center. Upon activation with diethylaluminum chloride (Et₂AlCl), all the title nickel complexes performed high activities toward ethylene polymerization, obtaining polyethylenes with high molecular weights ranging from 0.86–5.58 × 10⁵ g mol⁻¹ and narrow polydispersity (1.22–1.99). Moreover, the significant influences of polymerization parameters on the resultant polyethylenes have been examined and discussed.

Introduction

Late-transition metal precatalysts in ethylene polymerization have been extensively investigated since the emergence of α -diiminonickel complexes polymerizing ethylene for the polyethylenes with high molecular weights,¹ the research progresses have been timely summarized in the review articles.^{2,3} The *N,N*-bidentate nickel complex precatalysts have been extensively investigated including the derivatives of α -diiminonickel complexes^{2,4,5} and alternative nickel complex models bearing ligands of 2-aryliminopyridines,⁶ 8-arylamino-5,6,7-trihydroquinolines⁷ and 9-arylamino-5,6,7-trihydrocycloheptapyridines.⁸ Though polymerization parameters have been generally emphasized regarding the catalytic activities of complex precatalysts, the influences on the polymer properties are not commonly considered. Targeting the practicing catalytic systems in industry, the most important factor is the properties and the scope of applications of obtained polyethylenes, which were reflected by the structural information of obtained polyethylenes such as their molecular weights and polydispersity. Besides our efforts of exploring new and highly active complex precatalysts of α -diiminonickel complexes, therefore, the polymerization parameters and

resultant polyethylenes are investigated.

To enhance the catalytic behaviors of α -diiminonickel complexes,¹ bulky benzhydryl-substituted 1,2-diiminoacenaphthylene⁹ and 2,3-diiminobutane derivatives¹⁰ were developed and approved positive efficiencies as well as naphthyl-substituted α -diiminoacenaphthylene derivatives.¹¹ In addition, the positive effects of ligands containing electron-withdrawing substituents were confirmed by experimental results^{9f-h, 10b} and computational simulation.¹² Extensively, a series of 1-[2,4-bis(bis(4-fluorophenyl)methyl)naphthylimino]-2-aryliminoacenaphthylene derivatives (**L1–L5**) was synthesized and used to prepare their nickel complexes (**C1–C5**). All the nickel complexes, when activated by Et₂AlCl, exhibited high activities towards ethylene polymerization; in addition, the polymerization parameters heavily affected properties of the obtained polyethylenes. Herein, the synthesis and characterization of the 1-[2,4-bis(bis(4-fluorophenyl)methyl)naphthylimino]-2-aryliminoacenaphthylene derivatives and their corresponding nickel complexes are investigated systematically as well as their catalytic behaviour toward ethylene polymerization, and the properties of the resultant polyethylenes.

Results and discussion

Synthesis and Characterization of 1-[2,4-bis(bis(4-fluorophenyl)methyl)naphthylimino]-2-aryliminoacenaphthylene derivatives (**L1–L5**) and their nickel bromide complexes (**C1–C5**)

According to the literature procedure (Scheme 1),⁹ the condensation reaction of acenaphthylene-1,2-dione with 2,4-

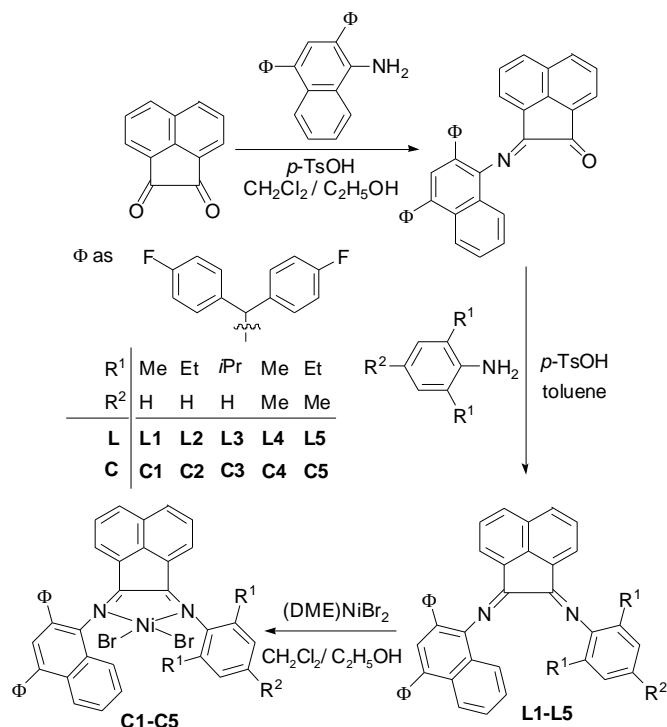
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† Electronic supplementary information (ESI) available: CCDC 1435888 for **C1**. For crystallographic data in CIF see DOI: 10.1039/x0xx00000x

bis[bis(4-fluorophenyl)methyl]naphthylamine was conducted to form the 1-[2,4-bis(bis(4-fluorophenyl)methyl)naphthyl imino]acenaphthylene-2-one, which further reacted with various anilines to form the 1-[2,4-bis(bis(4-fluorophenyl)methyl)naphthylimino]-2-arylimino-acenaphthylene derivatives (**L1–L5**). These compounds (**L1–L5**) reacted with a stoichiometric amount of (DME)NiBr₂ in the mixture of dichloromethane and ethanol, respectively; and the corresponding nickel complexes, 1-[2,4-bis(bis(4-fluorophenyl)methyl)naphthylimino]-2-aryliminoacenaphthylnickel bromides (**C1–C5**) were obtained in good yields (Scheme 1). All organic compounds were characterized by ¹H/¹³C NMR, FT-IR spectra and elemental analysis, meanwhile the nickel complexes were analyzed by the FT-IR spectra and elemental analysis without the NMR measurement due to their paramagnetic nature. According to their FT-IR spectra, the C=N stretching vibrations of complexes **C1–C5** were observed in the region 1620–1652 cm⁻¹ with weaker intensity in the comparison with those vibrations of corresponding organic compounds in the range of 1635–1675 cm⁻¹, indicating the effective coordination between imino-N atom with the cationic nickel center. Furthermore, the molecular structure of complex **C1** was confirmed by the single crystal X-ray diffraction.



Scheme 1 Synthetic procedures of ligands (**L1–L5**) and nickel complexes (**C1–C5**)

X-ray Crystallographic Study

Crystals of the complex **C1** suitable for the X-ray diffraction were grown by the slow diffusion of heptane into its dichloromethane solution at room temperature. The molecular structure of complex **C1** was shown in Figure 1, and the selected bond lengths and angles were tabulated in Table 1.

As shown in Figure 1, the nickel center is coordinated with two imino-nitrogen atoms of the organic ligand and two bromides,

adopting distorted tetrahedron geometry around the nickel center; in which the N1, N2, and Br2 atoms form its basal plane along with the apical position occupied by the Br1 atom. Such structural geometry is consistent to its analogous complexes.⁹ In complex **C1**, the nickel atom deviated by 1.072 Å from the basal plane; and the Ni–N bonds are quite similar with the values of 2.023(2) Å (Ni1–N1) and 2.025(3) Å (Ni1–N2), indicating the highly equal coordination ability between the nickel with two nitrogen atoms (N1 and N2), meanwhile the C=N bonds are also highly similar with the lengths as C1–N1 for 1.282(4) Å and C2–N2 for 1.281(4) Å. The dihedral angles between the basal plane comprising N1, N2 and Br2 with the naphthyl ring on N1-aryl ring and the aryl ring on N2-aryl ring are 55.2° and 53.7°, respectively; such observation is similar to its previous nickel analogue containing the naphthyl substituents.¹¹

Table 1 Selected bond lengths and angles for **C1**

Bond lengths (Å)		Bond angles(°)	
Ni(1)–N(1)	2.023(2)	N(1)–Ni(1)–N(2)	82.79(10)
Ni(1)–N(2)	2.025(3)	N(1)–Ni(1)–Br(2)	101.44(7)
Br(1)–Ni(1)	2.305(6)	N(2)–Ni(1)–Br(2)	118.62(2)
Br(2)–Ni(1)	2.347(6)	N(1)–Ni(1)–Br(1)	119.57(7)
C(1)–N(1)	1.282(4)	N(2)–Ni(1)–Br(1)	122.44(8)
C(2)–N(2)	1.281(4)	Br(2)–Ni(1)–Br(1)	118.62(2)
C(13)–N(1)	1.442(4)	C(1)–N(1)–C(13)	119.90(3)
C(49)–N(2)	1.439(4)	C(2)–N(2)–C(49)	120.70(3)

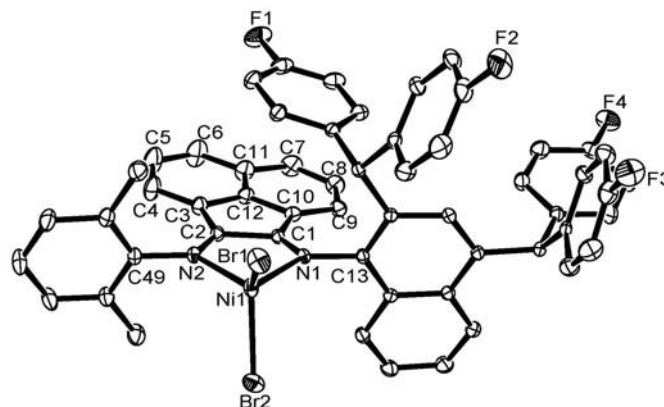


Fig. 1 ORTEP drawing of **C1**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms and free dichloromethane molecules have been omitted for clarity.

Ethylene Polymerization

To find the suitable co-catalyst toward ethylene polymerization, the complex **C3** was screened with different alkylaluminum reagents such as methylaluminoxane (MAO), modified methylaluminoxane (MMAO), diethylaluminum chloride (Et₂AlCl) and ethylaluminum sesquichloride (Et₃Al₂Cl₃, EASC) at 30 °C under 10 atm of ethylene (Entries 1–4 in Table 2). Most catalytic systems produced trace polyethylene, however, the system **C3**/Et₂AlCl exhibited high activity toward ethylene polymerization. Therefore, the Et₂AlCl was further explored to activate these nickel complexes for ethylene polymerization as well as detail investigations of

polymerization parameters and the properties of obtained polyethylenes.

Table 2 Ethylene polymerization by **C3** with various co-catalysts^a

Entry	Co-cat.	Al/Ni	Yield(g)	Act. ^b	M_w^c (10^5 g mol ⁻¹)	M_w/M_n^c	T_m^d (°C)
1	MAO	1000	trace	-	-	-	-
2	MMAO	1000	trace	-	-	-	-
3	EASC	600	trace	-	-	-	-
4	Et ₂ AlCl	600	2.89	385	3.68	1.73	116.8

^a Conditions: 1.5 μmol of Ni; 30 min; 30 °C; 10 atm of ethylene; total volume 100 mL. ^b In units of g of PE (mmol of Ni)⁻¹ h⁻¹ bar⁻¹. ^c Determined by GPC. ^d Determined by DSC.

To optimize the conditions of ethylene polymerization, in the presence of Et₂AlCl, the catalytic performance of complex **C3** was extensively investigated with changing reaction parameters of the Al/Ni ratio, reaction temperature, reaction time as well as the ethylene pressure, and results were collected in Table 3. Along with increasing the Al/Ni ratio from 300 to 700 (entries 1–5 in Table 3), the activities were observed gradually higher up to 4.79×10^6 g of PE (mol of Ni)⁻¹ h⁻¹ at the Al/Ni ratio of 700 (entry 5 in Table 3); however, with the Al/Ni ratio up to 800, the significant decrease was appeared with the activity as 2.76×10^6 g of PE (mol of Ni)⁻¹ h⁻¹ (entry 6 in Table 3). The higher ratio of Al/Ni used (entries 2–6 in Table 3), the slightly higher molecular weights of the polyethylenes resulted (Figure 2), however, the narrower polydispersity of the polyethylenes achieved. This case is different to the common observation by its nickel analogs:^{9,10} the catalytic system with the higher ratio of co-catalyst produced polyethylenes with lower molecular weight because of higher possibility of the chain transfer from the nickel species to aluminum for termination at higher ratio of co-catalyst. In current complexes incorporating the bulky-substituent of 2,4-bis[bis(4-fluorophenyl)methyl]naphthyl group, the cationic nickel active species is well stabilized, and more co-catalyst uniforms the single-site active species for the resultant polyethylene with narrower polydispersity. In another word, the chain propagations are generally superior to chain migrations to produce polyethylenes with higher molecular weights; such phenomenon was previously observed binuclear nickel complex analogs.^{5a}

On fixing the Al/Ni ratio at 700, the reaction temperature was changed from 20 to 80 °C (entry 5 and entries 7–11 in Table 3), and the highest activity was observed with 5.45×10^6 g of PE (mol of Ni)⁻¹ h⁻¹ at 40 °C (entry 8 in Table 3). Even the optimum temperature is 40 °C, which is still generally higher than the optimum temperature of the nickel precatalysts previously reported.^{1,4,9,11} Considering the correlation of ethylene concentration in toluene at different temperature,¹³ the adjusted activities were additionally obtained through calculating and shown in Table 3, indicating the close similar activities at 40 and 50 °C (entries 8 and 9 in Table 3); but the significant decrease of the activity was happened at 60 °C (entry 10 in Table 3), assuming the deactivation of active species occurred at higher temperature. The GPC curves

significantly indicated that the resultant polyethylenes had gradually lower molecular weights along with elevating the reaction temperature (entries 5, 7–10 in Table 3 and Fig. 3); this is ascribed to the more chain transfer and termination at the higher temperature.^{4,9}

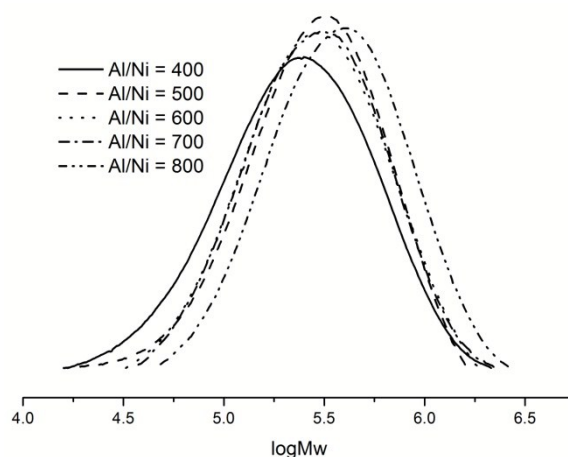


Fig. 2 GPC curves for the polyethylene obtained using the **C3**/Et₂AlCl system with various Al/Ni ratios (entries 2–6 in Table 3).

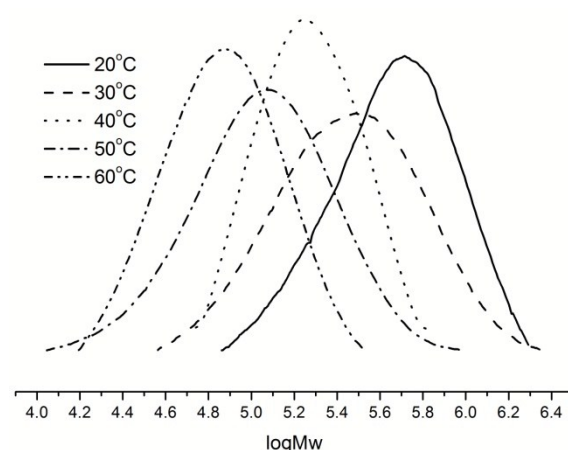


Fig. 3 GPC curves for the polyethylene obtained using the **C3**/Et₂AlCl system at different temperatures (entries 5, 7–10 in Table 3).

Pondering over the lifetime of the **C3**/Et₂AlCl system, the ethylene polymerization was conducted with the different periods within 15, 30, 45, and 60 min (entries 8 and 12–14 in Table 3). Along with prolonging time, the observing activities gradually decreased, indicating no initiation time required in such catalysis and partly deactivated species happened; meanwhile the obtained polyethylenes possessed the higher molecular weights (Figure 4), being consistent to the observation of its analogs.^{4,9} Besides the deactivation of active species, the increased viscosity of the reaction medium due to the formation of polyethylene disfavor the diffusion of ethylene into the solution and less coordination of ethylene onto active species, also resulting lower activity.

Table 3 Ethylene Polymerization by **C1–C5**/Et₂AlCl^a

Entry	Cat.	Al/Ni	<i>t</i> (min)	<i>T</i> (°C)	Yield (g)	Activity ^b	Adjusted activity ^c	<i>M_w</i> ^d (10 ⁵ g mol ⁻¹)	<i>M_w</i> / <i>M_n</i> ^d	<i>T_m</i> ^e (°C)
1	C3	300	30	30	trace	-	-	-	-	-
2	C3	400	30	30	0.14	18	14	3.20	1.99	116.20
3	C3	500	30	30	2.05	274	218	3.63	1.74	119.84
4	C3	600	30	30	2.89	385	306	3.68	1.73	116.78
5	C3	700	30	30	3.59	479	381	3.73	1.72	119.93
6	C3	800	30	30	2.07	276	219	4.80	1.70	126.50
7	C3	700	30	20	0.55	73	50	5.58	1.48	129.06
8	C3	700	30	40	4.08	545	496	2.11	1.29	95.88
9	C3	700	30	50	3.43	458	474	1.44	1.67	85.25
10	C3	700	30	60	1.57	209	244	0.86	1.40	63.16
11	C3	700	30	80	trace	-	-	-	-	-
12	C3	700	15	40	2.51	669	609	2.10	1.66	106.48
13	C3	700	45	40	4.84	430	392	2.13	1.89	105.32
14	C3	700	60	40	5.13	342	311	2.30	1.82	102.82
15 ^f	C3	700	30	40	2.56	342	623	1.58	1.33	87.60
16 ^g	C3	700	30	40	0.34	46	419	1.27	1.84	55.25
17	C1	700	30	40	3.45	461	420	0.96	1.22	112.05
18	C2	700	30	40	2.68	358	326	2.17	1.81	114.31
19	C4	700	30	40	3.35	446	406	0.92	1.99	108.28
20	C5	700	30	40	3.75	500	455	2.17	1.97	108.33

^a Conditions: 1.5 μmol of Ni; 30 min; 10 atm of ethylene; total volume 100 mL. ^b In units of g of PE (mmol of Ni)⁻¹ h⁻¹ bar⁻¹. ^c In units of g of PE (mmol of Ni)⁻¹ h⁻¹ C⁻¹ ethylene bar⁻¹. ^d Determined by GPC. ^e Determined by DSC. ^f 5 atm of ethylene. ^g 1 atm of ethylene; total volume 30 mL.

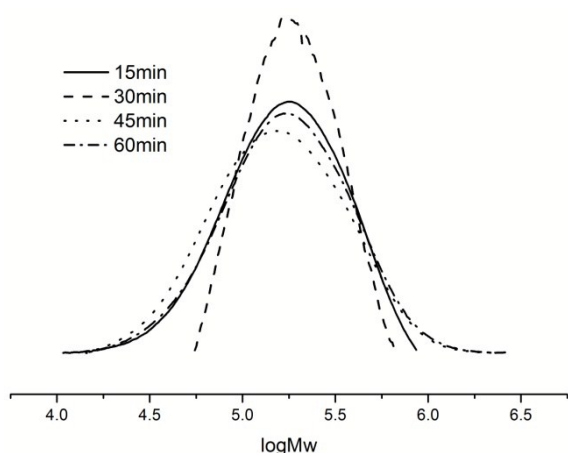


Fig. 4 GPC curves for the polyethylene obtained using the **C3**/Et₂AlCl system at different time (entries 8, 12–14 in Table 3).

Another factor, to significantly affect the ethylene concentration in solution, is the ethylene pressure. The polymerization of ethylene was conducted under the different pressures such as 1 atm, 5 atm and 10 atm (entries 8, 15–16 in Table 3), the higher activities were always achieved with the higher pressure of ethylene, moreover, the higher ethylene pressure led to produce the polyethylenes with higher molecular weights, being clearly reflected with their GPC curves (Figure 5).

Under the optimum conditions of an Al/Ni ratio of 700 at 40 °C under 10 atm pressure of ethylene, other nickel complexes were investigated and all showed high activities toward ethylene polymerization (entries 17–20 in Table 3). In general,

their activities were close similar, but with the differences in the order as **C3** [2,6-di(i-Pr)] > **C1** [2,6-di(Me)] > **C2** [2,6-di(Et)], **C5** [2,6-di(Et)-4-Me] > **C4** [2,4,6-tri(Me)], which were somewhat random regarding different substituents. The variations from anilines with relative less bulky substituents made the differences through the bulkiness and electronic affects, moreover, the solubility of complex precatalysts would be affected with substituents. In fact, the same substituent of bulky 2,4-bis[bis(4-fluorophenyl)methyl]naphthyl group play more important role of steric influence around the nickel center, resulting activities closer.

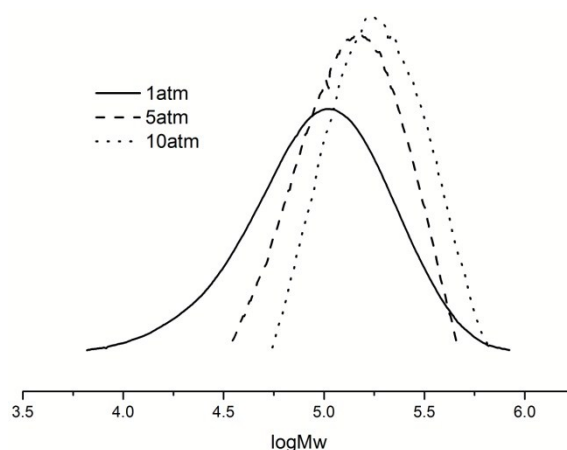


Fig. 5 GPC curves for the polyethylene obtained using the **C3**/Et₂AlCl system at different pressure of ethylene (entry 8 and entries 15–16 in Table 3).

Compared with the polyethylenes obtained by their analogs,⁹ the obtained polyethylenes possessed relatively lower

molecular weights and narrower polydispersity, meanwhile their T_m values were verified from low to high. The polyethylene with a lower T_m value indicates higher branches present. To confirm high branched polyethylenes formed, the ^{13}C NMR spectrum of the polyethylene by **C3**/ Et_2AlCl at 60°C (entry 10, Table 3) was obtained, indicating 164 branches/1000 carbons including methyl (41.7 %), ethyl (6.28 %), propyl (15.4 %), butyl (9.72 %) and long branches (26.9 %) according to the interpretation method.¹⁴

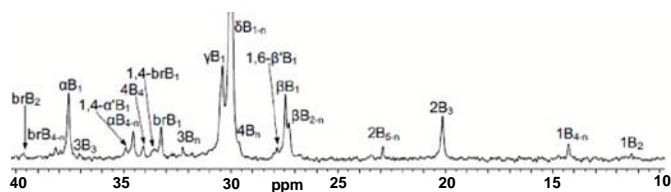


Fig. 6 ^{13}C NMR spectrum of polyethylene by **C3**/ Et_2AlCl at 60°C (entry 10, Table 3).

Conclusions

The series of 1-[2,4-bis(bis(4-fluorophenyl)methyl)naphthylimino]-2-aryliminoacenaphthylene derivatives (**L1–L5**) and their nickel bromide complexes (**C1–C5**) were synthesized and well characterized. On activation with Et_2AlCl , all the nickel precatalysts exhibited high activities toward ethylene polymerization (up to $5.45 \times 10^6 \text{ g}\cdot\text{mol}^{-1}(\text{Ni})\cdot\text{h}^{-1}$) as the similar range of their analogs,^{9,11} but having the optimum temperature of 40°C higher than the optimum temperatures observed by their analogs.^{9,11} In addition, the polymerization parameters heavily affected the properties of obtained polyethylenes, finely controlling molecular weights and branches (being reflected with their T_m values). Therefore the resultant polyethylenes could be tailored through using different parameters as well as the modified-substituents within ligands.

Experimental

General Considerations. All manipulations of air- and/or moisture-sensitive compounds were carried out under a nitrogen atmosphere using standard Schlenk techniques. Toluene was refluxed over sodium benzophenone and distilled under nitrogen prior to use. Methylaluminoxane (MAO, 1.46 M solution in toluene) and modified methylaluminoxane (MMAO, 1.93 M in heptane, 3A) were purchased from Akzo Nobel Corp. Diethylaluminum chloride (Et_2AlCl , 1.17 M in toluene) and ethylaluminum sesquichloride ($\text{Et}_3\text{Al}_2\text{Cl}_3$, 0.87 M in hexane) was purchased from Acros Chemicals. High-purity ethylene was purchased from Beijing Yansan Petrochemical Co. and used as received. 2,4-Bis(bis(4-fluorophenyl)methyl)naphthylamine was prepared according to our previous literature.^{6h} Other reagents were purchased from Aldrich, Acros, or local suppliers. NMR spectra were recorded on a Bruker DMX 400 MHz instrument at ambient temperature using TMS as an internal standard. IR spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrometer. Elemental analysis was

carried out using a Flash EA 1112 microanalyzer. Molecular weights and molecular weight distribution (MWD) of polyethylene were determined by a PL-GPC 220 at 150°C , with 1,2,4-trichlorobenzene as the solvent. Melting points of polyethylenes were measured from the second scanning run on a Perkin-Elmer DSC-7 differential scanning calorimetry (DSC) analyzer under a nitrogen atmosphere; in the procedure, a sample of about 3.8–4.5 mg was heated to 180°C at a rate of $20^\circ\text{C}/\text{min}$ and kept for 5 min at 180°C to remove the thermal history and then cooled at a rate of $20^\circ\text{C}/\text{min}$ to -40°C . ^{13}C NMR spectra of the polyethylenes were recorded on a Bruker DMX-300MHz instrument at 135°C in deuterated 1,1,2,2-tetrachloroethane with TMS as an internal standard.

Synthesis and Characterization

1-[2,4-bis(bis(4-fluorophenyl)methyl)naphthylimino]acenaphthylene-2-one. A mixture of acenaphthylene-1,2-dione (0.73 g, 4.0 mmol), 2,4-bis(bis(4-fluorophenyl)methyl)naphthylamine (2.19 g, 4.0 mmol) and a catalytic amount of *p*-toluenesulfonic acid (0.15 g, 0.80 mmol) was dissolved in 40 mL of CH_2Cl_2 and 2 mL of EtOH and stirred for 24 h at room temperature. After solvent evaporation at reduced pressure, the residue was purified by column chromatography on silica gel with the eluent of petroleum ether–ethyl acetate ($v : v = 100 : 1$) to afford a red powder (0.80 g) in 53 % isolated yield. ^1H NMR (400 MHz, CDCl_3 , TMS): δ 8.12 (t, $J = 8.8$ Hz, 2H), 7.93 (d, $J = 8.4$ Hz, 1H), 7.85–7.77 (m, 2H), 7.67 (d, $J = 8.0$ Hz, 1H), 7.39 (t, $J = 7.6$ Hz, 1H), 7.29–7.27 (m, 1H), 7.06–7.00 (m, 5H), 6.94–6.87 (m, 4H), 6.80 (d, $J = 7.2$ Hz, 4H), 6.67–6.64 (m, 2H), 6.47 (s, 1H), 6.20 (s, 1H), 6.13 (t, $J = 8.4$ Hz, 2H), 5.78 (d, $J = 7.6$ Hz, 1H), 5.66 (s, 1H).

1-[2,4-Bis(bis(4-fluorophenyl)methyl)naphthylimino]-2-(2,6-dimethylphenylimino)acenaphthylene (**L1**). A mixture of 1-[2,4-bis(bis(4-fluorophenyl)methyl)naphthylimino]acenaphthylene-2-one (1.27 g, 1.78 mmol), 2,6-dimethylphenylamine (0.215 g, 1.78 mmol) and a catalytic amount of *p*-toluenesulfonic acid (0.068 g, 0.35 mmol) in toluene (50 mL) was refluxed for 10 h. After solvent evaporation at reduced pressure, the residue was purified by column chromatography on silica gel with the eluent of petroleum ether–ethyl acetate ($v : v = 200 : 1$) to afford a red powder (0.21 g) in 14 % isolated yield. Mp: 149°C . IR (KBr, cm^{-1}): 2864 (w), 2730 (w), 1888 (w), 1669 (m), 1635 (m), 1600 (s), 1504 (vs), 1225 (vs), 1156 (s), 1017 (m), 821 (vs), 771 (vs), 723 (m). Anal. Calcd for $\text{C}_{56}\text{H}_{38}\text{F}_4\text{N}_2$ (814.91): C, 82.54; H, 4.70; N, 3.44. Found: C, 82.15; H, 4.66; N, 3.65. ^1H NMR (400 MHz, CDCl_3 , TMS): δ 7.93 (d, $J = 8.4$ Hz, 1H), 7.81 (d, $J = 8.4$ Hz, 2H), 7.72 (d, $J = 8.0$ Hz, 1H), 7.41–7.28 (m, 4H), 7.20 (t, $J = 8.2$ Hz, 2H), 7.00 (t, $J = 8.6$ Hz, 3H), 6.96–6.89 (m, 5H), 6.86–6.81 (m, 5H), 6.76 (t, $J = 7.0$ Hz, 2H), 6.65 (d, $J = 7.2$ Hz, 1H), 6.47 (s, 1H), 6.21 (s, 1H), 6.17 (d, $J = 8.6$ Hz, 2H), 5.83 (s, 1H), 5.78 (d, $J = 7.2$ Hz, 1H), 2.27 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 164.0, 162.4, 161.3, 140.5, 139.4, 130.5, 129.1, 128.3, 127.1, 126.0, 124.5, 123.7, 122.4, 115.1, 114.3, 51.4, 50.8, 18.2, 18.0.

1-[2,4-Bis(bis(4-fluorophenyl)methyl)naphthylimino]-2-(2,6-diethylphenylimino)acenaphthylene (**L2**). Using the same procedure as for the synthesis of **L1**, **L2** was obtained as a red

powder in 36 % yield (0.30 g). Mp: 160 °C. IR (KBr, cm^{-1}): 2963 (w), 2927 (w), 2870 (w), 1890 (w), 1668 (m), 1636 (m), 1599 (s), 1504 (vs), 1224 (vs), 1157 (s), 1016 (m), 820 (vs), 772 (vs), 723 (m). Anal. Calcd for $\text{C}_{58}\text{H}_{42}\text{F}_4\text{N}_2$ (842.96): C, 82.64; H, 5.02; N, 3.32. Found: C, 82.23; H, 5.06; N, 3.71. ^1H NMR (400 MHz, CDCl_3 , TMS): δ 7.93 (d, $J = 8.4$ Hz, 1H), 7.80 (d, $J = 8.0$ Hz, 2H), 7.71 (d, $J = 8.4$ Hz, 1H), 7.39 (t, $J = 7.4$ Hz, 1H), 7.34–7.29 (m, 2H), 7.27–7.20 (m, 2H), 7.07 (t, $J = 6.0$ Hz, 2H), 7.01 (t, $J = 8.4$ Hz, 2H), 6.97–6.87 (m, 6H), 6.83 (t, $J = 6.2$ Hz, 4H), 6.74 (t, $J = 6.6$ Hz, 2H), 6.63 (d, $J = 7.2$ Hz, 1H), 6.48 (s, 1H), 6.22 (s, 1H), 6.18 (t, $J = 8.2$ Hz, 2H), 5.84 (s, 1H), 5.76 (d, $J = 7.2$ Hz, 1H), 2.77–2.68 (m, 1H), 2.66–2.55 (m, 2H), 2.50–2.40 (m, 1H), 1.25 (t, $J = 7.2$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 164.1, 162.7, 161.2, 160.3, 148.2, 145.2, 140.5, 139.5, 138.6, 135.1, 130.6, 129.4, 128.8, 127.1, 126.2, 124.3, 123.6, 115.2, 114.3, 51.4, 50.8, 24.8, 24.6, 14.4, 14.1.

1-[2,4-Bis(bis(4-fluorophenyl)methyl)naphthylimino]-2-(2,6-diisopropylphenylimino)acenaphthylene (**L3**). Using the same procedure as for the synthesis of **L1**, **L3** was obtained as a red powder in 17 % yield (0.30 g). Mp: 231 °C. IR (KBr, cm^{-1}): 2925 (w), 2927 (w), 2866 (w), 1893 (w), 1675 (m), 1646 (w), 1600 (m), 1505 (vs), 1225 (vs), 1157 (s), 1016 (w), 822 (s), 772 (vs), 721 (m). Anal. Calcd for $\text{C}_{60}\text{H}_{46}\text{F}_4\text{N}_2$ (871.01): C, 82.74; H, 5.32; N, 3.22. Found: C, 82.49; H, 5.53; N, 3.27. ^1H NMR (400 MHz, CDCl_3 , TMS): δ 7.94 (d, $J = 8.4$ Hz, 1H), 7.80 (d, $J = 6.0$ Hz, 2H), 7.71 (d, $J = 8.4$ Hz, 1H), 7.40 (t, $J = 7.4$ Hz, 1H), 7.32 (t, $J = 7.4$ Hz, 5H), 7.09 (t, $J = 6.4$ Hz, 2H), 7.02 (t, $J = 8.4$ Hz, 2H), 6.96–6.80 (m, 9H), 6.76 (t, $J = 6.4$ Hz, 2H), 6.60 (d, $J = 7.2$ Hz, 1H), 6.49 (s, 1H), 6.23 (s, 1H), 6.17 (t, $J = 8.4$ Hz, 2H), 5.84 (s, 1H), 5.74 (d, $J = 7.2$ Hz, 1H), 3.23–3.16 (m, 1H), 3.07–3.00 (m, 1H), 1.34 (d, $J = 6.8$ Hz, 3H), 1.28 (d, $J = 6.8$ Hz, 3H), 1.13 (d, $J = 6.8$ Hz, 3H), 0.97 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 164.1, 162.7, 162.6, 161.6, 161.4, 160.3, 160.2, 147.0, 145.2, 140.6, 139.5, 135.4, 130.7, 130.4, 128.8, 128.4, 126.5, 126.0, 124.5, 124.3, 123.6, 123.3, 115.3, 114.6, 51.4, 50.8, 28.7, 28.6, 23.8, 23.6, 23.5, 23.2.

1-[2,4-Bis(bis(4-fluorophenyl)methyl)naphthylimino]-2-(2,4,6-trimethylphenylimino)acenaphthylene (**L4**). Using the same procedure as for the synthesis of **L1**, **L4** was obtained as a red powder (0.17 g) in 21 % isolated yield. Mp: 140 °C. IR (KBr, cm^{-1}): 2956 (w), 2920 (w), 2857 (w), 1889 (w), 1668 (m), 1636 (m), 1600 (m), 1504 (vs), 1224 (vs), 1157 (s), 1016 (m), 820 (s), 775 (s), 722 (m). Anal. Calcd for $\text{C}_{57}\text{H}_{40}\text{F}_4\text{N}_2$ (828.93): C, 82.59; H, 4.86; N, 3.38. Found: C, 82.23; H, 5.17; N, 3.53. ^1H NMR (400 MHz, CDCl_3 , TMS): δ 7.85 (d, $J = 8.4$ Hz, 1H), 7.73 (d, $J = 8.4$ Hz, 2H), 7.64 (d, $J = 8.0$ Hz, 1H), 7.29 (t, $J = 6.2$ Hz, 1H), 7.23–7.18 (m, 2H), 7.00 (t, $J = 6.8$ Hz, 2H), 6.95–6.90 (m, 4H), 6.88–6.81 (m, 5H), 6.79–6.73 (m, 4H), 6.69 (t, $J = 6.8$ Hz, 2H), 6.64 (d, $J = 7.2$ Hz, 1H), 6.39 (s, 1H), 6.14 (s, 1H), 6.08 (t, $J = 8.4$ Hz, 2H), 5.76 (s, 1H), 5.69 (d, $J = 7.2$ Hz, 1H), 2.32 (s, 3H), 2.16 (s, 3H), 2.07 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 164.2, 162.8, 162.6, 161.7, 160.4, 159.2, 146.6, 145.3, 140.5, 139.1, 137.4, 133.3, 132.4, 130.8, 129.2, 127.1, 126.0, 124.6, 123.8, 115.3, 114.5, 51.5, 50.9, 21.0, 19.3, 18.2.

1-[2,4-Bis(bis(4-fluorophenyl)methyl)naphthylimino]-2-(2,6-diethyl-4-methylphenylimino)acenaphthylene (**L5**). Using the same procedure as for the synthesis of **L1**, **L5** was obtained as

red powder (0.27 g) in 32 % isolated yield. Mp: 221 °C. IR (KBr, cm^{-1}): 2963 (w), 2926 (w), 2867 (w), 1892 (w), 1660 (m), 1635 (m), 1598 (m), 1504 (vs), 1223 (vs), 1158 (s), 1016 (w), 821 (vs), 770 (vs), 722 (m). Anal. Calcd for $\text{C}_{59}\text{H}_{44}\text{F}_4\text{N}_2$ (856.99): C, 82.69; H, 5.18; N, 3.27. Found: C, 82.47; H, 5.22; N, 3.50. ^1H NMR (400 MHz, CDCl_3 , TMS): δ 7.93 (d, $J = 8.4$ Hz, 1H), 7.80 (d, $J = 8.4$ Hz, 2H), 7.70 (d, $J = 8.4$ Hz, 1H), 7.40–7.34 (m, 2H), 7.32–7.25 (m, 1H), 7.09–6.98 (m, 6H), 6.95–6.89 (m, 5H), 6.86–6.81 (m, 4H), 6.78–6.74 (m, 2H), 6.70 (d, $J = 6.8$ Hz, 1H), 6.48 (s, 1H), 6.21 (s, 1H), 6.17 (t, $J = 8.4$ Hz, 2H), 5.83 (s, 1H), 5.74 (d, $J = 6.8$ Hz, 1H), 2.73–2.64 (m, 2H), 2.62–2.53 (m, 2H), 2.44 (s, 3H), 1.23 (t, $J = 7.6$ Hz, 3H), 1.14 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 164.3, 163.0, 161.6, 160.4, 146.0, 140.7, 138.9, 135.3, 133.7, 131.0, 130.7, 129.2, 127.4, 124.5, 115.3, 114.7, 51.7, 51.0, 25.0, 24.8, 21.4, 14.7, 14.1.

1-[2,4-Bis(bis(4-fluorophenyl)methyl)naphthylimino]-2-(2,6-dimethylphenylimino)acenaphthynickel bromide (**C1**). The 1-[2,4-bis(bis(4-fluorophenyl)methyl)naphthylimino]-2-(2,6-dimethylphenylimino)acenaphthylene (**L1**) (0.114 g, 0.14 mmol) was dissolved in 10 mL CH_2Cl_2 and then added to a solution of (DME)NiBr₂ (0.043 g, 0.14 mmol) in 5 mL ethanol. The mixture was stirred for 24 h, and then diethyl ether was poured into the mixture to precipitate the complex. The precipitate was collected by filtration, washed with diethyl ether (3 × 5 mL), and dried in vacuum to obtain a deep red powder of **C1** (0.12 g) in 82 % yield. IR (KBr, cm^{-1}): 2800 (w), 2771 (w), 1889 (w), 1649 (w), 1622 (m), 1602 (s), 1507 (vs), 1227 (vs), 1155 (s), 1017 (m), 830 (s), 776 (vs), 737 (m). Anal. Calcd for $\text{C}_{56}\text{H}_{38}\text{Br}_2\text{F}_4\text{N}_2\text{Ni}$ (1033.41): C, 65.09; H, 3.71; N, 2.71. Found: C, 62.22; H, 3.72; N, 2.60.

1-[2,4-Bis(bis(4-fluorophenyl)methyl)naphthylimino]-2-(2,6-diethylphenylimino)acenaphthynickel bromide (**C2**). Yield: 72 % (0.08 g), deep red powder. IR (KBr, cm^{-1}): 2974 (w), 2937 (w), 2876 (w), 1908 (w), 1647 (w), 1621 (m), 1600 (s), 1505 (vs), 1225 (vs), 1157 (s), 1016 (m), 835 (s), 776 (m), 723 (m). Anal. Calcd for $\text{C}_{58}\text{H}_{42}\text{Br}_2\text{F}_4\text{N}_2\text{Ni}$ (1061.46): C, 65.63; H, 3.99; N, 2.64. Found: C, 65.55; H, 4.31; N, 2.43.

1-[2,4-Bis(bis(4-fluorophenyl)methyl)naphthylimino]-2-(2,6-diisopropylphenylimino)acenaphthynickel bromide (**C3**). Yield: 93 % (0.15 g), deep red powder. IR (KBr, cm^{-1}): 2968 (w), 2930 (w), 2867 (w), 1889 (w), 1650 (w), 1621 (m), 1602 (m), 1505 (vs), 1227 (s), 1154 (s), 1018 (w), 827 (s), 772 (s), 723 (w). Anal. Calcd for $\text{C}_{60}\text{H}_{46}\text{Br}_2\text{F}_4\text{N}_2\text{Ni}$ (1089.52): C, 66.14; H, 4.26; N, 2.57. Found: C, 66.25; H, 4.47; N, 2.26.

1-[2,4-Bis(bis(4-fluorophenyl)methyl)naphthylimino]-2-(2,4,6-trimethylphenylimino)acenaphthynickel bromide (**C4**). Yield: 32 % (0.03 g), deep red powder. IR (KBr, cm^{-1}): 2950 (w), 2913 (w), 2853 (w), 1900 (w), 1652 (w), 1624 (m), 1600 (s), 1503 (vs), 1220 (vs), 1157 (s), 1015 (m), 827 (vs), 777 (s), 713 (w). Anal. Calcd for $\text{C}_{57}\text{H}_{40}\text{Br}_2\text{F}_4\text{N}_2\text{Ni}$ (1047.44): C, 65.36; H, 3.85; N, 2.67. Found: C, 65.45; H, 3.49; N, 2.43.

1-[2,4-Bis(bis(4-fluorophenyl)methyl)naphthylimino]-2-(2,6-diethyl-4-methylphenylimino)acenaphthynickel bromide (**C5**). Yield: 93 % (0.10 g), deep red powder. IR (KBr, cm^{-1}): 2971 (w), 2934 (w), 2874 (w), 1910 (w), 1647 (w), 1620 (w), 1599 (m), 1505 (vs), 1225 (vs), 1158 (s), 1015 (w), 828 (s), 777 (m), 717

(w). Anal. Calcd for $C_{59}H_{44}Br_2F_4N_2Ni$ (1075.49): C, 65.89; H, 4.12; N, 2.60. Found: C, 65.52; H, 4.27; N, 2.58.

General Procedure for Ethylene Polymerization

Ethylene Polymerization at Ambient Pressure. The precatalyst was dissolved in toluene using standard Schlenk techniques, and the reaction solution was stirred with a magnetic stir bar under ethylene atmosphere (1 atm) with a steam bath for controlling the desired temperature. Finally, the required amount of co-catalyst (Et_2AlCl) was added by a syringe. After the reaction was carried out for the required period, the reaction solution was collected and terminated by the addition of 10 % aqueous hydrogen chloride immediately. The precipitated polymer was collected, washed with ethanol, and finally dried.

Ethylene Polymerization at Elevated Pressure (5 or 10 atm). A 300 mL stainless steel autoclave, equipped with a mechanical stirrer and a temperature controller, was employed for the reaction. Firstly, 50 mL toluene (freshly distilled) was injected to the clave which is full of ethylene. When the temperature required was reached, another 30 mL toluene which dissolved the complex (1.5 μ mol of nickel) before, the required amount of co-catalyst (Et_2AlCl), the residual toluene were added by

syringe successively. The reaction mixture was intensively stirred for the desired time under corresponding pressure of ethylene through the entire experiment. The reaction was terminated and analyzed using the same procedure as above for ethylene polymerization.

X-ray Crystallographic Studies

Crystals of **C1** suitable for X-ray diffraction analysis were obtained by the slow diffusion of heptane into dichloromethane solution at room temperature. With graphite-monochromated Mo K_α radiation ($\lambda = 0.71073 \text{ \AA}$) at 173(2) K, cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least squares on F^2 . All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package.¹⁵ Details of the X-ray structure determinations and refinements are provided in Table 4.

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Notes and references

- (a) L. K. Johnson, C. M. Killian and M. Brookhart, *J. Am. Chem. Soc.*, 1995, **117**, 6414; (b) C. M. Killian, D. J. Tempel, L. K. Johnson and M. Brookhart, *J. Am. Chem. Soc.*, 1996, **118**, 11664.
- (a) S. D. Ittel, L. K. Johnson and M. Brookhart, *Chem. Rev.*, 2000, **100**, 1169; (b) F. Speiser, P. Braunstein and L. Saussine, *Acc. Chem. Res.*, 2005, **38**, 784; (c) V. C. Gibson, C. Redshaw and G. A. Solan, *Chem. Rev.*, 2007, **107**, 1745; (d) C. Bianchini, G. Giambastiani, L. Luconi and A. Meli, *Coord. Chem. Rev.*, 2010, **254**, 431; (e) R. Gao, W.-H. Sun and C. Redshaw, *Catal. Sci. Technol.*, 2013, **3**, 1172; (f) S. Wang, W.-H. Sun and C. Redshaw, *J. Organomet. Chem.*, 2014, **751**, 717.
- (a) W. Zhang, W.-H. Sun and C. Redshaw, *Dalton Trans.*, 2013, **42**, 8988; (b) Z. Flisak and W.-H. Sun, *ACS Catal.*, 2015, **5**, 4713; (c) B. Burcher, P.-A.R. Breuil, L. Magna, H. Olivier-Bourbigou, *Top. Organomet. Chem.*, 2015, **50**, 217; (d) B. L. Small, *Acc. Chem. Res.*, 2015, **48**, 2599; (e) J. Ma, C. Feng, S. Wang, K.-Q. Zhao, W.-H. Sun, C. Redshaw and G. A. Solan, *Inorg. Chem. Front.*, 2014, **1**, 14.
- (a) C. M. Killian, L. K. Johnson and M. Brookhart, *Organometallics*, 1997, **16**, 2005; (b) S. A. Svejda and M. Brookhart, *Organometallics*, 1999, **18**, 65; (c) M. Helldorfer, J. Backhaus, W. Milius and H. J. Alt, *J. Mol. Catal. A: Chem.*, 2003, **193**, 59; (d) D. H. Camacho, E. V. Salo, J. W. Ziller and Z. Guan, *Angew. Chem. Int. Ed.*, 2004, **43**, 1821; (e) A. E. Cherian, J. M. Rose, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 2005, **127**, 13770; (f) F.-S. Liu, H.-B. Hu, Y. Xu, L.-H. Guo, S.-B. Zai, K.-M. Song, H.-Y. Gao, L. Zhang, F.-M. Zhu and Q. Wu, *Macromolecules*, 2009, **42**, 7789; (g) C. S. Popeney, A. L. Rheingold and Z. Guan, *Organometallics*, 2009, **28**, 4452; (h) M. M. Wegner, A. K. Ott and B. Rieger, *Macromolecules*, 2010, **43**, 3624; (i) F. Wang, J. Yuan, F. Song, J. Li, Z. Jia and B. Yuan, *Appl. Organometal. Chem.*, 2013, **27**,

Table 4 Crystal data and structure refinements for **C1**

C1	
Empirical formula	$C_{58}H_{42}Br_2Cl_4F_4N_2Ni$
Formula weight	1203.27
Temperature (K)	173(2)
Wavelength (\AA)	0.71073
Crystal system	Triclinic
space group	P -1
a (\AA)	11.224
b (\AA)	11.341
c (\AA)	22.484
α ($^\circ$)	92.60
β ($^\circ$)	96.06
γ ($^\circ$)	113.86
V (\AA^3)	2590.5
Z	2
D_{calc} (mg m^{-3})	1.543
μ (mm^{-1})	2.179
F(000)	1212
Crystal size (mm)	$0.39 \times 0.23 \times 0.18$
θ range ($^\circ$)	$0.91 - 27.49$
Limiting indices	$-14 \leq h \leq 14$, $-14 \leq k \leq 14$, $-29 \leq l \leq 29$
No. of reflections collected	36070
No. of unique reflections	11811
R_{int}	0.0333
Completeness to θ (%)	99.4 ($\theta = 27.49^\circ$)
No. of parameters	642
Goodness-of-fit on F^2	1.069
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0619$, $wR2 = 0.1776$
R indices (all data)	$R1 = 0.0655$, $wR2 = 0.1818$

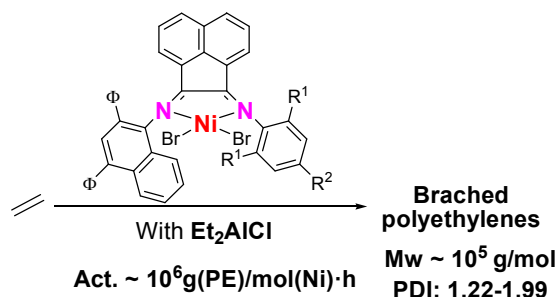
- 319; (j) F. Wang, J. Yuan, Q. Li, R. Tanaka, Y. Nakayama and T. Shiono, *Appl. Organometal. Chem.*, 2014, **28**, 477.
- 5 (a) Q. Xing, K. Song, T. Liang, Q. Liu, W.-H. Sun and C. Redshaw, *Dalton Trans.*, 2014, **43**, 7830; (b) K. Song, W. Yang, B. Li, Q. Liu, C. Redshaw, Y. Li and W.-H. Sun, *Dalton Trans.*, 2013, **42**, 9166.
- 6 (a) T. V. Laine, M. Klinga and M. Leskelä, *Eur. J. Inorg. Chem.*, 1999, 959; (b) T. V. Laine, U. Piironen, K. Lappalainen, M. Klinga, E. Aitola and M. Leskel, *J. Organomet. Chem.*, 2000, **606**, 112; (c) A. Köppl and H. G. Alt, *J. Mol. Catal. A: Chem.*, 2000, **154**, 45; (d) G. J. P. Britovsek, S. P. D. Baugh, O. Hoarau, V. C. Gibson, D. F. Wass, A. J. P. White and D. J. Williams, *Inorg. Chim. Acta*, 2003, **345**, 279; (e) V. C. Gibson, C. M. Halliwell, N. J. Long, P. J. Oxford, A. M. Smith, A. J. P. White and D. J. Williams, *Dalton Trans.*, 2003, 918; (f) S. Jie, D. Zhang, T. Zhang, W.-H. Sun, J. Chen, Q. Ren, D. Liu, G. Zheng and W. Chen, *J. Organomet. Chem.*, 2005, **690**, 1739; (g) W.-H. Sun, S. Song, B. Li, C. Redshaw, X. Hao, Y.-S. Li and F. Wang, *Dalton Trans.*, 2012, **41**, 11999; (h) E. Yue, L. Zhang, Q. Xing, X.-P. Cao, X. Hao, C. Redshaw and W.-H. Sun, *Dalton Trans.*, 2014, **43**, 423; (i) E. Yue, Q. Xing, L. Zhang, Q. Shi, X.-P. Cao, L. Wang, C. Redshaw and W.-H. Sun, *Dalton Trans.*, 2014, **43**, 3339.
- 7 (a) J. Yu, X. Hu, Y. Zeng, L. Zhang, C. Ni, X. Hao and W.-H. Sun, *New J. Chem.*, 2011, **35**, 178; (b) J. Yu, Y. Zeng, W. Huang, X. Hao, and W.-H. Sun, *Dalton Trans.*, 2011, **40**, 8436; (c) L. Zhang, X. Hao, W.-H. Sun and C. Redshaw, *ACS Catal.*, 2011, **1**, 1213; (d) X. Hou, Z. Cai, X. Chen, L. Wang, C. Redshaw and W.-H. Sun, *Dalton Trans.*, 2012, **41**, 1617; (e) W. Chai, J. Yu, L. Wang, X. Hu, C. Redshaw and W.-H. Sun, *Inorg. Chim. Acta*, 2012, **385**, 21; (f) Z. Sun, E. Yue, M. Qu, I. V. Oleynik, I. I. Oleynik, K. Li, T. Liang, W. Zhang and W.-H. Sun, *Inorg. Chem. Front.*, 2015, **2**, 223; (g) I. E. Soshnikov, N. V. Semikolenova, K. P. Bryliakov, V. A. Zakharov, W.-H. Sun and E. P. Talsi, *Organometallics*, 2015, **34**, 3222.
- 8 (a) F. Huang, Z. Sun, S. Du, E. Yue, J. Ba, X. Hu, T. Liang, G. B. Galland and W.-H. Sun, *Dalton Trans.*, 2015, **44**, 14281; (b) Z. Sun, F. Huang, M. Qu, E. Yue, I. V. Oleynik, I. I. Oleynik, Y. Zeng, T. Liang, K. Li, W. Zhang and W.-H. Sun, *RSC Adv.*, 2015, **5**, 77913.
- 9 (a) H. Liu, W. Zhao, X. Hao, C. Redshaw, W. Huang and W.-H. Sun, *Organometallics*, 2011, **30**, 2418; (b) H. Liu, W. Zhao, J. Yu, W. Yang, X. Hao, C. Redshaw, L. Chen and W.-H. Sun, *Catal. Sci. Technol.*, 2012, **2**, 415; (c) S. Kong, C.-Y. Guo, W. Yang, L. Wang, W.-H. Sun and R. Glaser, *J. Organomet. Chem.*, 2013, **725**, 37; (d) C. Wen, S. Yuan, Q. Shi, E. Yue, D. Liu and W.-H. Sun, *Organometallics*, 2014, **33**, 7223; (e) J. L. Rhinehart, N. E. Mitchell and B. K. Long, *ACS Catal.*, 2014, **4**, 2501; (f) S. Du, S. Kong, Q. Shi, J. Mao, C. Guo, J. Yi, T. Liang and W.-H. Sun, *Organometallics*, 2015, **34**, 582; (g) L. Fan, S. Du, C.-Y. Guo, X. Hao and W.-H. Sun, *J. Polym. Sci. Part A: Polym. Chem.*, 2015, **53**, 1369; (h) S. Du, Q. Xing, Z. Flisak, E. Yue, Y. Sun, and W.-H. Sun, *Dalton Trans.*, 2015, **44**, 12282.
- 10 (a) D. Jia, W. Zhang, W. Liu, L. Wang, C. Redshaw and W.-H. Sun, *Catal. Sci. Technol.*, 2013, **3**, 2737; (b) Q. Liu, W. Zhang, D. Jia, X. Hao, C. Redshaw and W.-H. Sun, *Applied Catalysis A: General*, 2014, **475**, 195.
- 11 C. Wen, S. Yuan, E. Yue, Q. Shi, D. Liu and W.-H. Sun, *Organometallics*, 2014, **33**, 7223.
- 12 (a) T. Zhang, D. Guo, S. Jie, W.-H. Sun, T. Li and X. Yang, *J. Polym. Sci., Part A: Polym. Chem.*, 2004, **42**, 4765; (b) W. Yang, Y. Chen and W.-H. Sun, *Macromol. Chem. Phys.*, 2014, **215**, 1810; (c) Y. Chen, W. Yang, R. Sha, R. Fu and W.-H. Sun, *Inorg. Chim. Acta*, 2014, **423**, 450; (d) D. Guo, L. Han, T. Zhang, W.-H. Sun, T. Li, X. Yang, *Macromol. Theory Simul.*, 2002, **11**, 1006.
- 13 W. Krauss and W. Gestrich, *Chem.-Tech.*, 1977, **6**, 513.
- 14 G. B. Galland, R. F. de Souza, R. S. Mauler and F. F. Nunes, *Macromolecules*, 1999, **32**, 1620.
- 15 G. M. Sheldrick, *SHELXTL-97, Program for the Refinement of Crystal Structures*; University of Göttingen, Germany, 1997.

Graphical Abstract

for

**Synthesis, characterization, and ethylene polymerization of
1-[2,4-bis(bis(4-fluorophenyl) methyl)naphthylimino]-2-aryliminoacenaphthyl
nickel bromides: Influences of polymerization parameters on polyethylenes**

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The 1-[2,4-bis(bis(4-fluorophenyl) methyl)naphthylimino]-2-aryliminoacenaphthylnickel bromides (C1–C5), upon activation with diethylaluminum chloride (Et_2AlCl), exhibited high activities toward ethylene polymerization obtaining polyethylenes with Mw from $0.86\text{--}5.58 \times 10^5 \text{g mol}^{-1}$ and narrower PDI (1.22–1.99).