Alkylaluminum activator effects on polyethylene branching using a *N,N'*-nickel precatalyst appended with bulky 4,4'-dimethoxybenzhydryl groups

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Abstract

Ten unsymmetrical *N,N'*-bis(imino)acenaphthene-nickel(II) halide complexes, [1-[2,6-((4-MeOC₆H₄)₂CH)₂-4-MeC₆H₂N]-2-(ArN)C₂C₁₀H₆]NiX₂, each appended with one *N*-2,6-bis(4,4'-dimethoxybenzhydryl)-4-methylphenyl group, have been synthesized and characterized. The molecular structures of **Ni1**, **Ni3**, **Ni5** and **Ni6** highlight the variation in steric protection afforded by the inequivalent *N*-aryl groups; a distorted tetrahedral geometry is conferred about each nickel center. On activation with diethylaluminum chloride (Et₂AlCl) or methylaluminoxane (MAO), all complexes showed high activity at 30 °C for the polymerization of ethylene with the least bulky bromide precatalysts (**Ni1**, **Ni4**) generally the most productive, forming polyethylenes with narrow dispersities [M_w/M_n : < 3.4 (Et₂AlCl), < 4.1 (MAO)] and various levels of branching. Significantly, this level of branching can be influenced by the type of co-catalyst employed with Et₂AlCl having a predilection towards polymers displaying significantly higher branching contents than with MAO [T_m : 33.0 – 82.5 °C (Et₂AlCl) vs. 117.9 – 119.4 °C (MAO)]. On the other hand, the molecular weights of the materials obtained with each co-catalyst were high and, in some cases, entering the ultra-high molecular weight range [M_w range: 6.8 - 12.2 × 10⁵ g mol⁻¹ (Et₂AlCl), 7.2 - 10.9 × 10⁵ g mol⁻¹ (MAO)]. Furthermore, good tensile strength (ϵ_b up to 553.5%) and elastic recovery (up to 84%) have been displayed by selected more branched polymers highlighting their elastomeric properties.

Keywords: Bis(imino)acenaphthene-Nickel(II) precatalyst; Ethylene polymerization; Co-catalyst effects

Introduction

The propensity of α -diimine-nickel catalysts to promote the formation of polyethylenes with various levels of branching and molecular weight has provided the impetus behind numerous metal-mediated polymerization studies since the first report in the mid 1990's [1]. Indeed, the branching properties displayed by these homo-polymerized materials are attracting attention due to their relevance to thermoplastic elastomers (TPEs) [2]. While the structural properties of the catalyst play a key role on determining the polymer properties, the effects of temperature and pressure have also been shown as important [3].

With regard to the precatalyst, many different types of nickel(II) halide complexes have now been reported, in which the structural features of the particular chelating ligand have been found to be crucial to performance [4]. In the case of α -diimine precatalysts (**A**, Figure 1), manipulation of the ligand backbone or the substituents belonging to the *N*-aryl groups allows a means of both tuning the catalyst and the polymer microstructure. For example, the integration of the imine-carbon substituents of the diimine unit into a rigid five-membered ring has seen the development of bis(imino)acenaphthene-type nickel precatalysts (**A**, Figure 1) that have proved highly active for ethylene polymerization [5]. Furthermore, the activity, thermal stability and polymer molecular weight can be improved by installing sterically encumbered benzhydryl (CHPh₂) substituents to the 2,6-positions of the *N*-aryl groups [6]; other bulky substituents have also shown promise [7].

< Figure 1 >

In recent years, our group has also been drawn to the bis(imino)acenaphthene family of nickel precatalysts, and in particular the unsymmetrical variation in which one *N*-2,6-bis(benzhydryl)-4-*R*-phenyl group is fixed while the other *N*-aryl group can be interchanged (**B**, Figure 1). Indeed, by varying the steric and electronic profile of the second *N*-aryl group, some degree of modulation of the activity and the properties of the polymers can be achieved; changes to the *para*-*R* substituent (*R* = Me, F, *t*-Bu) have also been shown to be influential [6b]. As an extension to this approach, we have also developed unsymmetrical precatalysts that contain one *N*-2,6-(bis(4,4'-difluorobenzhydryl)-4-*R*-phenyl group (**C**, Figure 1), and have noted distinct variations in performance in terms of activity and thermal stability of the catalyst. For example, difluorobenzhydryl-containing **C** (Figure 1), was found to display superior productivity for ethylene polymerization at 70 °C when compared to its non-fluorinated counterpart **B** at the same

temperature (Figure 1) [7].

In this work we again focus on unsymmetrical bis(imino)acenaphthene-nickel precatalysts for ethylene polymerization that, in this case, contain one *N*-2,6-bis(4,4'-dimethoxybenzhydryl)-4-methylphenyl group (**D**, Figure 1). A study is then conducted using ten examples of **D**, differing in the substitution pattern of the second *N*-aryl group and the halide ligand, to ascertain how precatalyst structure, type/amount of co-catalyst and temperature, affect catalytic activity and in particular the branching and molecular weight of the polymer. In addition, selected branched samples will be the subject of an investigation of their mechanical properties (*e.g.*, tensile stress-strain and elastic recovery tests). Details of the synthesis and characterization of all new compounds are also reported.

Experimental section

General considerations

All operations involving air and/or moisture sensitive compounds were performed under an atmosphere of nitrogen using standard Schlenk techniques. Solvents were distilled under nitrogen from appropriate drying agents prior to use. Modified methylaluminoxane (MMAO, 1.93 M in heptane) and methylaluminoxane (MAO, 1.46 M in toluene) were purchased from Akzo Nobel Corporation. Diethylaluminum chloride (Et_2AlCl , 1.17 M in toluene) and dimethylaluminum chloride (EASC, 0.87 M in toluene) were supplied from Acros Chemical. High purity ethylene was purchased from Beijing Yanshan Petrochemical Company and used as received. Other reagents were purchased from Aldrich, Acros or local suppliers. The compound 2,6-bis(4,4'-dimethoxybenzhydryl)-4-methylaniline was prepared using a procedure based on a literature route [8]. The ^1H and ^{13}C NMR spectroscopic measurements for the ligands, precursors as well as the nickel complexes were performed on a Bruker DMX 400 MHz and Bruker DMX 300 MHz instrument at room temperature. Chemical shifts are measured in ppm for the ^1H and ^{13}C NMR spectra and are relative to TMS as an internal standard. Coupling constants (*J* values) are given in Hz. FT-IR spectra were carried out using a PerkinElmer System 2000 FT-IR spectrometer. Elemental analyses were conducted on a Flash EA 1112 microanalyzer. The molecular weights (M_w) and molecular weight distributions (M_w/M_n) of the polyethylenes were determined using a PL-GPC220 instrument at 150 °C with 1,2,4-trichlorobenzene as the solvent. The melting

temperatures of the polyethylenes were measured from the second scanning run on a Perkin-Elmer TA-Q2000 DSC analyzer under a nitrogen atmosphere. In the procedure, a sample of about 4.0–6.0 mg was heated to 160 °C at a heating rate of 20 °C min⁻¹ and maintained for 5 min at 160 °C to remove the thermal history and then cooled at a rate of 20 °C min⁻¹ to –20 °C. For the ¹³C NMR spectra of the polyethylenes, a weighed amount of polyethylene (80 – 100 mg) was combined with 1,1,2,2-tetrachloroethane-*d*₂ (2 mL) with TMS as an internal standard. Inverse gated ¹³C spectra recorded on a Bruker DMX 300 spectrometer at 75.47 MHz in 5 mm standard glass tubes at 100 °C with the number of scans between 3000 and 4000. Operating conditions used: spectral width 17.9856 kHz; acquisition time 1.8219 s; relaxation delay 2 s. An estimation of the branching content was made by integration of the corresponding peaks in the ¹³C NMR spectra using approaches described in the literature [9]. The stress–strain curves were obtained using a universal tester (Instron 1122, UK). The stress–strain recovery tests at different temperatures were carried out using a dynamic mechanical analyzer (DMA800, TA) under controlled force mode and performed as described elsewhere.

Synthesis of 1-[2,6-{(4-MeOC₆H₄)₂CH}₂-4-MeC₆H₂N]-2-OC₂C₁₀H₆ (1).

To a mixture of 2,6-bis(4,4'-dimethoxybenzhydryl)-4-methylaniline (8.39 g, 15.0 mmol), acenaphthylen-1,2-dione (2.73 g, 15.0 mmol) and a catalytic amount of *para*-toluene-sulfonic acid (*ca.* 20 mol%) was added dichloromethane (500 mL) and ethanol (50 mL). After stirring for 24 h at room temperature, the resulting solution was concentrated on the rotary evaporator to give the crude product, which was then recrystallized from methanol to give **1** as an orange solid (8.95 g, 83%). Mp: 150 - 152 °C. ¹H NMR (400 MHz, CDCl₃, TMS): δ 8.03 (t, *J* = 7.2 Hz, 2H, Ph-H), 7.71 (t, *J* = 9.0 Hz, 2H, Ph-H), 6.96 (d, *J* = 8.4 Hz, 4H, Ph-H), 6.75 (m, 12H, Ph-H), 6.07 (d, *J* = 8.4 Hz, 4H, Ph-H), 5.30 (s, 2H, 2 × CH), 3.76 (s, 6H, 2 × OCH₃), 3.25 (s, 6H, 2 × OCH₃), 2.26 (s, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃, TMS): δ 190.0 (C=O), 162.5 (C=N), 157.5, 145.9, 142.4, 135.6, 134.4, 133.2, 132.2, 131.8, 130.4, 129.9, 128.3, 128.1, 127.6, 126.8, 121.5, 113.4, 55.0, 50.8, 21.6. FT-IR (KBr, cm⁻¹): 2952 (w), 2832 (w), 1721 (ν_{C=O}, s), 1653 (ν_{C=N}, m), 1604 (m), 1507 (s), 1457 (s), 1341 (w), 1301 (m), 1242 (s), 1173 (s), 1112 (w), 1032 (s), 909 (m), 831 (s), 778 (m), 731 (w).

Syntheses of 1-[2,6-{(4-MeOC₆H₄)₂CH}₂-4-MeC₆H₂N]-2-(ArN)C₂C₁₀H₆

(a) Ar = 2,6-Me₂C₆H₃ (**L1**). To a mixture of 2-(2,6-bis(4,4'-dimethoxydibenzyl)-4-methylphenylimino)acenaphthylen-1-one (1.80 g, 2.50 mmol), 2,6-dimethylaniline (0.33 g, 2.75 mmol) and a catalytic amount of *para*-toluene-sulfonic acid (*ca.* 20 mol%) was added dry toluene (100 mL). The reaction mixture was stirred and heated to reflux for 5 h. After cooling to room temperature, the solvent was removed under reduced pressure and the residue purified by alumina column chromatography using petroleum ether–ethyl acetate (v/v = 50:1) as the eluent affording **L1** as an orange crystalline solid (0.23 g, 11%). Mp: 248 - 250 °C. ¹H NMR (400 MHz, CDCl₃, TMS): δ 7.72 (d, *J* = 8.4 Hz, 1H, Ph–H), 7.58 (d, *J* = 8.3 Hz, 1H, Ph–H), 7.17 (d, *J* = 7.4 Hz, 2H, Ph–H), 7.10–6.96 (m, 6H, Ph–H), 6.83–6.75 (m, 11H, Ph–H), 6.54 (d, *J* = 7.1 Hz, 1H, Ph–H), 6.05 (d, *J* = 8.4 Hz, 4H, Ph–H), 5.94 (d, *J* = 7.1 Hz, 1H, Ph–H), 5.49 (s, 2H, 2 × CH), 3.77 (s, 6H, 2 × OCH₃), 3.21 (s, 6H, 2 × OCH₃), 2.27 (s, 3H, CH₃), 2.23 (s, 6H, 2 × CH₃). ¹³C NMR (100 MHz, CDCl₃, TMS): δ 161.5 (C=N), 157.8 (C=N), 156.9, 149.3, 146.6, 135.8, 134.4, 132.6, 130.8, 130.4, 129.8, 128.9, 128.5, 128.3, 128.2, 127.4, 126.9, 124.7, 124.3, 123.6, 121.6, 113.4, 113.1, 55.2, 54.6, 50.6, 21.5, 18.1. FT-IR (KBr, cm⁻¹): 2925 (w), 2897 (w), 2829 (w), 1670 (ν_{C=N}, m), 1645 (ν_{C=N}, m), 1507 (s), 1445 (m), 1353 (w), 1299 (w), 1280 (w), 1246 (s), 1174 (m), 1106 (m), 1033 (m), 920 (m), 870 (w), 825 (m), 776 (s), 752 (w), 730 (w). Anal. calcd for C₅₇H₅₀N₂O₄ (826.38): C, 82.78; H, 6.09; N, 3.39%. Found: C, 82.42; H, 5.95; N, 3.28%.

(b) Ar = 2,6-Et₂C₆H₃ (**L2**). Using similar experimental steps and molar ratios of reactants as described for **L1**, **L2** was isolated as a yellow solid (0.35g, 16%). Mp: 212 - 214 °C. ¹H NMR (300 MHz, CDCl₃, TMS): δ 7.70 (d, *J* = 5.4 Hz, 1H, Ph-H), 7.54 (d, *J* = 4.8 Hz, 1H, Ph-H), 7.23 (t, *J* = 4.5 Hz, 3H, Ph-H), 7.03 (d, *J* = 8.7 Hz, 4H, Ph-H), 6.93 (t, *J* = 7.8 Hz, 1H, Ph-H), 6.83 - 6.76 (m, 11H, Ph-H), 6.53 (d, *J* = 7.2 Hz, 1H, Ph-H), 6.03 (d, *J* = 8.7 Hz, 4H, Ph-H), 5.85 (d, *J* = 7.2 Hz, 1H, Ph-H), 5.50 (s, 2H, 2 × CH), 3.77 (s, 6H, 2 × OCH₃), 3.20 (s, 6H, 2 × OCH₃), 2.77 - 2.65 (m, 2H, CH₂), 2.61 - 2.48 (m, 2H, CH₂), 2.27 (s, 3H, CH₃), 1.17 (t, *J* = 7.5 Hz, 6H, 2 × CH₃). ¹³C NMR (100 MHz, CDCl₃, TMS): δ 163.6 (C=N), 161.7 (C=N), 157.8, 156.9, 148.4, 146.6, 139.8, 136.0, 134.3, 132.6, 130.7, 130.6, 130.4, 129.7, 128.9, 128.4, 128.3, 128.2, 127.2, 127.1, 126.9, 126.1, 124.4, 124.6, 122.1, 113.4, 113.1, 55.2, 54.6, 53.4, 50.5, 24.4, 21.5, 14.4. FT-IR (KBr, cm⁻¹): 2957 (w), 2904 (w), 2831 (w), 1655 (ν_{C=N}, w), 1631 (ν_{C=N}, w), 1608 (w), 1586 (w), 1507 (s), 1438 (s), 1333 (w), 1330 (w), 1242 (s), 1175 (s), 1109 (w), 1034 (s), 949 (w), 923 (m), 868 (w), 828 (m), 780 (m), 761 (w), 732 (w). Anal. calcd for C₅₉H₅₄N₂O₄ (854.41): C, 82.87; H, 6.37; N, 3.28%. Found: C,

82.55; H, 6.34; N, 3.26%.

(c) Ar = 2,6-*i*-Pr₂C₆H₃ (**L3**). Using similar experimental steps and molar ratios of reactants as described for **L1**, **L3** was isolated as a yellow solid (0.26 g, 12%). Mp: 230 - 232 °C. ¹H NMR (300 MHz, CDCl₃, TMS): δ 7.68 (d, *J* = 8.4 Hz, 1H, Ph-H), 7.51 (d, *J* = 8.8 Hz, 1H, Ph-H), 7.31-7.27 (m, 3H, Ph-H), 7.22 (t, *J* = 7.7 Hz, 1H, Ph-H), 7.03 (d, *J* = 8.6 Hz, 4H, Ph-H), 6.89 (t, *J* = 7.7 Hz, 1H, Ph-H), 6.82 - 6.77 (m, 10H, Ph-H), 6.45 (d, *J* = 7.2 Hz, 1H, Ph-H), 6.01 (d, *J* = 8.5 Hz, 4H, Ph-H), 5.75 (d, *J* = 7.1 Hz, 1H, Ph-H), 5.51 (s, 2H, 2 × CH), 5.30 (s, 2H, 2 × CH), 3.77 (s, 6H, 2 × OCH₃), 3.19 (s, 6H, 2 × OCH₃), 2.28 (s, 3H, CH₃), 1.28 (t, *J* = 6.9 Hz, 6H, 2 × CH₃), 1.03 (d, *J* = 6.9 Hz, 6H, 2 × CH₃). ¹³C NMR (100 MHz, CDCl₃, TMS): δ 157.8 (C=N), 156.9 (C=N), 136.1, 135.7, 134.2, 132.7, 130.7, 130.4, 128.4, 127.1, 123.6, 113.4, 113.2, 55.2, 54.6, 50.5, 28.5, 24.2, 23.7, 21.6. FT-IR (KBr, cm⁻¹): 2951 (m), 2925 (w), 2830 (w), 1669 (ν_{C=N}, w), 1647 (ν_{C=N}, w), 1603 (m), 1588 (w), 1507 (s), 1457 (m), 1439 (w), 1382 (w), 1359 (w), 1328 (w), 1298 (m), 1245 (s), 1176 (s), 1106 (m), 1032 (s), 924 (m), 867 (w), 830 (s), 811 (w), 785 (m), 758 (m), 732 (w). Anal. calcd for C₆₁H₅₈N₂O₄ (882.44): C, 82.96; H, 6.62; N, 3.17%. Found: C, 82.89; H, 6.65; N, 3.13%.

(d) Ar = 2,4,6-Me₃C₆H₂ (**L4**). Using similar experimental steps and molar ratios of reactants as described for **L1**, **L4** was isolated as an orange solid (0.21 g, 10%). Mp: 236 - 238 °C. ¹H NMR (400 MHz, CDCl₃, TMS): δ 7.72 (d, *J* = 8.2 Hz, 1H, Ph-H), 7.58 (d, *J* = 8.2 Hz, 1H, Ph-H), 7.03 - 6.96 (m, 7H, Ph-H), 6.83 - 6.75 (m, 11H, Ph-H), 6.61 (d, *J* = 7.2 Hz, 1H, Ph-H), 6.04 (d, *J* = 8.5 Hz, 4H, Ph-H), 5.93 (d, *J* = 7.2 Hz, 1H, Ph-H), 5.48 (s, 2H, 2 × CH), 3.76 (s, 6H, 2 × OCH₃), 3.20 (s, 6H, 2 × OCH₃), 2.38 (s, 3H, CH₃), 2.26 (s, 3H, CH₃), 2.19 (s, 6H, 2 × CH₃). ¹³C NMR (100 MHz, CDCl₃, TMS): δ 161.6 (C=N), 157.8 (C=N), 135.8, 134.4, 132.6, 130.7, 130.4, 129.0, 124.5, 121.6, 113.4, 113.0, 55.2, 54.6, 53.4, 50.6, 18.1. FT-IR (KBr, cm⁻¹): 2950 (w), 2903 (w), 2830 (w), 1666 (ν_{C=N}, m), 1642 (ν_{C=N}, m), 1605 (m), 1507 (s), 1448 (m), 1298 (w), 1281 (w), 1245 (s), 1174 (m), 1108 (w), 1034 (m), 920 (w), 830 (m), 778 (m), 733 (w). Anal. calcd for C₅₈H₅₂N₂O₄ (840.39): C, 82.83; H, 6.23; N, 3.33%. Found: C, 82.55; H, 6.41; N, 3.37%.

(e) Ar = 2,6-Et₂-4-MeC₆H₂ (**L5**). Using similar experimental steps and molar ratios of reactants as described for **L1**, **L5** was isolated as a deep yellow solid (0.28 g, 13%). Mp: 240 - 242 °C. ¹H NMR (400 MHz, CDCl₃, TMS): δ 7.69 (d, *J* = 8.3 Hz, 1H, Ph-H), 7.54 (d, *J* = 8.3 Hz, 1H, Ph-H), 7.02 (d, *J* = 7.6 Hz, 6H, Ph-H), 6.92 (t, *J* = 7.7 Hz, 1H, Ph-H), 6.82-6.76 (m, 11H, Ph-H), 6.59 (d, *J* = 7.1

Hz, 1H, Ph-H), 6.03 (d, $J = 8.5$ Hz, 4H, Ph-H), 5.84 (d, $J = 7.0$ Hz, 1H, Ph-H), 5.50 (s, 2H, $2 \times \text{CH}$), 3.77 (s, 6H, $2 \times \text{OCH}_3$), 3.19 (s, 6H, $2 \times \text{OCH}_3$), 2.70 - 2.61 (m, 2H, CH_2), 2.56 - 2.46 (m, 2H, CH_2), 2.43 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 1.15 (t, $J = 7.5$ Hz, 6H, $2 \times \text{CH}_3$). ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 161.8 (C=N), 157.7 (C=N), 156.9, 139.7, 136.0, 134.3, 132.6, 130.7, 130.5, 130.4, 129.6, 128.2, 126.9, 126.8, 124.3, 122.2, 113.4, 113.1, 55.2, 54.6, 50.5, 24.4, 21.5, 21.2, 14.5. FT-IR (KBr, cm^{-1}): 2931 (w), 2899 (w), 2830 (w), 1665 ($\nu_{\text{C=N}}$, m), 1644 ($\nu_{\text{C=N}}$, m), 1606 (m), 1505 (s), 1455 (m), 1387 (w), 1299 (w), 1241 (s), 1173 (s), 1107 (m), 1033 (s), 920 (w), 831 (m), 807 (w), 778 (m), 757 (w), 680 (m). Anal. calcd for $\text{C}_{60}\text{H}_{56}\text{N}_2\text{O}_4$ (868.42): C, 82.97; H, 6.49; N, 3.22%. Found: C, 82.73; H, 6.61; N, 3.29%.

Syntheses of [1-[2,6- $\{(4\text{-MeOC}_6\text{H}_4)_2\text{CH}\}_2\text{-4-MeC}_6\text{H}_2\text{N}\]$ -2-(ArN) $\text{C}_2\text{C}_{10}\text{H}_6$]NiBr₂

(a) Ar = 2,6-Me₂C₆H₃ (**Ni1**). To a mixture of **L1** (0.165 g, 0.20 mmol) and (DME)NiBr₂ (0.062 g, 0.20 mmol) was added dichloromethane and ethanol (20/5 mL). The reaction mixture was stirred for 24 h at ambient temperature and excess diethyl ether added to precipitate the product. The precipitate was collected by filtration, washed with diethyl ether (3×10 mL) and then dried under reduced pressure to give **Ni1** as a deep red solid (0.201 g, 95%). ^1H NMR (400 MHz, CDCl_3 , TMS): -16.14 (s, 1H, Ar-H_p), 2.71 (s, 6H, -OCH₃), 3.66 (s, 6H, -OCH₃), 4.98 (s, 1H, An-H), 5.20 (s, 5H, Ar-H), 6.05 (s, 1H, An-H), 6.82 (s, 6H, Ar-H), 8.07 (s, 5H, Ar-H), 12.70 (broad, 1.56H, Ar-CH(Ph)₂), 15.87 (s, 1H, An-H), 16.80 (s, 1H, An-H), 20.39 (s, 1H, An-H), 22.50 (s, 2H, Ar-H), 24.64 (s, 1H, An-H), 25.48 (s, 2H, Ar-H), 28.62 (s, 6H, $2 \times \text{CH}_3$), 33.98 (s, 3H, CH_3). FT-IR (KBr, cm^{-1}): 2952 (w), 2905 (w), 2834 (w), 1646 ($\nu_{\text{C=N}}$, w), 1609 ($\nu_{\text{C=N}}$, m), 1583 (w), 1509 (s), 1463 (w), 1444 (w), 1424 (w), 1299 (m), 1262 (s), 1255 (s), 1246 (s), 1199 (w), 1179 (s), 1111 (w), 1034 (m), 867 (w), 831 (s), 775 (m), 732 (w). Anal. calcd for $\text{C}_{57}\text{H}_{50}\text{Br}_2\text{N}_2\text{O}_4\text{Ni}$ (1042.15): C, 65.48; H, 4.82; N, 2.68. Found: C, 65.14; H, 4.81; N, 2.67%.

(b) Ar = 2,6-Et₂C₆H₃ (**Ni2**). **Ni2** was prepared using similar experimental steps and molar ratios to that described for **Ni1** affording a deep red solid (0.208 g, 97%). ^1H NMR (400 MHz, CDCl_3 , TMS): -16.00 (s, 1H, Ar-H_p), 0.75 (s, 6H, $2 \times \text{CH}_3$), 2.74 (s, 6H, -OCH₃), 3.65 (s, 6H, -OCH₃), 4.98 (s, 1H, An-H), 5.25 (s, 5H, Ar-H), 6.03 (s, 1H, An-H), 6.81 (s, 6H, Ar-H), 8.06 (s, 5H, Ar-H), 12.63 (broad, 1.45H, Ar-CH(Ph)₂), 15.94 (s, 1H, An-H), 16.82 (s, 1H, An-H), 20.49 (s, 1H, An-H), 22.64

(s, 2H, Ar-H), 24.87 (s, 1H, An-H), 25.32 (s, 2H, Ar-H), 26.77 (s, 2H, CH₂), 28.05 (s, 2H, CH₂), 34.23 (s, 3H, CH₃). FT-IR (KBr, cm⁻¹): 2964 (w), 2931 (w), 2834 (w), 1647 (ν_{C=N}, m), 1606 (ν_{C=N}, m), 1582 (m), 1508 (s), 1459 (m), 1298 (m), 1246 (s), 1177 (s), 1112 (m), 1032 (s), 958 (m), 832 (s), 777 (s), 734 (m). Anal. calcd for C₅₉H₅₄Br₂N₂O₄Ni (1070.18): C, 66.01; H, 5.07; N, 2.61. Found: C, 65.83; H, 5.10 N, 2.63%.

(c) Ar = 2,6-*i*-Pr₂C₆H₃ (**Ni3**). **Ni3** was prepared using similar experimental steps and molar ratios to that described for **Ni1** affording a deep red solid (0.210 g, 96%). ¹H NMR (400 MHz, CDCl₃, TMS): -15.46 (s, 1H, Ar-H_p), 1.75 (s, 12H, 4 × CH₃), 2.74 (s, 6H, -OCH₃), 3.62 (s, 6H, -OCH₃), 4.52 (broad, 1.76H, Ar-CH(Me)₂), 5.01 (s, 1H, An-H), 5.38 (s, 5H, Ar-H), 5.70 (s, 1H, An-H), 6.75 (s, 6H, Ar-H), 7.97 (s, 5H, Ar-H), 13.34 (broad, 1.63H, Ar-CH(Ph)₂), 16.07 (s, 1H, An-H), 17.24 (s, 1H, An-H), 21.21 (s, 1H, An-H), 23.07 (s, 2H, Ar-H), 24.89 (s, 2H, Ar-H), 25.18 (s, 1H, An-H), 34.85 (s, 3H, CH₃). FT-IR (KBr, cm⁻¹): 2961 (w), 2832 (w), 1648 (ν_{C=N}, m), 1606 (ν_{C=N}, m), 1582 (m), 1508 (s), 1459 (m), 1296 (m), 1246 (s), 1177 (s), 1109 (m), 1033 (s), 829 (s), 777 (s), 733 (m). Anal. calcd for C₆₁H₅₈Br₂N₂O₄Ni (1098.21): C, 66.51; H, 5.31; N, 2.54. Found: C, 66.52; H, 5.31; N, 2.63%.

(d) Ar = 2,4,6-Me₃C₆H₂ (**Ni4**). **Ni4** was prepared using similar experimental steps and molar ratios to that described for **Ni1** affording a deep red solid (0.199 g, 94%). ¹H NMR (400 MHz, CDCl₃, TMS): 2.71 (s, 6H, -OCH₃), 3.67 (s, 6H, -OCH₃), 4.91 (s, 1H, An-H), 5.18 (s, 5H, Ar-H), 6.13 (s, 1H, An-H), 6.83 (s, 6H, Ar-H), 8.09 (s, 5H, Ar-H), 12.42 (broad, 1.57H, Ar-CH(Ph)₂), 15.87 (s, 1H, An-H), 16.76 (s, 1H, An-H), 20.21 (s, 1H, An-H), 22.51 (s, 2H, Ar-H), 25.25 (s, 1H, An-H), 25.25 (s, 2H, Ar-H), 28.72 (s, 6H, 2×CH₃), 33.76 (s, 3H, CH₃), 34.08 (s, 3H, CH₃). FT-IR (KBr, cm⁻¹): 2924 (w), 2834 (w), 1649 (ν_{C=N}, m), 1605 (ν_{C=N}, m), 1582 (m), 1509 (s), 1459 (m), 1299 (m), 1252 (s), 1178 (s), 1112 (m), 1032 (s), 960 (m), 831 (s), 775 (s), 735 (m). Anal. calcd for C₅₈H₅₂Br₂N₂O₄Ni (1056.16): C, 65.75; H, 4.95; N, 2.64. Found: C, 65.58; H, 4.96; N, 2.66%.

(e) Ar = 2,6-Et₂-4-MeC₆H₂ (**Ni5**). **Ni5** was prepared using similar experimental steps and molar ratios to that described for **Ni1** affording a deep red solid (0.213 g, 98%). ¹H NMR (400 MHz, CDCl₃, TMS): 0.80 (s, 6H, 2CH₃), 2.74 (s, 6H, -OCH₃), 3.66 (s, 6H, -OCH₃), 4.93 (s, 1H, An-H), 5.25 (s, 5H, Ar-H), 6.12 (s, 1H, An-H), 6.83 (s, 6H, Ar-H), 8.09 (s, 5H, Ar-H), 12.27 (broad, 1.45H, Ar-CH(Ph)₂), 15.93 (s, 1H, An-H), 16.77 (s, 1H, An-H), 20.28 (s, 1H, An-H), 22.58 (s, 2H, Ar-H),

25.00 (s, 2H, Ar-H), 25.40 (s, 1H, An-H), 26.84 (s, 2H, CH₂), 27.78 (s, 2H, CH₂), 33.76 (s, 3H, CH₃), 34.19 (s, 3H, CH₃). FT-IR (KBr, cm⁻¹): 2967 (w), 2900 (w), 2831 (w), 1647 (ν_{C=N}, m), 1606 (ν_{C=N}, m), 1582 (m), 1509 (s), 1459 (m), 1299 (m), 1251 (s), 1179 (s), 1110 (m), 1034 (s), 956 (m), 827 (s), 772 (s), 733 (m). Anal. calcd for C₆₀H₅₆Br₂N₂O₄Ni (1084.20): C, 66.26; H, 5.19; N, 2.58. Found: C, 65.89; H, 5.19; N, 2.65%.

Syntheses of [1-[2,6- $\{$ (4-MeOC₆H₄)₂CH₂ $\}_2$ -4-MeC₆H₂N]-2-(ArN)C₂C₁₀H₆]NiCl₂

(a) Ar = 2,6-Me₂C₆H₃ (**Ni6**). To a mixture of **L1** (0.165 g, 0.20 mmol) and NiCl₂·6H₂O (0.047 g, 0.20 mmol) was added dichloromethane and ethanol (20/5 mL). The reaction mixture was stirred for 24 h at ambient temperature and excess diethyl ether added to precipitate the product. The precipitate was collected by filtration, washed with diethyl ether (3 × 10 mL) and then dried under reduced pressure to give **Ni6** as a brown solid (0.177 g, 93%). ¹H NMR (400 MHz, CDCl₃, TMS): -14.22 (s, 1H, Ar-H_p), 2.48 (s, 6H, -OCH₃), 3.60 (s, 6H, -OCH₃), 4.76 (s, 5H, Ar-H), 5.30 (s, 1H, An-H), 5.93 (s, 1H, An-H), 6.75 (s, 6H, Ar-H), 8.15 (s, 5H, Ar-H), 10.99 (broad, 1.34H, Ar-CH(Ph)₂), 15.68 (s, 1H, An-H), 16.57 (s, 1H, An-H), 20.80 (s, 1H, An-H), 23.65 (s, 2H, Ar-H), 24.62 (s, 1H, An-H), 26.29 (s, 2H, Ar-H), 26.68 (s, 6H, 2 × CH₃), 34.18 (s, 3H, CH₃). FT-IR (KBr, cm⁻¹): 2932 (w), 2835 (w), 1651 (ν_{C=N}, m), 1605 (ν_{C=N}, m), 1585 (m), 1509 (s), 1463 (m), 1382 (w), 1352 (w), 1298 (m), 1255 (w), 1246 (m), 1176 (s), 1112 (m), 1031 (s), 958 (w), 868 (w), 831 (s), 776 (s), 734 (m). Anal. calcd for C₅₇H₅₀Cl₂N₂O₄Ni (954.25): C, 71.57; H, 5.27; N, 2.93. Found: C, 71.18; H, 5.20; N, 2.93%.

(b) Ar = 2,6-Et₂C₆H₃ (**Ni7**). **Ni7** was prepared using similar experimental steps and molar ratios to that described for **Ni6** affording a brown solid (0.130 g, 66%). ¹H NMR (400 MHz, CDCl₃, TMS): -13.93 (s, 1H, Ar-H_p), 0.50 (s, 6H, 2 × CH₃), 2.50 (s, 6H, -OCH₃), 3.58 (s, 6H, -OCH₃), 4.81 (s, 5H, Ar-H), 5.02 (s, 1H, An-H), 5.29 (s, 1H, An-H), 6.79 (s, 6H, Ar-H), 8.14 (s, 5H, Ar-H), 11.29 (broad, 1.76H, Ar-CH(Ph)₂), 15.73 (s, 1H, An-H), 16.55 (s, 1H, An-H), 21.08 (s, 1H, An-H), 23.63 (s, 2H, CH₂), 23.89 (s, 2H, Ar-H), 24.65 (s, 1H, An-H), 25.70 (s, 2H, CH₂), 26.12 (s, 2H, Ar-H), 34.48 (s, 3H, CH₃). FT-IR (KBr, cm⁻¹): 2931 (w), 2834 (w), 1649 (ν_{C=N}, m), 1606 (ν_{C=N}, m), 1584 (m), 1509 (s), 1460 (m), 1338 (w), 1296 (m), 1248 (s), 1176 (s), 1132 (w), 1110 (w), 1030 (s), 956 (w), 869 (w), 829 (s), 812 (w), 776 (s), 730 (m). Anal. calcd for C₅₉H₅₄Cl₂N₂O₄Ni (982.28): C,

71.97; H, 5.53; N, 2.84. Found: C, 71.64; H, 5.42; N, 2.78%.

(c) Ar = 2,6-*i*-Pr₂C₆H₃ (**Ni8**). **Ni8** was prepared using similar experimental steps and molar ratios to that described for **Ni6** affording a dark orange solid (0.164 g, 81%). ¹H NMR (400 MHz, CDCl₃, TMS): -13.45 (s, 1H, Ar-H_p), 1.28 (s, 12H, 4 × CH₃), 2.47 (s, 6H, -OCH₃), 3.55 (s, 6H, -OCH₃), 4.89 (s, 5H, Ar-H), 5.04 (s, 1H, An-H), 5.76 (s, 1H, An-H), 6.67 (s, 6H, Ar-H), 8.04 (s, 5H, Ar-H), 11.70 (broad, 1.66H, Ar-CH(Ph)₂), 15.86 (s, 1H, An-H), 16.95 (s, 1H, An-H), 21.75 (s, 1H, An-H), 24.39 (s, 2H, Ar-H), 25.14 (s, 1H, An-H), 25.94 (s, 2H, Ar-H), 35.22 (s, 3H, CH₃). FT-IR (KBr, cm⁻¹): 2962 (w), 2833 (w), 1651 (ν_{C=N}, m), 1606 (ν_{C=N}, m), 1585 (m), 1509 (s), 1460 (m), 1386 (w), 1358 (w), 1297 (m), 1247 (s), 1177 (s), 1131 (w), 1110 (w), 1034 (s), 957 (w), 934 (w), 870 (w), 830 (s), 812 (w), 777 (s), 759 (w), 731 (w). Anal. calcd for C₆₁H₅₈Cl₂N₂O₄Ni (1010.31): C, 72.35; H, 5.77; N, 2.77. Found: C, 71.97; H, 5.76; N, 2.76%.

(d) Ar = 2,4,6-Me₃C₆H₂ (**Ni9**). **Ni9** was prepared using similar experimental steps and molar ratios to that described for **Ni6** affording a light orange solid (0.167 g, 86%). ¹H NMR (400 MHz, CDCl₃, TMS): 2.47 (s, 6H, -OCH₃), 3.61 (s, 6H, -OCH₃), 4.91 (s, 5H, Ar-H), 5.30 (s, 1H, An-H), 5.99 (s, 1H, An-H), 6.76 (s, 6H, Ar-H), 8.20 (s, 5H, Ar-H), 10.94 (broad, 1.33H, Ar-CH(Ph)₂), 15.69 (s, 1H, An-H), 16.54 (s, 1H, An-H), 20.63 (s, 1H, An-H), 23.65 (s, 2H, Ar-H), 25.12 (s, 1H, An-H), 26.04 (s, 2H, Ar-H), 26.79 (s, 6H, 2 × CH₃), 33.74 (s, 3H, CH₃), 34.22 (s, 3H, CH₃). FT-IR (KBr, cm⁻¹): 2925 (w), 2832 (w), 1647 (ν_{C=N}, m), 1605 (ν_{C=N}, m), 1584 (m), 1509 (s), 1448 (m), 1383 (w), 1354 (w), 1299 (m), 1243 (s), 1174 (s), 1110 (m), 1028 (s), 960 (w), 830 (s), 771 (s), 735 (m). Anal. calcd for C₅₈H₅₂Cl₂N₂O₄Ni (968.27): C, 71.77; H, 5.40; N, 2.89. Found: C, 71.44; H, 5.45; N, 2.86%.

(e) Ar = 2,6-Et₂-4-MeC₆H₂ (**Ni10**). **Ni10** was prepared using similar experimental steps and molar ratios to that described for **Ni6** affording a light orange solid (0.151 g, 76%). ¹H NMR (400 MHz, CDCl₃, TMS): 0.55 (s, 6H, 2 × CH₃), 2.50 (s, 6H, -OCH₃), 3.58 (s, 6H, -OCH₃), 4.80 (s, 5H, Ar-H), 4.95 (s, 1H, An-H), 5.52 (s, 1H, An-H), 6.73 (s, 6H, Ar-H), 8.15 (s, 5H, Ar-H), 10.93 (broad, 1.33H, Ar-CH(Ph)₂), 15.72 (s, 1H, An-H), 16.48 (s, 1H, An-H), 20.85 (s, 1H, An-H), 23.63 (s, 2H, CH₂), 23.79 (s, 2H, Ar-H), 25.13 (s, 1H, An-H), 25.46 (s, 2H, CH₂), 25.79 (s, 2H, Ar-H), 33.64 (s, 3H, CH₃), 34.38 (s, 3H, CH₃). FT-IR (KBr, cm⁻¹): 2931 (w), 2831 (w), 1649 (ν_{C=N}, m), 1605 (ν_{C=N}, m), 1583 (m), 1508 (s), 1457 (m), 1297 (m), 1242 (s), 1176 (s), 1110 (w), 1031 (s), 954 (w), 866

(w), 827 (s), 772 (s), 731 (w). Anal. calcd for C₆₀H₅₆Cl₂N₂O₄Ni (996.30): C, 72.16; H, 5.65; N, 2.81. Found: C, 71.83; H, 5.74; N, 2.87%.

X-ray crystallographic studies

The single crystal X-ray determinations of **Ni1**, **Ni3**, **Ni5** and **Ni6** were carried out on a Rigaku Saturn 724⁺ CCD with graphite-monochromatic Mo-K α radiation ($\lambda = 0.71073$ Å) at 173(2) K and their 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 Olex2 1.2 package. Details of the crystal data and structure refinements for **Ni1**, **Ni3**, **Ni5** and **Ni6** are shown in Table S3.

Typical procedure for ethylene polymerization

The polymerization at 10 atm ethylene pressure was carried out in a stainless steel autoclave (0.25 L) equipped with an ethylene pressure control system, a mechanical stirrer and a temperature controller. At the required reaction temperature, freshly distilled toluene (30 mL) was injected into the autoclave, followed by the complex (2.0 μ mol) dissolved in toluene (50 mL). The required amount of co-catalyst (MAO, MMAO, Et₂AlCl or EASC) and more toluene (20 mL) were then injected successively to take the total volume of solvent to 100 mL. The autoclave was immediately pressurized to 10 atm and the stirring commenced. After the required reaction time, the ethylene pressure was released and the polymer was collected and washed with ethanol. Following drying under reduced pressure at 50 °C, the polymer sample was weighed.

Results and discussion

Synthesis and Characterization

The free bis(arylimino)acenaphthenes, 1-[2,6-{(4-MeOC₆H₄)₂CH}₂-4-MeC₆H₂N]-2-(ArN)C₂C₁₀H₆ (Ar = 2,6-Me₂C₆H₃ **L1**, 2,6-Et₂C₆H₃ **L2**, 2,6-*i*-Pr₂C₆H₃ **L3**, 2,4,6-Me₃C₆H₂ **L4**, 2,6-Et₂-4-MeC₆H₂ **L5**), have been prepared in moderate yield by treating 2-(2,6-bis(4,4'-dimethoxydibenzyl)-4-methylphenylimino)acenaphthylen-1-one (**1**) with the

corresponding aniline in toluene at reflux (Scheme 1). Imine-ketone **1** is novel and could be readily prepared in good yield by the Schiff base condensation reaction of acenaphthylene-1,2-dione with one equivalent of 2,6-bis(4,4'-dimethoxybenzhydryl)-4-methylaniline at room temperature. Compounds **1** and **L1** – **L5** have been characterized by ^1H , ^{13}C NMR and FT-IR spectroscopy as well as by elemental analysis.

Reaction of **L1** – **L5** with either (DME)NiBr₂ (DME = 1,2-dimethoxyethane) in dichloromethane or NiCl₂·6H₂O in a mixture of dichloromethane and ethanol at room temperature afforded the corresponding nickel complexes [1-[2,6-{(4-MeOC₆H₄)₂CH}₂-4-MeC₆H₂N]-2-(ArN)C₂C₁₀H₆]NiBr₂ (Ar = 2,6-Me₂C₆H₃ **Ni1**, 2,6-Et₂C₆H₃ **Ni2**, 2,6-*i*-Pr₂C₆H₃ **Ni3**, 2,4,6-Me₃C₆H₂ **Ni4**, 2,6-Et₂-4-MeC₆H₂ **Ni5**) and [1-[2,6-{(4-MeOC₆H₄)₂CH}₂-4-MeC₆H₂N]-2-(ArN)C₂C₁₀H₆]NiCl₂ Ar = 2,6-Me₂C₆H₃ **Ni6**, 2,6-Et₂C₆H₃ **Ni7**, 2,6-*i*-Pr₂C₆H₃ **Ni8**, 2,4,6-Me₃C₆H₂ **Ni9**, 2,6-Et₂-4-MeC₆H₂ **Ni10**), in good yield (66 – 98%), respectively (Scheme 1). FT-IR and ^1H NMR spectroscopy as well as elemental analysis have been used to characterize **Ni1** – **Ni10**, while crystals of **Ni1**, **Ni3**, **Ni5** and **Ni6** have been used for single crystal X-ray diffraction studies.

< Scheme 1 >

Single crystals of **Ni1**, **Ni3**, **Ni5** and **Ni6** suitable for the X-ray determinations were grown by slow diffusion of diethyl ether into their dichloromethane solutions. Views of each structure are shown in Figures 1 – 4; selected bond lengths and angles for all four are compiled in Table 1. The structures are similar and will be discussed together. Each comprises a nickel center bound by two halides ligands [Br (**Ni1**, **Ni3** and **Ni5**); Cl (**Ni6**)] and two nitrogen donors belonging to the *N,N*-chelating bis(imino)acenaphthene (**L1** for **Ni1** and **Ni6**, **L3** for **Ni3** and **L5** for **Ni5**) so as to form a distorted tetrahedral geometry. The N(1)–Ni(1)–N(2) bite angles in each complex are comparable at 83.04(12)° (**Ni1**), 82.88(8)° (**Ni3**), 82.95(9)° (**Ni5**) and 82.74(9)° (**Ni6**) and highlight the distortion imposed by the *N,N*-chelating ligand on the geometry. The consequence is that the X(1)–Ni(1)–X(2) angles are more open at 119.93(3)° (**Ni1**), 121.29(3)° (**Ni3**), 120.90(2)° (**Ni5**) and 121.87(4)° (**Ni6**). There is some modest variation in the nickel–nitrogen bond lengths in each complex with the N(1)–Ni(1) distances [2.034(3) Å (**Ni1**), 2.036(2) Å (**Ni3**), 2.038(2) Å (**Ni5**), 2.041(2) Å (**Ni6**)] longer than those involving N(2)–Ni(1) [2.016(3) Å (**Ni1**), 2.013(2) Å (**Ni3**), 2.014(2) Å (**Ni5**), 2.020(2) Å (**Ni6**)], in line with the more bulky

2,6-bis(4,4'-dimethoxydibenzyl)-4-methylphenyl group located on N(1). Related nickel(II) halide structures containing unsymmetrical 1,2-bis(imino)acenaphthenes have been previously reported and indeed the structural features of **Ni1**, **Ni3**, **Ni5** and **Ni6** compare favorably [10].

< Table 1 >

< Figure 2 >

< Figure 3 >

< Figure 4 >

< Figure 5 >

The ^1H NMR spectra of these Ni(II) ($S = 1$) complexes display broad paramagnetically shifted peaks that can be assigned through a comparison with data for related species [4a], relative integration and closeness to the paramagnetic center (Figures S1 – S10). Using **Ni1** as an example, the acenaphthene protons can be identified as six distinct signals between δ 4.96 and 24.45 reflecting the presence of the two inequivalent *N*-aryl groups. A broad 2H-peak around δ 12.8 was assigned to the $\text{CH}(\text{4-MeOC}_6\text{H}_4)_2$ protons, while the single *para*-aryl proton can be seen upfield at δ -16.0. On the other hand, two resonances are seen for the protons of each methoxy methyl group which is consistent with some restricted C_{ortho} -aryl rotation leading to inequivalent $\text{CH}(\text{4-OMeC}_6\text{H}_4)_a(\text{4-OMeC}_6\text{H}_4)_b$ groups. In the IR spectra of **Ni1** – **Ni10**, two distinct $\nu(\text{C}=\text{N})_{\text{imine}}$ stretching vibrations are visible in the range $1605 - 1651\text{ cm}^{-1}$ which are viewable at lower wavenumber than that seen in the corresponding free ligand which is as expected following metal coordination.

Catalytic evaluation for ethylene polymerization

(a) *Co-catalyst screen*. Four types of alkylaluminum activator were initially assessed namely, ethylaluminum sesquichloride ($\text{Et}_3\text{Al}_2\text{Cl}_3$, EASC), methylaluminoxane (MAO), modified methylaluminoxane (MMAO) and diethylaluminum chloride (Et_2AlCl), with **Ni1** selected as the test precatalyst. Typically, these preliminary runs were performed at $30\text{ }^\circ\text{C}$ in toluene under 10 atm C_2H_4 over a period of 30 minutes; the results are gathered in Table 2 (entries 1 – 4). On examination of the data, the highest activities were achieved using MAO followed by Et_2AlCl , while the results obtained with EASC and MMAO were of a similar but lower level. On the basis of the numerical values of the catalytic activities coupled with their differences in structural composition, subsequent more in-depth studies were conducted using MAO and Et_2AlCl as the co-catalysts.

< Table 2 >

(b) *Catalytic testing of Ni1 – Ni10 with Et₂AlCl as the co-catalyst.* With a view to optimizing the catalytic conditions, **Ni1** was again employed as the test precatalyst and the molar ratio of Al:Ni, run temperature and reaction time were each studied with Et₂AlCl as the co-catalyst; the results are compiled in Table 3.

< Table 3 >

Firstly, with the temperature maintained at 30 °C, the Al:Ni molar ratio was progressively increased from 400 to 900 (entries 1 - 6, Table 3), resulting in 700 being identified as the optimum ratio with the catalytic activity of **Ni1**/Et₂AlCl reaching a maximum of 9.32×10^6 g PE mol⁻¹ (Ni) h⁻¹. Above 700 equivalents, the activity was found to show only a modest fall (entries 5 and 6, Table 3). On the other hand, the molecular weights of the resultant polyethylenes revealed no clear trend on increasing the molar ratio.

Secondly, to examine the stability of **Ni1**/Et₂AlCl towards changes in temperature, the polymerizations runs were conducted over increments of 10 °C between 20 and 60 °C with the Al:Ni ratio fixed at 700 (entries 4, 7 - 10, Table 3). The topmost activity of 9.32×10^6 g PE mol⁻¹ (Ni) h⁻¹ was observed at 30 °C (entry 4, Table 3) while higher temperatures led to a steady decrease reaching its lowest value of 3.75×10^6 g PE mol⁻¹ (Ni) h⁻¹ at 60 °C (entry 10, Table 4). This drop in activity with temperature can be attributed to a combination of partial deactivation of the active species at higher temperature and lower solubility of the ethylene monomer in toluene at these temperatures ^[11]. Furthermore, as the temperature was raised, the molecular weight of the polymers was found to reduce which can be ascribed to an increased rate of chain termination with respect to chain propagation at higher temperatures (Figure 5). In addition, the melt temperatures (*T_m*) of the polymers were found to gradually fall on increasing the reaction temperature (*T_m*: 94.9 to 17.3 °C) with the materials generated during the runs performed at 60 °C adopting waxy-like compositions. These findings are consistent with the gradual loss of crystallinity due to increased branching as the temperature was raised (*vide infra*).

< Figure 6 >

Thirdly, the effect of run time on the performance of **Ni1**/Et₂AlCl at 30 °C was explored by conducting separate polymerizations over 5, 15, 30, 45 and 60 minutes with the Al:Ni molar ratio in

each case fixed at 700 (entries 11 – 15, Table 3). The results reveal that the highest activity of 11.86×10^6 g PE mol⁻¹ (Ni) h⁻¹ was observed after 5 minutes (entry 11, Table 3) indicating that the induction period required to fully generate the active species was relatively short and then slow deactivation ensued. Nonetheless, **Ni1**/Et₂AlCl still maintained a good level even after one hour [5.06×10^6 g PE mol⁻¹ (Ni) h⁻¹], highlighting the good catalytic lifetime displayed by the active species (entry 15, Table 3). Conversely, no clear trend regarding the effect of time on the molecular weight of the polyethylenes could be identified^[12].

Using the optimized conditions established for **Ni1**/Et₂AlCl [Al:Ni ratio = 700, Temp. = 30 °C, run time = 30 minutes], the nine other precatalysts, **Ni2** – **Ni10**, were also screened for the polymerization of ethylene and these data compared with that obtained using **Ni1**; the results are summarized in Table 3 (entries 16 - 24). All the bromide complexes (**Ni1** – **Ni5**) (entries 4, 16 - 19, Table 3) displayed very high activities and afforded high molecular weight polyethylene. In terms of their relative performance, their catalytic activities were found to fall in the order, **Ni4** [2,4,6-tri(Me)] > **Ni1** [2,6-di(Me)] > **Ni5** [2,6-di(Et)-4-Me] > **Ni3** [2,6-di(i-Pr)] > **Ni2** [2,6-di(Et)]. Evidently, both steric and electronic factors are at play with the less sterically demanding precatalysts tending to be the most active; similar trends have been noted elsewhere^[13]. On the other hand, the precatalysts containing a *para*-methyl group (**Ni4**, **Ni5**) are more active than the corresponding ones without it (**Ni1**, **Ni2**), highlighting a positive electronic effect.

Likewise, the catalytic activities of the nickel chlorides (**Ni6** – **Ni10**) were high but generally lower than that seen for the bromides, but nevertheless showed a similar trend: **Ni9** [2,4,6-tri(Me)] > **Ni6** [2,6-di(Me)] > **Ni10** [2,6-di(Et)-4-Me] > **Ni8** [2,6-di(i-Pr)] > **Ni7** [2,6-di(Et)] (entries 20 – 24, Table 3). Indeed, the activities of all the nickel bromide complexes were generally above 5.61×10^6 g PE mol⁻¹ (Ni) h⁻¹, which compares with 3.18×10^6 g PE mol⁻¹ (Ni) h⁻¹ for the chlorides. Similar activity variations between chloride and bromide precatalysts have been observed in other catalytic systems and can be accounted for by differences in the activation process and the nature of the counterion generated^[14]. In common to both bromide and chloride series, the diethyl-substituted precatalysts, **Ni2** and **Ni7**, formed the highest molecular weight polyethylene [12.2×10^5 g mol⁻¹ and 11.1×10^5 g mol⁻¹] and indeed their values fall in the ultra-high molecular weight range. In general, the polyethylenes showed narrow polydispersities [M_w/M_n : < 3.4], an observation that is consistent with single-site behavior for these catalytic systems.

In terms of the melt temperatures (T_m), all the nickel catalysts, **Ni1** – **Ni10**/Et₂AlCl, operating under optimized conditions, generated polymers with T_m 's of less than 82.5 °C (entries 4, 16 – 24, Table 3). Such relatively low values imply that these materials possess significant levels of branching. To confirm this conclusion, a sample of polymer obtained using **Ni1**/Et₂AlCl at 30 °C ($T_m = 61.3$ °C) was subject to a ¹³C NMR spectroscopic study (entry 4, Table 3). The spectrum, recorded in deuterated 1,2-dichlorobenzene at 100 °C, reveals a highly branched polymer with multiple resonances visible in the aliphatic δ 40.0 – 11.0 region (Figure 6). The assignment and the number of branches was calculated using procedures previously reported [9]. Specifically, the analysis revealed that this polymer sample contained 115 branches per 1000 Cs which included methyl (81.2%), ethyl (4.1%), longer chain branches (3.3%) and 1,6-paired methyl branches (7.0%) (Table S1).

< Figure 7 >

(c) *Catalytic testing of **Ni1** – **Ni10** with MAO as the co-catalyst.* Complex **Ni1** was again used as the test precatalyst this time using MAO as the co-catalyst. To facilitate the optimization, the molar ratio of Al:Ni, run time and temperature were all once more systematically examined; the results are tabulated in Table 4.

< Table 4 >

With temperature set at 30 °C, the Al:Ni molar ratio was varied between 1500 and 3000 and the catalytic activity monitored (entries 1 – 6, Table 4). The highest activity of 9.29×10^6 g PE mol⁻¹ (Ni) h⁻¹ using **Ni1**/MAO was achieved with a ratio of 2750 (entry 5, Table 4). Indeed, this level is similar to that observed using **Ni1**/Et₂AlCl under optimized conditions [9.32×10^6 g PE mol⁻¹ (Ni) h⁻¹]. With reference to the molecular weight, a maximum of 11.7×10^5 g mol⁻¹ was obtained with a Al:Ni ratio of 2000 and then steadily lowered with larger amounts of MAO (entries 2 - 6, Table 4).

With regard to the optimal temperature, **Ni1**/MAO exhibited its highest activity of 9.29×10^6 g PE mol⁻¹ (Ni) h⁻¹ at 30 °C (entry 5, Table 4). On raising the temperature to 40 °C the activity dropped by close to half [5.61×10^6 g PE mol⁻¹ (Ni) h⁻¹] (entry 8, Table 4) and then at 50 °C a further drop of half was observed [2.67×10^6 g PE mol⁻¹ (Ni) h⁻¹] (entry 9, Table 4). On the other hand, at 60 °C the activity remained reasonably constant with only a small decrease observable [2.51×10^6 g PE mol⁻¹ (Ni) h⁻¹] (entry 10, Table 4). As was the case with **Ni1**/Et₂AlCl, the

molecular weights of the polymer gradually decreased with a rise in the temperature with the highest M_w of 11.2×10^5 g mol⁻¹ observed at 20 °C and the lowest of 5.7×10^5 g mol⁻¹ at 60 °C (Figure 7) [15]. In general, the polyethylene obtained between 20 and 60 °C exhibited narrow dispersities indicative of well-behaved catalyst (M_w/M_n range: 3.0 – 3.2) (see GPC curves in Figure 7).

< Figure 8 >

To explore the lifetime of these MAO-promoted polymerizations, the runs using **Ni1** were performed at fixed times between 5 and 60 minutes with the temperature maintained at 30 °C and the Al:Ni ratio at 2750. As with **Ni1**/Et₂AlCl, peak activity was noted after a period of 5 minutes (11.9×10^6 g PE mol⁻¹ (Ni) h⁻¹; entry 12, Table 4) after which a gradual drop was observed reaching its lowest value of 5.02×10^6 g PE mol⁻¹ (Ni) h⁻¹ at the one hour mark which compares favorably to that seen with Et₂AlCl after the same time [5.06×10^6 g PE mol⁻¹ (Ni) h⁻¹].

With the optimized conditions established for **Ni1**, *i.e.*, Al:Ni ratio = 2750, Temp. = 30 °C and run time = 30 minutes, **Ni2** – **Ni10** were similarly evaluated with MAO; the data are summarized in Table 3. As with the Et₂AlCl study all the precatalysts display high activities and form high molecular weight polyethylene. Indeed, the molecular weights of the polymers obtained using **Ni1** – **Ni10** fall in similar ranges for each co-catalyst [M_w : 7.2 - 10.9×10^5 g mol⁻¹ (MAO) *vs.* 6.8 - 12.2×10^5 g mol⁻¹ (Et₂AlCl)] as do the catalytic activities [$5.92 - 9.29 \times 10^6$ g PE mol⁻¹ (Ni) h⁻¹ (MAO) *vs.* $3.18 - 9.67 \times 10^6$ g PE mol⁻¹ (Ni) h⁻¹ (Et₂AlCl)].

As to the influence of the precatalyst structure, the activities for the bromides with MAO as co-catalyst fall in the order: **Ni1** [2,6-di(Me)] > **Ni4** [2,4,6-tri(Me)] > **Ni2** [2,6-di(Et)] > **Ni3** [2,6-di(*i*-Pr)] > **Ni5** [2,6-di(Et)-4-Me]. Once again both electronic and steric properties of the chelating ligand are important on influencing productivity with the least bulky precatalysts, **Ni1** and **Ni4**, once more the most active. In contrast to that seen with Et₂AlCl, the presence of the *para*-methyl group has a negative effect on the catalytic activity with **Ni1** [2,6-di(Me)] > **Ni4** [2,4,6-tri(Me)] and **Ni2** [2,6-di(Et)] > **Ni5** [2,6-di(Et)-4-Me]; similar findings have been noted elsewhere [3]. As to the nickel chlorides (**Ni6** – **Ni10**) (entries 19 - 23, Table 4), these displayed comparatively lower activities when compared to the bromides. Nonetheless, they showed a similar but not identical order of activity: **Ni9** [2,4,6-tri(Me)] > **Ni6** [2,6-di(Me)] ~ **Ni10** [2,6-di(Et)-4-Me] > **Ni7** [2,6-di(Et)] > **Ni8** [2,6-di(*i*-Pr)]. Unexpectedly, the presence of the

para-methyl groups in **Ni9** now appears to have had a positive effect on performance when compared to **Ni6**; the origin of this difference is unclear but may be related to solubility. Structure/molecular weight correlations similar to that seen earlier with Et₂AlCl are again evident with the diethyl systems having a tendency to form higher molecular weight polyethylene (*e.g.*, **Ni2**: $M_w = 10.9 \times 10^5 \text{ g mol}^{-1}$).

On comparison of **Ni4** (**D**) with its analogues **B**_{2,4,6-Me2Ph}^[6b] and **C**_{2,4,6-Me2Ph}^[11a] (Figure 1, R = Me), **Ni4** under similar polymerization conditions (MAO as co-catalyst and at 10 atm C₂H₄), displayed higher activity as well as higher molecular weight for the resulting polyethylene. For instance, **C**_{2,4,6-Me2Ph} (Figure 1) bearing a 2,6-bis(bis-(4-fluorophenyl)methyl)-4-methylphenyl group showed an activity of $6.67 \times 10^6 \text{ g PE mol}^{-1} (\text{Ni}) \text{ h}^{-1}$ and gave polyethylene with molecular weight of $4.0 \times 10^5 \text{ g mol}^{-1}$. On the other hand, **Ni4** (**D**) gave an activity of $8.95 \times 10^6 \text{ g PE mol}^{-1} (\text{Ni}) \text{ h}^{-1}$ and polyethylene with molecular weight of $7.3 \times 10^5 \text{ g mol}^{-1}$, respectively (entry 17, Table 4).

While the catalytic activities and polymer molecular weight obtained using the different co-catalysts show similarities, the melt temperatures for the polymers obtained show some distinct differences. With **Ni1** – **Ni10**/MAO, these fall in the range 113.3 – 119.4 °C which are significantly higher than that seen with Et₂AlCl as the co-catalyst [T_m : 33.0 – 82.5 °C]. These findings would suggest that these MAO-derived materials are less branched and more crystalline. To confirm this suggestion a sample of the polymer obtained using **Ni1**/MAO at 30 °C was characterized by high temperature ¹³C NMR spectroscopy (Figure 8). Analysis of the data reveals a polymer containing only 29 branches per 1000 Cs, which included methyl (96.2%) and 1,4-paired methyl branches (3.8%) (Table S2). In marked contrast, the polymer sample generated using **Ni1**/Et₂AlCl at 30 °C gave 115 branches per 1000 Cs along with more varied branch composition. It is unclear how the nature of the co-catalyst affects the branching properties of the polymer, but it would seem likely that it is connected to the 4,4'-dimethoxybenzhydryl *ortho*-substituents on the precatalyst. In particular, the MAO-promoted polymerizations have a reduced inclination to form branches which implies chain isomerization/walking is somehow impeded during chain propagation. It is possible that interactions between the methoxy groups on the catalyst and the sterically bulky MAO counterion are influential.

< Figure 9 >

Mechanical properties of the polyethylene

The mechanical properties of the more branched polyethylene samples designated PE-40_{E/NiI}, PE-50_{E/NiI} and PE-60_{E/NiI} (entries 9 - 11 in Table 3), in which NiI/Et₂AlCl was employed as the catalyst, were initially studied by stress–strain measurements; the resulting data are presented in Table 5 while stress–strain curves are illustrated in Figure 9 ^[16]. Each mechanical test was performed with three specimens in order to achieve consistent results. Notably, the lowest ultimate tensile stress (3.06 MPa) and highest strain at break ($\epsilon_b = 553.5\%$) was observed for PE-60_{E/NiI}, which can be attributed to it being the least crystalline owing to its higher branching content.

< Table 5 >

Secondly, the corresponding less branched but higher molecular weight samples formed with MAO as co-catalyst namely, PE-40_{M/NiI}, PE-50_{M/NiI} and PE-60_{M/NiI} (entries 8 – 10, Table 4), were also tested for stress–strain measurements; the resulting data are given in Table 7 while stress–strain curves are shown in Figures 9 and 10. As a general point, these MAO-derived polymers show, for a given temperature, higher values of stress and strain as compared to the Et₂AlCl ones highlighting their better mechanical properties. For example, the ultimate tensile strength and maximum elongation at break for PE-40_{M/NiI} is 11.71 MPa and 308.4% which compares with 4.60 MPa and 151.8% for PE-40_{E/NiI}, respectively. Essentially, the reduced branching content and higher molecular weight make these samples more rigid leading to the observed higher values of stress and strain.

< Figure 10 >

< Figure 11 >

To explore the elastomeric properties, stress–strain recovery tests were performed by dynamic mechanical analysis (DMA) on the more branched and less crystalline samples, PE-40_{E/NiI}, PE-50_{E/NiI} and PE-60_{E/NiI}; the results are shown in Figure 11. Typically, these tests were performed at –10 and 30 °C and each cycle was repeated up to ten times. Following the first cycle, where the residual deformation gradually increases, all the materials display an essentially constant level of recovery. This behavior is quite typical of thermoplastic elastomers and can be credited to the alignment of the polymer microstructure ^[2]. After an initial change in morphology, a largely constant structure is assumed and hysteresis is observed. Moreover, as the temperature of the stress–strain recovery tests was increased from –10 °C to 30 °C, the elastic recovery of PE-40_{E/NiI}

was improved from 62 to 75%. Likewise, the elastic recovery of PE-50_{E/Ni1} increased from 59 to 84% and PE-60_{E/Ni1} from 60 to 83%. Hence, the specimen of PE-50_{E/Ni1} displayed the best elastic recovery. These results suggest that the high branching content of these polyethylenes leads to high physical crosslinks, properties that are characteristic of thermoplastic elastomers ^[17].

< Figure 12 >

Conclusions

Ten distinct 1,2-bis(arylimino)acenaphthene-nickel(II) complexes, each bearing one *N*-2,6-bis(4,4'-dimethoxybenzhydryl)-4-methylphenyl group, have been successfully synthesized and characterized by a range of techniques including in four cases by single crystal X-ray diffraction. With either MAO or Et₂AlCl as the co-catalyst, all the nickel precatalysts exhibited high activities at 30 °C for ethylene polymerization with the bromides generally more active than the chlorides while these least bulky precatalysts (**Ni1** (Me, Me), **Ni4** (Me, Me)) the most productive. Notably, all the materials are of high molecular weight and in some cases entering the ultra-high molecular weight window (i.e., > 1 × 10⁶ g mol⁻¹). In addition, the degree of branching of the resultant polyethylenes has been found to be dependent on the type of co-catalyst employed. With Et₂AlCl, the polyethylene exhibits a relatively high degree of branching (*ca.* 115 branches per 1000 carbons), while with MAO this is significantly lower (*ca.* 29 branches per 1000 carbons). Meanwhile, all the polyethylenes obtained showed narrow molecular weight distributions (*M_w/M_n* range: 1.9 - 4.3) in agreement with single-site type behavior. Overall, this work shows i) how fine tuning of the chelating ligand frame can influence catalytic performance and ii) how the choice of co-catalyst can, with a suitably appended precatalyst, influence the branching properties of a polyethylene formed in a highly active nickel-mediated ethylene homo-polymerization.

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Captions of Tables, Figures, Chart and Scheme

Table 1 Selected bond lengths (Å) and angles (°) for **Ni1**, **Ni3**, **Ni5** and **Ni6**.

Table 2 Ethylene polymerization using **Ni1** with a range of different co-catalysts.

Table 3 Ethylene polymerization runs using **Ni1** – **Ni10**/Et₂AlCl.

Table 4 Ethylene polymerization runs using **Ni1** – **Ni10**/MAO.

Table 5 Selected properties of PE-40_{E/Ni1}, PE-50_{E/Ni1}, PE-60_{E/Ni1}, PE-40_{M/Ni1}, PE-50_{M/Ni1} and PE-60_{M/Ni1}.

Figure 1 Symmetrical α -diimine-nickel precatalyst **A** and its unsymmetrical bis(imino)acenaphthene counterparts (**B** – **D**).

Figure 2 ORTEP representation of **Ni1** with thermal ellipsoids set at 30% probability level; all hydrogen atoms have been omitted for clarity.

Figure 3 ORTEP representation of **Ni3** with thermal ellipsoids set at 30% probability level; all hydrogen atoms have been omitted for clarity.

Figure 4 ORTEP representation of **Ni5** with thermal ellipsoids set at 30% probability level; all hydrogen atoms have been omitted for clarity.

Figure 5 ORTEP representation of **Ni6** with thermal ellipsoids set at 30% probability level; all hydrogen atoms have been omitted for clarity.

Figure 6 GPC curves of the polyethylenes obtained using **Ni1**/Et₂AlCl at different reaction temperatures (entries 6 – 10, Table 3).

Figure 7 ¹³C NMR spectrum of the polyethylene obtained using **Ni1**/Et₂AlCl at 30 °C (entry 4, Table 3); recorded in deuterated 1,2-dichlorobenzene at 100 °C. Peak assignments are with respect to the depicted polymer backbone.

Figure 8 GPC curves of the polyethylenes obtained using **Ni1**/MAO at different reaction temperatures (entries 7 – 11, Table 4).

Figure 9 ¹³C NMR spectrum of the polyethylene obtained using **Ni1**/MAO at 30 °C (entry 5, Table 4); recorded in deuterated 1,2-dichlorobenzene at 135 °C. Peak assignments are with respect to the depicted polymer backbone.

Figure 10 Stress–strain curves for PE-40_{E/Ni1}, PE-50_{E/Ni1} and PE-60_{E/Ni1}; the vertical line represents the breakage point.

Figure 11 Stress–strain curves for PE-40_{M/Ni1}, PE-50_{M/Ni1} and PE-60_{M/Ni1}; the vertical line represents the breakage point.

Figure 12 Stress–strain recovery tests for PE-40_{E/Ni1}, PE-50_{E/Ni1} and PE-60_{E/Ni1} at –10 and 30 °C.

Scheme 1 Synthetic route to **L1** – **L5** and their complexes **Ni1** – **Ni10**.

Table 1 Selected bond lengths (Å) and angles (°) for **Ni1**, **Ni3**, **Ni5** and **Ni6**

	Ni1	Ni3	Ni5	Ni6
X	Br	Br	Br	Cl
Bond lengths (Å)				
Ni(1)-X(1)	2.3179(9)	2.3373(13)	2.3319(8)	2.1965(11)
Ni(1)-X(2)	2.3471(9)	2.3285(9)	2.3382(8)	2.1951(10)
Ni(1)-N(1)	2.034(3)	2.036(2)	2.038(2)	2.041(2)
Ni(1)-N(2)	2.016(3)	2.013(2)	2.014(2)	2.020(2)
N(1)-C(1)	1.295(4)	1.291(3)	1.286(3)	1.283(3)
N(1)-C(13)	1.441(4)	1.451(3)	1.446(3)	1.447(3)
N(2)-C(11)	1.288(4)	1.282(3)	1.282(3)	1.283(3)
N(2)-C(50)	1.446(5)	1.446(3)	1.443(3)	1.446(3)
Bond Angles (°)				
X(1)-Ni(1)-X(2)	119.93(3)	121.29(3)	120.90(2)	121.87(4)
N(1)-Ni(1)-N(2)	83.04(12)	82.88(8)	82.95(9)	82.74(9)
N(1)-Ni(1)-X(1)	107.22(8)	113.70(6)	117.06(6)	104.89(7)
N(1)-Ni(1)-X(2)	116.12(8)	111.39(7)	107.30(6)	117.75(7)
N(2)-Ni(1)-X(1)	112.06(9)	107.75(7)	110.26(7)	116.86(7)
N(2)-Ni(1)-X(2)	103.21(9)	113.34(7)	112.15(7)	106.48(7)

Table 2 Ethylene polymerization using **Ni1** with a range of different co-catalysts^a

Runs	Cocat.	Al:Ni	Activity ^b	M_w^c	M_w/M_n^c	T_m (°C) ^d
1	MAO	2500	8.81	9.2	2.5	119.1
2	MMAO	2500	5.72	10.5	1.9	110.3
3	Et ₂ AlCl	600	7.90	9.6	2.6	60.6
4	EASC	600	5.80	6.8	2.3	61.0

^a General conditions: 2.0 μ mol of **Ni1**, 100 mL of toluene, 10 atm C₂H₄, 30 min, 30 °C;

^b $\times 10^6$ g PE mol⁻¹ (Ni) h⁻¹;

^c M_w : $\times 10^5$ g mol⁻¹, determined by GPC;

^d Determined by DSC.

Table 3 Ethylene polymerization runs using **Ni1 – Ni10**/Et₂AlCl^a

Runs	Precat.	T (°C)	t (min)	Al:Ni	Activity ^b	M_w^c	M_w/M_n^c	$T_m(^{\circ}\text{C})^d$
1	Ni1	30	30	400	2.61	10.7	2.8	91.5
2	Ni1	30	30	500	2.83	8.9	2.5	76.9
3	Ni1	30	30	600	7.90	9.6	2.6	60.6
4	Ni1	30	30	700	9.32	7.5	2.5	61.3
5	Ni1	30	30	800	7.12	7.2	2.5	94.0
6	Ni1	30	30	900	6.19	8.4	2.7	78.6
7	Ni1	20	30	700	6.42	8.2	2.6	94.9
8	Ni1	40	30	700	5.48	7.3	2.3	51.4
9	Ni1	50	30	700	4.17	5.1	2.3	38.1
10	Ni1	60	30	700	3.75	3.3	2.7	17.3
11	Ni1	30	5	700	11.86	7.9	1.9	65.6
12	Ni1	30	15	700	11.24	6.0	3.4	54.9
13	Ni1	30	30	700	9.32	7.5	2.5	61.3
14	Ni1	30	45	700	6.48	7.1	2.6	76.4
15	Ni1	30	60	700	5.06	8.7	2.6	84.1
16	Ni2	30	30	700	5.61	12.2	1.8	61.6
17	Ni3	30	30	700	8.19	9.3	3.3	40.9
18	Ni4	30	30	700	9.67	6.8	2.2	52.1
19	Ni5	30	30	700	9.17	9.0	2.2	33.0
20	Ni6	30	30	700	6.99	8.0	2.3	79.0
21	Ni7	30	30	700	3.18	11.1	2.1	64.7
22	Ni8	30	30	700	5.68	6.9	2.7	82.5
22	Ni9	30	30	700	9.56	6.5	2.6	44.6
24	Ni10	30	30	700	6.42	9.2	2.8	51.4

^a General conditions: 2.0 μmol of precatalyst, 100 mL of toluene, 10 atm C₂H₄;^b $\times 10^6$ g PE mol⁻¹ (Ni) h⁻¹;^c M_w : $\times 10^5$ g mol⁻¹, determined by GPC;^d Determined by DSC.

Table 4 Ethylene polymerization runs using **Ni1 – Ni10**/MAO^a

Run	Precat.	T (°C)	t (min)	Al:Ni	Activity	M_w	M_w/M_n	T_m (°C)
1	Ni1	30	30	1500	4.17	9.8	2.3	118.3
2	Ni1	30	30	2000	5.79	11.7	3.3	118.4
3	Ni1	30	30	2250	8.39	10.3	4.3	117.9
4	Ni1	30	30	2500	8.81	9.2	2.5	119.1
5	Ni1	30	30	2750	9.29	9.2	3.1	117.9
6	Ni1	30	30	3000	6.69	7.0	2.7	119.6
7	Ni1	20	30	2750	7.11	11.2	3.0	120.9
8	Ni1	40	30	2750	5.61	8.3	3.1	116.8
9	Ni1	50	30	2750	2.67	6.9	3.2	116.7
10	Ni1	60	30	2750	2.51	5.7	3.2	104.9
11	Ni1	30	5	2750	11.58	9.8	1.9	115.6
12	Ni1	30	15	2750	10.34	7.8	2.5	117.0
13	Ni1	30	45	2750	6.44	9.7	2.8	118.9
14	Ni1	30	60	2750	5.02	8.3	2.9	116.6
15	Ni2	30	30	2750	7.12	10.9	2.7	118.2
16	Ni3	30	30	2750	6.74	9.4	3.0	113.7
17	Ni4	30	30	2750	8.95	7.3	2.7	118.9
18	Ni5	30	30	2750	6.19	8.3	2.6	115.0
19	Ni6	30	30	2750	6.67	7.2	2.7	116.6
20	Ni7	30	30	2750	6.52	8.8	1.9	116.6
21	Ni8	30	30	2750	5.92	10.0	2.3	113.3
22	Ni9	30	30	2750	7.59	8.0	3.2	119.4
23	Ni10	30	30	2750	6.59	7.5	2.8	116.6

^a General conditions: 2.0 μmol of precatalyst, 100 mL of toluene, 10 atm C_2H_4 ;^b $\times 10^6$ g PE mol^{-1} (Ni) h^{-1} ;^c M_w : $\times 10^5$ g mol^{-1} , determined by GPC;^d Determined by DSC.

Table 5 Selected properties of PE-40_{E/NiI}, PE-50_{E/NiI}, PE-60_{E/NiI}, PE-40_{M/NiI}, PE-50_{M/NiI} and PE-60_{M/NiI}

Sample	M_w^a	T_m (°C) ^b	Stress (MPa) ^c	Strain (%) ^c
PE-40 _{E/NiI}	7.3	51.4	4.60	151.8
PE-50 _{E/NiI}	5.1	38.1	3.14	210.3
PE-60 _{E/NiI}	3.3	17.3	3.06	553.5
PE-40 _{M/NiI}	8.3	116.8	11.71	308.4
PE-50 _{M/NiI}	6.9	116.7	10.53	390.2
PE-60 _{M/NiI}	5.7	104.9	11.57	638.7

^a M_w : $\times 10^5$ g mol⁻¹, determined by GPC;

^b Determined by DSC.

^c The stress-strain curves were obtained using a universal tester (Instron 1122, UK).