Olefin Polymerization

Design of Thermally Stable Amine–Imine Nickel Catalyst Precursors for Living Polymerization of Ethylene: Effect of Ligand Substituents on Catalytic Behavior and Polymer Properties

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Abstract: Nickel complexes bearing amine–imine ligands with various backbone substituents were synthesized and employed as ethylene polymerization catalysts on activation with Et_2AICI . The substituent on the backbone carbon atom of the amine moiety is decisive for the living nature of ethylene polymerization. A bulky amine–imine nickel precursor with a *tert*-butyl group on the carbon atom of the amine group can polymerize ethylene in a living fashion at an ele-

Introduction

A striking feature of olefin coordination polymerization is that stereoselectivity, regiospecificity, and the architecture (density, length, and topology) of branches can be controlled at will by means of tailor-made catalysts.^[1] The development of polyole-fin materials with well-defined polymer structure and composition, stereochemistry, and branch architecture has become increasingly attractive.^[2] Early transition-metal catalysts have been developed that give precise control over polymer stereo-chemistry.^[3] In contrast, late transition-metal catalysts, such as α -diimine nickel and palladium catalysts, are outstanding in control of branch topology due to the chain-walking process.^[4] Polyethylenes (PEs) with branch architectures ranging from linear to hyperbranched can be readily prepared by tuning reaction parameters and ligand structure.^[4, 5]

Living catalytic olefin polymerization is unsurpassed in terms of microstructure control of polymers, which allows controlled synthesis of polyolefins with precise structure and composition, such as monodisperse polymers and block copolymers.^[6] Combining the chain-walking characteristic of late transition-metal catalysts with living polymerization can provide effective access to the synthesis of well-defined block polyolefins with novel architectures such as regioblock,^[7] hyperbranched-linear,^[8] core–shell,^[9] and large dendritic structures.^[10] Currently,

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vated temperature of 65 $^{\circ}$ C, which is the highest temperature of living polymerization of ethylene with late transitionmetal catalysts. The wide applicable temperature range for living polymerization and sensitivity of the branch structure of the polyethylene to temperature enable precise synthesis of di- and triblock polyethylenes featuring different branched segments by sequential tuning of the polymerization temperature.

living coordination polymerization of olefins remains a challenge because of the processes of chain termination/transfer and poor thermal stability of catalysts, especially at elevated temperature. The main limitations for living polymerization of olefins with late transition-metal catalysts are scarce catalyst systems and low practicable temperatures (<5 °C),^[11] which restrict precise tuning of branch architecture. A noteworthy sample is a cyclophane-based α -diimine nickel catalyst that can polymerize propylene in a living fashion at 50 °C but exhibits a nonliving mode of ethylene polymerization.^[12] The temperature of 50 °C is the highest reported in the literature for living olefin polymerization with late transition-metal catalysts.

Recently, we reported that a bulky amine–imine nickel catalyst precursor (1 in Scheme 1) affords PE with low polydispersity (polydispersity index (PDI) < 1.10) in a living fashion above



Scheme 1. Amine-imine nickel complexes.

room temperature.^[13] Two methyl substituents on the backbone carbon atom (Me₂CNH) increase the axial steric hindrance of the amine–imine nickel complex, which seems to be responsible for living polymerization of ethylene at high temperature. This prompted us to elucidate the key site of amine–imine nickel catalysts for living polymerization of ethylene. We found that substituents on the carbon atom of the amine group of



amine–imine nickel catalyst are decisive for living polymerization of ethylene, and developed a new amine–imine nickel catalyst precursor (**7** in Scheme 1) with a *tert*-butyl group on carbon atom C1 of the amine group that can polymerize ethylene in a living fashion at 65 °C. The high thermal stability of the amine–imine nickel precursors allowed us to regulate the branch architecture of PE, and novel di- and triblock PEs featuring different branched segments could be precisely synthesized by tuning the living-polymerization temperature.

Results and Discussion

Synthesis and characterization of amine-imine nickel complexes

Potentially, N,N-bidentate hybrid amine–imine ligands can exhibit distinct influences of the amine and imine functional groups on the metal center with regard to both polymer structure and reactivity control.^[14] Therefore, amine–imine ligands with various substituents on the carbon atoms of the imine and amine groups were designed and synthesized in order to evaluate substituent effects. The ligands were prepared by reduction of α -diimine compounds (see Supporting Information), and new nickel complexes **2–8** (Scheme 1) were obtained by addition of the ligands to a stirred suspension of (DME)NiBr₂ in CH₂Cl₂. Single crystals of **4**, **5**, and **7** suitable for X-ray diffraction analysis (Figure 1) were obtained by slow diffusion of hexane into solutions of the nickel complexes in CH₂Cl₂.

The molecular structure of 7 clearly showed steric effects on the different nitrogen atoms. Aryl moiety 2 of the imine (sp² N) is roughly perpendicular to the slightly distorted five-membered coordination plane (dihedral angle of 82.2°), similar to the α -diimine nickel analogue.^[15] For the amine moiety of complex 7, deflection of the bulky tert-butyl group to one side of the slightly distorted chelate ring is indicative of an axial steric effect on the metal center, which may effectively prohibit chain-transfer reactions. Aryl moiety 1 of the amine group lies on the other side of the chelate ring due to the distorted tetrahedral configuration of the amine nitrogen atom (sp³ N) and is closer to the nickel center than aryl moiety 2 of the imine because of repulsion of the tert-butyl group. Complex 4 also shows a large axial steric effect due to the introduction of methyl and phenyl groups on the amine carbon atom. Moreover, aryl moiety 1 of the amine exerts equatorial hindrance on coordination sites. On the contrary, complex 5 without substituents on the carbon atom adjacent to the amino group has relatively open equatorial and axial environments around the nickel center, which may facilitate both chain-propagation and chain-transfer reactions.

Effect of ligand substituents on ethylene polymerization

Ethylene polymerization was carried out with nickel complexes 1-8 after activation with Et₂AlCl under the same reaction conditions to probe substituent effects of the ligand backbone. The polymerization results, which were reproducible, are listed in Table 1. Firstly, it is informative to compare the different be-



Figure 1. Molecular structures of nickel complexes 4, 5, and 7 (50% probability ellipsoids, H atoms except H2N and H15 omitted).

haviors of amine-imine nickel complexes and classical α -diimine nickel complex [(ArN=C(Me)-C(Me)=NAr)NiBr₂] (9, Ar= 2,6-diisopropylphenyl) in ethylene polymerization. Generally, amine-imine nickel precursors show lower catalytic activity for ethylene polymerization than the α -diimine nickel precursor, but they can afford PE with lower polydispersity (Table 1, entries 1-8 versus 9). In amine-imine nickel complexes 1-4, replacement of one of the methyl groups on bridging carbon atom C1 with a longer alkyl substituent (Et or nBu) or a rigid phenyl group leads to a decrease in both catalytic activity and polymer molecular weight. Interestingly, all four catalysts can polymerize ethylene in a living fashion at 50 °C and afford branched polymers with almost the same molecular weight distribution (PDI; Table 1, entries 1-4). This indicates that two methyl substituents on the backbone carbon atom of the amine moiety (Me₂CNH) are bulky enough to inhibit chaintransfer reactions in ethylene polymerization. Bulkier substituents lead to decreased activity because equatorial hindrance exerted by aryl moiety 1 on the amine retards trapping and coordination of ethylene. The molecular weight distribution of the polymer obtained by using catalyst precursor 5, which has no substituents on the amine-adjacent carbon atom C1, is

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Table 1. Ethylene polymerization with nickel complexes $1-9$ /Et ₂ AlCl. ^[a]								
Entry	Cat.	$T_{p} [^{\circ}C]$	Yield [g]	Activity ^[b]	$M_n^{[c]}$	PDI ^[c]	Br ^[d]	<i>T</i> _m ^[e] [°C]
1	1	50	0.358	35.8	48.2	1.08	96	_ ^[f]
2	2	50	0.162	16.2	21.2	1.07	99	_ ^[f]
3	3	50	0.151	15.1	20.0	1.09	108	_[f]
4	4	50	0.047	4.7	10.8	1.08	102	_ ^[f]
5	5	50	1.226	122.6	46.7	1.56	85	_ ^[f]
6	6	50	0.728	72.8	72.9	1.07	57	42, 73
7	7	50	0.305	30.5	41.1	1.02	50	50, 65
8	8	50	0.277	27.7	29.4	1.02	56	25
9 ^[g]	9	50	2.411	241.1	140.2	1.63	87	_ ^[f]
10	7	-40	0.035	3.5	12.8	1.29	19	120
11	7	20	0.211	21.1	26.3	1.08	38	68, 86
12	7	35	0.279	27.9	27.4	1.02	40	57, 70
13	7	65	0.306	30.6	41.2	1.06	54	46, 60
14	7	75	0.229	22.9	24.5	1.39	55	50, 63
15 ^[h]	7	65	1.352	541	138.8	1.12	48	57
16 ^[h]	7	65	2.967	1187	398.9	1.16	47	61

[a] Polymerization conditions: 10 mmol of nickel, 60 min, 28 mL of toluene and 2 mL of CH₂Cl₂, Al(Et₂AlCl)/Ni = 200, 3 psig ethylene for entries 1–14. [b] Activity [kg_{PE} mol_{Ni}⁻¹ h⁻¹]. [c] M_n [kg mol⁻¹] and PDI were determined by GPC in 1,2,4-trichlorobenzene at 150°C with a light-scattering detector. [d] Branching density in number of branches per 1000 C atoms, determined by ¹H NMR spectroscopy. [e] Determined by DSC. [f] Broad melting endotherm. [g] **9** is classical α -diimine nickel complex [(ArN= C(Me)–C(Me)–NAr)NiBr₂] (Ar=2,6-diisopropylphenyl). [h] Polymerization conditions: 10 mmol of nickel, 15 min, 58 mL of toluene and 2 mL of CH₂Cl₂, Al(Et₂AlCl)/Ni=200, 75 psig ethylene for entry 15 and 300 psig ethylene for entry 16.

clearly broader (PDI = 1.56), but it shows the highest activity among the tested catalyst precursors (Table 1, entry 5), which suggests that a lack of steric bulk on the adjacent carbon atom leads to loss of control over the molecular weight distribution of the polymer.

In an attempt to achieve both high activity and low polydispersity by introducing only a single substituent on C1, nickel catalyst precursors **6–8** were designed and synthesized. Polymers with low polydispersity could be obtained when *i*Pr or *t*Bu was attached to C1 (**6** and **7**), and the catalytic activities were considerable. In particular, catalyst precursor **7** afforded PE with low polydispersity even at a high temperature of 65 °C. Thus, this catalyst system is also a rare example of a thermally stable late transition-metal catalyst.^[5e, 12, 13, 16] On the basis of the evaluation of the ligand substituent effects, we concluded that the substituents on carbon atom C1 adjacent to the amine group of the amine–imine nickel catalyst are strategically located for production of low-polydispersity PE, presumably due to effective prohibition of chain transfer/elimination because of axial steric hindrance on the metal center.

The steric effect of the substituent on carbon atom C2 of the imine moiety is distinct from that of the substituent on carbon atom C1 of the amine moiety because of the two different coordinating groups [imine (sp² N) versus amine (sp³ N)]. Comparison of complexes **7** and **8** (Table 1, entries 7 and 8) demonstrates that increasing steric hindrance of C2 leads to an increase in polymerization activity and molecular weight of the PE product. This is in contrast to the above-mentioned steric effect of the amine moiety but similar to that of the α - diimine nickel analogue.^[15,17] In contrast to the α -diimine nickel catalyst,^[5a,b] amine–imine nickel catalysts contain different nitrogen atoms, which can provide additional tunable positions to control polymerization reactivity.

Living polymerization of ethylene

As reported previously, the 1/Et₂AlCl system catalyzes living polymerization of ethylene at 50 °C for dozens of minutes and then decays slightly.^[13] Complexes 2-4 show similar catalytic behavior to 1 in ethylene polymerization. Complexes 7 and 8 with bulky tert-butyl ligand substituents can polymerize ethylene to afford extremely low polydispersity PE (PDI = 1.02) with symmetric gel permeation chromatography (GPC) traces at an elevated temperature of 50°C after activation with Et₂AlCl (Table 1, entries 7 and 8, and Figure S1 in the Supporting Information). The PDI values of the PEs obtained with 7/Et₂AlCl and 8/Et₂AlCl can be maintained below 1.10 over a reaction timescale of 3 h, and this indicating their high thermal stability. The 7/Et₂AlCl system exhibits the highest thermal stability among these catalyst systems, shows the highest activity at 65 °C, and produces low-PDI PE below 65 °C. Thus, living polymerization of ethylene catalyzed by 7/Et₂AlCl can be achieved over a wide range of reaction temperatures (Table 1, entries 7 and 10-14). The relatively broad molecular weight distribution of the polymer obtained at -40 °C may be attributed to slower initiation of the active center and precipitation of linear PE at low temperature. The living nature of ethylene polymerization with 7/ Et₂AlCl at 65 °C was further investigated. As shown in Figure 2, the number-average molecular weight M_n increased linearly



Figure 2. a) Plot of M_n (**△**) and M_w/M_n (**△**) as a function of polymerization time at 65 °C. b) GPC traces at different times for **7**/Et₂AlCl.

with polymerization time, and M_w/M_n values remained below 1.10 for 1 h. To the best of our knowledge, this is the highest temperature of living polymerization of ethylene with late transition-metal catalysts.^[11, 12]

Effects of ligand substituents on branch structure of PE

Polymer branch structure can be also affected by substituents on the different bridging carbon atoms. The branching density of the obtained PE varies from 108 to 50 per 1000 C atoms on tuning the substituent group on the carbon atom of the amine moiety, and this provides a viable means to control

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polymer branch structure. A general trend is that introduction of bulky substituents onto bridge carbon atom C1 of the amine moiety leads to a decrease in total branch density (Table 1, entries 1-8). ¹³C NMR experiments were conducted to detect the branching distributions of the PEs (Figure S4 in the Supporting Information), and detailed branching distributions of the PEs obtained with various catalysts are listed in Table S2 (Supporting Information). The branch-on-branch structure generated through tertiary carbon atoms can be seen in the methyl and ethyl resonances centered at 19.44 and 11.72 ppm for the PEs obtained with 2-6/Et₂AICI as opposed to 1/Et₂AICI, 7/Et₂AlCl, and 8/Et₂AlCl. It is assumed that the branch structure originates from the chain-walking mechanism involving repetitive β -hydrogen elimination/reinsertion processes.^[5a, 18] Despite the slight change in total branching density within the tested temperature range for 7/Et₂AICI, the content of long branches increased gradually with increasing temperature from 0/1000 C at $-40\,^\circ\text{C}$ to 33/1000C at 75 $^\circ\text{C},$ as revealed by $^{13}\text{C}\,\text{NMR}$ spectroscopy (Table S2 in the Supporting Information), which suggests a remarkable change in chain branch structure with variation in temperature. Dilute-solution properties also enabled us to examine the chain structure of PEs obtained at different temperatures. The dependence of intrinsic viscosity on polymer molecular weight detected by high-temperature GPC with a viscosity detector can directly reflect branch structure of the PE. As shown in Figure 3, the highest intrinsic viscosity was observed for the PE obtained at -40 °C, and the lowest for the



Figure 3. Dependence of intrinsic viscosity on molecular weight of the PEs obtained by using $7/Et_2$ AlCl at various reaction temperatures.

PE produced at 65 °C. The Mark–Houwink exponents α calculated from the slope of the intrinsic viscosity curves are 0.70 and 0.23 for the PEs obtained at -40 °C and 65 °C, respectively.^[9,19] This result shows that the **7**/Et₂AlCl system affords linear PE at -40 °C but highly branched PE at 65 °C, which is consistent with differential scanning calorimetric (DSC) analysis of polymer products.^[20,21]

Moreover, increasing ethylene pressure from atmospheric pressure of 15 psig to 300 psig (Table 1, entries 13, 15, and 16) for **7**/Et₂AlCl system leads to a significant increase in activity and affords higher molecular weight PE with slightly higher polydispersities. Usually, increasing ethylene pressure leads to more linear products.^[5c] In contrast, the total branching density

of the PE obtained with $7/Et_2AlCl$ is insensitive to ethylene pressure at high temperature (65 °C; Table S2 in the Supporting Information), which suggests that reaction temperature plays a dominant role in the chain-walking process for the $7/Et_2AlCl$ system. A basic trend is that the content of methyl groups increases while the content of long branches decreases with increasing ethylene pressure.

Synthesis of block PE featuring different branched segments

Living polymerization of ethylene over a wide range of temperature opens a way for precise synthesis of monodisperse PE with various branch structures and corresponding block polymers by changing the reaction temperature (Scheme 2). Amine–imine nickel catalyst precursors 1 and 7 were selected



Scheme 2. Synthesis of block PE featuring different branched segments by sequential tuning of polymerization temperature.

to prepare block polyethylenes featuring different branched segments due to their enormously different chain-walking abilities. When ethylene polymerization catalyzed by $7/Et_2AlCl$ at 65 °C was sequentially followed by a second stage of polymerization at -40 °C, low-polydispersity diblock PE (PDI=1.18) with different branched segments was obtained (Table 2, entry 3). Shifting of the GPC trace to lower retention times without obvious tail or shoulder peaks (Figure 4a) proves the successful occurrence of chain-extension reactions. The obtained diblock PE shows two melting temperatures of 45 and 115 °C (Figure 4b), corresponding to the PE segments obtained at 65 and -40 °C, respectively. Moreover, the intrinsic viscosity of the diblock polyethylene is intermediate between those of

Table 2. Synthesis of block PEs with 1/Et ₂ AlCl and 7/Et ₂ AlCl. ^[a]							
Entry	Cat.	t₁ [min]/ T₁ [°C]	t₂ [min]/ T₂ [°C]	t₃ [min]/ T₃ [°C]	<i>M</i> _n ^[b]	PDI ^[b]	<i>T</i> _m ^[c] [°C]
1	7	15/65	-	-	12	1.03	46, 60
2	7	60/-40	-	-	13	1.29	120
3	7	15/65	60/-40	-	26	1.18	45, 115
4	1	15/50	-	-	12	1.02	_[d]
5	1	60/-40	-	-	14	1.07	97
6	1	15/50	60/-40	-	27	1.09	97
7	1	15/50	60/-40	15/50	39	1.11	89
8	1	60/-40	15/50	-	29	1.07	93
9	1	60/-40	15/50	60/-40	42	1.16	93
[a] Polymerization conditions: 10 mmol nickel, 28 mL of toluene and 2 mL							

[a] Polymerization conditions: 10 mmol nickel, 28 mL of toluene and 2 mL of CH_2CI_2 , Al(Et₂AlCl)/Ni=200, 3 psig ethylene. [b] M_n [kg mol⁻¹] and PDI were determined by GPC in 1,2,4-trichlorobenzene at 150 °C with a light-scattering detector. [c] Determined by DSC. [d] Broad melting endotherm.



Figure 4. a) GPC and b) DSC curves of PE and diblock PE polymers produced by $7/Et_2AICI$.

the branched and linear segments, as indicated by the dependence of intrinsic viscosity on polymer molecular weight (Figure 3). Therefore, it is deduced that the obtained diblock PE has a linear-highly branched (L-HB) diblock structure.

Similarly, well-defined diblock PE (PDI=1.09) containing amorphous and semicrystallized segments with a broad melting endotherm at -8 °C and a sharp melting peak at 97 °C was synthesized by using 1/Et₂AlCl (entry 6 in Table 2 and Figure 5a) for sequential polymerization of ethylene at 50 and at -40 °C. Interestingly, the branch architecture of the polymer



Figure 5. GPC and DSC curves of PE and block PE polymers obtained with 1/ Et_2AICI . a) Branched-first strategy (HB–L–HB). b) Linear-first strategy (L–HB–L).

product remains almost the same on changing the synthetic approach from branched-first (high temperature first; Table 2, entry 6) to linear-first (low temperature first; Table 2, entry 8). This is distinctive from the α -diimine palladium catalyst, for which the synthetic procedure is restricted to branched-first, as walking back of the active center to the polymer chain occurred when the linear segment was prepared first.^[8] Triblock PE polymers can be also prepared by sequentially varying reaction temperature in the long-lived living polymerization of ethylene with $1/Et_2$ AlCl. An obvious increase in M_n , shifting GPC traces, and two distinctive endothermic peaks in DSC curves clearly support successful synthesis HB-L-HB or L-HB-L triblock PE polymers with low polydispersities (Figure 5). Our study provides a different access to precise synthesis of di- and triblock PE containing both amorphous and semicrystallized segments from ethylene monomer solely by changing reaction temperature, which is hardly achievable with other catalyst systems. These block PE materials with hybrid branch structures are readily amenable to applications such as compatibilizers, thermoplastic elastomers, and high-impact plastics.^[20d]

Conclusion

The two coordinating functionalities [imine (sp²) and amine (sp³)] of amine-imine nickel catalysts exert distinctive effects and reactivity control on ethylene polymerization, and bulky substituents on C1 of the amine group is strategically located for stability and living polymerization of ethylene. Bulky amine-imine nickel complex 7 activated by Et₂AlCl can polymerize ethylene in a living fashion with unprecedented molecular-weight control (PDI = 1.02) and thermal stability (65 $^{\circ}$ C). This is the highest temperature of living polymerization of ethylene with a late transition-metal catalyst. These long-lived and robust living-polymerization systems provide a viable access to the practical design of polyethylene with various branch architectures. Well-defined di- and triblock PEs (PDI < 1.20) with different branched segments were prepared from ethylene monomer solely by varying reaction temperature. The amineimine nickel catalyst system developed herein will provide additional possibilities for precise synthesis of monodisperse PEs, PE block polymers, and functional PEs with various branch structures.

Experimental Section

General remarks

All manipulations involving air- and moisture-sensitive compounds were carried out under an atmosphere of dried and purified nitrogen with standard vacuum-line, Schlenk, or glovebox techniques. Elemental analyses were performed on a Vario EL microanalyzer. Fast atom bombardment (FAB) mass spectra of nickel complexes were obtained on an LCQ DECA XP instrument. NMR spectra of organic compounds were recorded on a Bruker 300 MHz instrument in CDCl₃ with TMS as reference. ¹³C NMR spectra of polymers were recorded on an INOVA 400 MHz spectrometer at 120°C by using o-C₆D₄Cl₂ as solvent. DSC analyses were conducted with a PerkinElmer DSC-7 system. The DSC curves were recorded as second heating curves from -100 to $140\,^\circ\text{C}$ at a heating rate of $10\,^\circ\text{C}\,\text{min}^{-1}$ and a cooling rate of 10°C min⁻¹. GPC analysis of the molecular weights and molecular weight distributions (PDI = M_w/M_n) of the polymers at 150 °C were performed on a PL-GPC 220 high-temperature chromatograph equipped with a triple-detection array, including a differential refractive-index detector, a two-angle light-scattering detector, and a four-bridge capillary viscometer. The detection angles of the LS detector were 15 and 90°, and the laser wavelength was 658 nm. 1,2,4-Trichlorobenzene (TCB) was used as the eluent at a flow rate of 1.0 mL min⁻¹.

Materials

Dichloromethane was distilled from CaH_2 under nitrogen, and toluene and hexane were distilled from Na/K alloy. Glyoxal (40wt% aqueous solution), pyruvaldehyde (35wt% aqueous solution), 2,6-diisopropylaniline, and (DME)NiBr₂ were purchased from Aldrich and used as received. Diethylaluminum chloride (DEAC, 1.0 M in

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hexane), was purchased from Acros. Ethylene (99.99%) was purified by passing through Agilent moisture and oxygen traps. Other commercially available reagents were purchased and used without purification. Classical α -diimine nickel complex **9** and amine–imine nickel complex **1** were prepared according to reported methods.^[5c, 13]

Typical ethylene polymerization procedure

A round-bottom Schlenk flask with stirring bar was heated for 3 h at 150 °C under vacuum and then cooled to room temperature. The flask was pressurized to 15 psi of ethylene and vented three times. The appropriate alkyl aluminum compound as cocatalyst was introduced into the glass reactor under 3 psi of ethylene. The system was continuously stirred for 5 min, and then toluene and 2 mL of a solution of nickel complex in CH₂Cl₂ were added sequentially by syringe to the well-stirred solution, and the total reaction volume was kept at 30 mL. The ethylene pressure was kept constant at 3 psi by continuous feeding of gaseous ethylene throughout the reaction. Except for -40 °C, maintained with a cooler, the other polymerization temperatures were controlled with an external oil bath. The polymerizations were terminated by the addition of 200 mL of acidic methanol (ethanol/HCl 95/5) after continuous stirring for an appropriate period. The resulting precipitated polymers were collected by filtration, washed with methanol several times, and dried in vacuum at 40°C to constant weight.

High-pressure polymerization of ethylene

A mechanically stirred 100 mL Parr reactor was heated to $150 \,^{\circ}$ C for 2 h under vacuum and then cooled to room temperature. The autoclave was pressurized to 50 psi of ethylene and vented three times. The autoclave was then charged with 58 mL of a solution of Et₂AlCl in toluene under 50 psi of ethylene at initialization temperature. The system was continuously stirred for 5 min, and then 2 mL of a solution of nickel complex in CH₂Cl₂ was charged into the autoclave. The ethylene pressure was raised to the specified value, and the reaction was carried out for a certain time. Polymerization was terminated by addition of acidic methanol after releasing ethylene pressure. The resulting precipitated polymers were collected by filtration, washed with methanol several times, and dried under vacuum at 40 °C to constant weight.

Synthesis of block polyethylene

Typical procedure for highly branched-linear diblock polyethylene: A round-bottom Schlenk flask with stirring bar was heated for 3 h at 150 °C under vacuum and then cooled to room temperature. The flask was pressurized to 15 psi of ethylene and vented three times. The appropriate alkyl aluminum compound as cocatalyst was added to the flask under 3 psi of ethylene. The system was continuously stirred for 5 min, and then toluene and 2 mL of a solution of nickel complex in CH₂Cl₂ were added sequentially by syringe to the well-stirred solution, and the total reaction volume was kept at 30 mL. The ethylene pressure was kept constant at 3 psi. After ethylene polymerization for 15 min, the ethylene feed was stopped, and the reaction flask was charged with N₂ and vented three times. The flask was cooled to $-40\,^\circ\text{C}$ by using a cooler and kept at that temperature for about 60 min, and then the flask was exposed to vacuum to remove the N₂ and pressured to 3 psi of ethylene. After reaction for 60 min, the pressure was released and the polymerization was terminated by addition of 200 mL of acidic methanol (ethanol/HCl 95/5) after continuous stirring for an appropriate period. The precipitated polymer was collected by filtration, washed with methanol several times, and dried in vacuum at 40 $^\circ\text{C}$ to constant weight. The other block polyethylenes were prepared by similar procedures.

Synthesis of α -diimine compounds

 α -Diimine compounds ArN=C(Me)-CH=NAr and ArN=CH-CH=NAr (Ar = diisopropylphenyl) were prepared according to the literature. For detailed procedures and characterization of α -diimine compounds, see the Supporting Information.

Synthesis of ArN=C(Me)-C(Ph)=NAr (Ar = diisopropylphenyl)

PhLi was prepared according to the literature procedure by reaction of *n*-butyllithium with bromobenzene.^[22] The freshly prepared solution of PhLi (5.8 mL, 1.7 м in THF) was added dropwise to solution of α -diimine (Ar–N=C(Me) –CH=N–Ar (Ar=diisopropylphenyl) (3.83 g, 9.8 mmol) in diethyl ether (20 mL) under nitrogen atmosphere at 0°C. The mixture was stirred overnight at room temperature and terminated with a concentrated aqueous solution of NH₄Cl. The organic layer was separated and dried over ethyl acetate using anhydrous MgSO₄ as drying agent. The product was obtained as yellow crystals in 24.5% yield after removal of solvent and recrystallization from hot ethanol. ¹H NMR (300 MHz, CDCl₃): $\delta =$ 7.26–7.03 (m, 11 H, ArH), 2.88–2.74 (m, 4 H, CH(CH₃)₂), 1.27–0.99 (d, 24H, CH(CH₃)₂), 0.96–0.93 ppm (d, 3H, CCH₃); ¹³C NMR (75 MHz, CDCl₃): $\delta = 169.95$ (C=N), 166.14 (C=N), 146.39, 145.46, 135.51, 135.14, 129.39, 129.16, 127.82, 124.08, 123.18, 29.09, 28.89, 24.04, 23.58, 23.36, 22.40, 18.97 ppm (C-CH₃); elemental analysis calcd (%) for $C_{33}H_{42}N_2$: C 84.80, H 8.90, N 6.00; found: C 84.93, H 9.07, N 6.01.

Synthesis of ArN=C(Me)-C(Me)(Et)-NHAr (Ar = 2,6-diisopropylphenyl; L2)

Under nitrogen atmosphere, a solution of ArN=C(Me)-C(Me)=NAr (2.42 g, 6 mmol) in anhydrous diethyl ether (20 mL) was introduced into a 100 mL Schlenk flask, and then diethylzinc (4 mL, $1.5 \,\text{m}$ in hexane) was injected slowly by syringe at room temperature. The reaction mixture was stirred at room temperature for 2 h. After the solution was cooled to 0°C in an ice/water bath, the reaction mixture was carefully hydrolyzed by adding ice/water. The organic layer was separated and dried over MgSO4, and the solvent was evaporated. The desired product was obtained by slow evaporation of solvent after addition of ethanol to the residual oil. The crude product was purified by recrystallization from hot ethanol to give colorless crystals in 53 % yield (1.37 g). ^1H NMR (300 MHz, CDCl₃): $\delta = 7.16-7.04$ (m, 6H, ArH), 5.00 (s, 1H, NH), 3.55 (sept, 2H, CH(CH₃)₂), 2.88 (sept, 1H, CH(CH₃)₂), 2.80 (sept, 1H, CH(CH₃)₂), 1.90 (m, 1H, CH₂CH₃), 1.78 (m, 1H, CH₂CH₃), 1.78 (s, 3H, N=CCH₃), 1.24-1.16 (m, 24 H, CH(CH₃)₂, 1.07 (s, 3 H, CH₃), 1.06 ppm (t, 3 H, CH₃); ¹³C NMR (75 MHz, CDCl₃): δ = 174.80, 147.21, 145.77, 140.70, 136.63, 136.00, 124.34, 123.39, 12 3.13, 123.00, 64.88, 32.70, 28.10, 27.97, 27.79, 24.62, 24.48, 24.29, 24.13, 23.69, 23.39, 16.74, 8.59 ppm; elemental analysis calcd (%) for C₃₀H₄₆N₂: C 82.89, H 10.67, N 6.44; found: C 82.64, H 10.43, N 6.21.

Synthesis of ArN=C(Me)–C(Me)(*n*Bu)–NHAr (Ar = diisopropylphenyl; L3)

Under nitrogen atmosphere, a solution of ArN=C(Me)-C(Me)=NAr (2.04 g, 5.05 mmol) in anhydrous toluene (20 mL) was introduced into a 100 mL Schlenk flask, and then *n*-butyllithium (3.2 mL, 1.6 m in hexane) was injected slowly by syringe at room temperature.

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The reaction mixture was stirred at room temperature for 2 h. After the solution was cooled to $0\,^\circ\text{C}$ in an ice/water bath, the reaction mixture was carefully hydrolyzed by adding ice/water. The organic layer was separated and dried over MgSO4, and the solvent was evaporated. The desired product was obtained by slow evaporation of solvent after addition of ethanol to the residual oil. The crude product was purified by recrystallization from hot ethanol to give white crystals in 29% yield (0.68 g). ¹H NMR (300 MHz, CDCl₃): $\delta = 7.17 - 7.04$ (m, 6H, ArH), 4.96 (s, 1H, NH), 3.52 (sept, 2H, CH(CH₃)₂), 2.90 (sept, 1H, CH(CH₃)₂), 2.79 (sept, 1H, CH(CH₃)₂), 1.78 (s, 3 H, CH₃), 1.32 (m, 2 H, CH₂), 1.23-1.16 (m, 24 H, CH₃), 1.08 (s, 3 H, CH₃), 0.94 ppm (t, 3 H, CH₃); ¹³C NMR (75 MHz, CDCl₃): δ = 175.05, 146.97, 145.72, 140.81, 136.66, 135.95, 124.32, 123.41, 123.13, 123.00, 64.56, 40.59, 28.14, 27.88, 27.77, 26.79, 24.80, 24.58, 24.34, 24.05, 23.77, 23.69, 23.51, 23.11, 16.82, 14.45 ppm; elemental analysis calcd (%) for C₃₂H₅₀N₂: C 83.06, H 10.89, N 6.05; found: C 82.95, H 10.63, N 6.10%.

Synthesis of ArN=C(Me)-C(Me)(Ph)-NHAr (Ar = diisopropylphenyl; L4)

Under nitrogen atmosphere, a solution of ArN=C(Me)-C(Ph)=NAr (0.93 g, 2 mmol) in toluene (30 mL) was introduced into a 100 mL Schlenk flask, and then trimethylaluminum (1 mL, 2.0 M in toluene) was injected slowly by syringe at room temperature. The reaction mixture was heated to reflux for 4 h. After the solution was cooled to 0°C in an ice/water bath, the reaction mixture was carefully hydrolyzed with 5% aqueous NaOH solution. The organic layer was separated and dried over MgSO₄, and the solvent was evaporated. The crude product was recrystallized from hot ethanol to obtain ligand L4 as colorless crystals in 85.0% yield. ¹H NMR (300 MHz, CDCl₃): $\delta = 7.70$ (d, 2H, phenyl α -H), 7.40–7.07 (m, 9H, ArH), 6.45 (s, 1H, CNH), 3.17-2.83 (m, 4H, CH(CH₃)₂), 1.54-1.52 (d, 3H, C(CH₃)), 1.44–1.43 (d, 3 H, C(CH₃)), 1.31–0.96 ppm (m, 24 H, CH(CH₃)₂); ¹³C NMR (75 MHz, CDCl₃): $\delta = 174.10$ (C=N), 147.28 (C_{Ar}-N), 145.57, 141.83, 137.44, 136.77, 128.19, 127.66, 127.22, 124.09, 123.80, 123.42, 66.19 (C-NH), 28.68, 28.22, 25.08, 24.33, 24.24, 23.94, 0.79, 17.72 ppm; elemental analysis calcd (%) for $C_{34}H_{46}N_2\!\!:$ C 84.68, H 9.42, N 5.82; found: C 84.59, H 9.60, N 5.80.

Synthesis of $ArN=C(Me)-CH_2-NHAr$ (Ar = diisopropylphenyl; L5)

Under nitrogen atmosphere, a solution of ArN=CH-CH=NAr (2.82 g, 7.5 mmol) in toluene (50 mL) was introduced into a 100 mL Schlenk flask, and then trimethylaluminum (6 mL, 2.0 M in toluene) was injected slowly by syringe at room temperature. The reaction mixture was heated to reflux overnight. After the solution was cooled to 0°C in an ice/water bath, the reaction mixture was carefully hydrolyzed with 5% aqueous NaOH solution. The organic layer was separated and dried over MgSO₄, and the solvent was evaporated. The desired product was obtained by slow evaporation of solvent after addition of ethanol to the residual oil. The crude product was purified by reisolation from hot ethanol to give L5 as a light yellow liquid in 93% yield. The product was characterized as the methyl-transfer compound, as reported previously by others. ¹H NMR (300 MHz, CDCl₃): $\delta = 7.19-7.04$ (m, 6H, ArH), 5.04 (s, 1 H, NH), 3.99 (s, 2 H, CH₂), 3.45 (septet, 2 H, CH(CH₃)₂), 2.78 (septet, 2H, CH(CH₃)₂), 1.72 (s, 3H, CH₃), 1.29 (d, 12H, CH₃), 1.19-1.15 ppm (m, 12 H, CH₃); ¹³C NMR (75 MHz, CDCl₃): $\delta = 167.48$, 145.48, 144.59, 141.26, 136.58, 123.62, 123.48, 123.03, 122.79, 58.25, 28.06, 24.14, 23.62, 23.01, 19.24 ppm; elemental analysis calcd (%) for $C_{27}H_{40}N_2$: C 86.00, H 8.58, N 5.42; found: C 86.03, H 8.41, N 5.48.

Synthesis of ArN=C(Me)-CH(*i*Pr)-NHAr (Ar = diisopropylphenyl; L6)

Following the procedure used for ligand L3, the reaction of *i*PrMgBr and α -diimine compound ArN=C(Me)–CH=N–Ar (Ar = diisopropylphenyl) gave ligand L6 as colorless crystals in 83% yield. ¹H NMR (300 MHz, CDCl₃): δ = 7.08–6.86 (m, 6H, ArH), 4.10 (d, 1H, NH), 3.42–2.39 (m, 4H, CH(CH₃)₂), 2.53–2.39 (m, 2H), 2.21–2.15 (m, 1H, CH–NH), 2.27–2.18 (m, 1H), 1.29–1.20 (m, 20H, CH(CH₃)₂), 1.18–1.00 ppm (d, 14H, CCH₃); ¹³C NMR (75 MHz, CDCl₃): δ = 172.31 (C=N), 146.33 (C_{Ar}–N), 142.18 (C_{Ar}–NH), 139.60, 136.45, 136.28, 123.83, 123.44, 123.23, 122.97, 121.93, 71.59 (C–NH), 36.92 (C(CH₃)₃), 28.61, 28.18, 27.97, 24.49, 24.36, 24.26, 24.00, 23.33, 20.30, 19.80, 19.38 ppm (C–CH₃); elemental analysis calcd (%) for C₃₀H₄₆N₂: C 82.77, H 10.51, N 6.41; found: C 82.89, H 10.67, N 6.44.

Synthesis of ArN=C(Me)-CH(tBu)-NHAr (Ar = diisopropylphenyl; L7)

tBuMgCl was prepared according to the reported procedure and used freshly for subsequent reaction without further treatment.^[23] A solution of ArN=C(Me)-CH=NAr (2.25 g, 6 mmol) in anhydrous diethyl ether (10 mL) was added to the stirred Grignard reagent (60 mL, 1.2 м in diethyl ether) by syringe. The mixture was allowed to stir overnight at room temperature. The reaction was terminated by pouring into a concentrated aqueous solution of NH₄Cl. The organic layer was separated and dried over MgSO₄. A crude product was obtained after removal of organic solvent and purified by recrystallization from hot ethanol to give ligand L7 as a colorless crystals in 71% yield. ¹H NMR (300 MHz, CDCl₃): $\delta = 7.05-6.86$ (m, 6H, ArH), 4.22 (d, 1H, NH), 4.12-3.30 (m, 4H, CH(CH₃)₂), 2.44-2.53 (m, 1H, CH-NH), 2.27-2.18 (m, 1H), 1.29-1.21 (m, 24H, CH(CH₃)₂), 1.00–0.93 ppm (d, 11 H, CCH₃); ¹³C NMR(75 MHz, CDCl₃): δ = 173.00, 146.61, 142.32, 138.43, 136.37, 36.05, 123.51, 123.31, 123.13, 121.42, 74.12, 36.95, 28.76, 28.30, 28.07, 24.76, 24.39, 23.97, 23.36, 22.02 ppm; elemental analysis calcd (%) for C₃₁H₄₈N₂: C 82.98, H 10.78, N 6.24; found: C 82.89, H 10.80, N 6.17.

Synthesis of ArN=CH-CH(tBu)-NHAr (Ar = diisopropylphenyl; L8)

Following the procedure used for ligand **L7**, the reaction of tBuMgCl and ArN=CH-CH=NAr gave ligand **L8** as colorless crystal in 68% yield. ¹H NMR (300 MHz, CDCl₃): δ = 7.52-7.50 (d, 1 H, HC= N), 7.13-6.96 (m, 6H, ArH), 4.00-3.98 (d, 1 H, NH), 3.46-2.66 (m, 4 H, CH(CH₃)₂), 2.34-2.25 (m, 1 H, HC-NH), 1.29-1.13 (m, 24 H, CH(CH₃)₂), 0.93-0.90 ppm (m, 9 H, C(CH₃)₃); ¹³C NMR(75 MHz, CDCl₃): δ = 167.79, 149.06, 141.25, 140.63, 137.44, 124.04, 122.88, 71.78, 35.98, 28.61, 27.75, 27.58, 24.61, 24.07, 23.37 ppm; elemental analysis calcd (%) for C₃₀H₄₆N₂: C 82.89, H 10.67, N 6.44; found: C 82.97, H 10.54, N 6.49.

Synthesis of [NiBr₂(L2)] (2)

Ligand L2 (434 mg, 1 mmol) in dichloromethane (10 mL) was added to a stirred suspension of (DME)NiBr₂ (308 mg, 1 mmol) in dichloromethane (30 mL) at room temperature. Shortly after the addition of ligand, the solution began to turn brown. The suspension was allowed to stir for an additional 5 h at room temperature. The solution was filtered through Celite, and the solvent of the filtrate was removed in vacuum. The residue was recrystallized from $CH_2Cl_2/hexane$ to give complex **2** as a light brown powder in 45% yield. Elemental analysis calcd (%) for $C_{30}H_{46}Br_2N_2Ni$: C 55.16, H

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7.10, N 4.29; found: C 55.29, H 7.06, N 4.39; MS (FAB): m/z=573, 572, 571 [*M*-Br]⁺; 494, 493, 492 [*M*-2Br]⁺; 436, 435, 433 [ligand]⁺.

Synthesis of [NiBr₂(L3)] (3)

Following the above-described procedure, the reaction of (DME)-NiBr₂ and L3 gave complex 3 in 68% yield. Elemental analysis calcd (%) for C₃₂H₅₀Br₂N₂Ni: C 56.42, H 7.40, N 4.11; found: C 56.69, H 7.51, N 3.91; MS (FAB): m/z=601, 600, 599 [*M*-Br]⁺; 522, 521, 520 [*M*-2Br]⁺; 464, 463, 462 [ligand]⁺.

Synthesis of [NiBr₂(L4)] (4)

Following the above-described procedure, the reaction of (DME)-NiBr₂ and L4 gave complex 4 in 71% yield. Elemental analysis calcd (%) for $C_{34}H_{46}Br_2N_2Ni: C 54.75$, H 6.57, N 3.74; found: C 55.03, H 6.61, N 3.89; MS (FAB): m/z=619, 621, [*M*-Br]⁺; 538, 539, 540, [*M*-2 Br]⁺; 481, 483, 484, [*M*-NiBr₂]⁺.

Synthesis of [NiBr₂(L5)] (5)

Following the above-described

procedure, the reaction of (DME)NiBr₂ and L5 gave complex 5 in 86% yield. Elemental analysis calcd (%) for C₂₇H₄₀Br₂N₂Ni: C 53.06, H 6.60, N 4.58; found: C 52.87, H 6.67, N 4.46; MS (FAB): m/z=531, 532 [*M*–Br]⁺; 450, 451, 452 [*M*–2Br]⁺; 392, 393, 394 [ligand]⁺.

Synthesis of [NiBr₂(L6)] (6)

Following the above-described procedure, the reaction of (DME)-NiBr₂ and L6 gave complex 6 in 65% yield. Elemental analysis calcd (%) for C₃₀H₄₆Br₂N₂Ni: C 54.22, H 7.06, N 4.18; found: C 54.16, H 7.10, N 4.29; MS (FAB): m/z=572, 573, 574 [M-Br]⁺; 492, 493 [*M*-2Br]⁺; 434, 435, 436 [ligand]⁺.

Synthesis of [NiBr₂(L7)] (7)

Following the above-described procedure, the reaction of (DME)- $NiBr_{2}$ and $\boldsymbol{L7}$ gave complex $\boldsymbol{7}$ in 92% yield. Elemental analysis calcd (%) for C₃₁H₄₈Br₂N₂Ni: C 55.80, H 7.25, N 4.20; found: C 55.56, H 7.35, N 4.08; MS (FAB): m/z=587, 586 [M-Br]+; 506, 505 [M-2Br]⁺; 451, 450, 449, 448 [ligand]⁺.

Synthesis of [NiBr₂(L8)] (8)

Following the above-described procedure, the reaction of (DME)-NiBr₂ and L8 gave complex 8 in 83% yield. Elemental analysis calcd (%) for $C_{30}H_{46}Br_2N_2Ni$: C 55.16, H 7.10, N 4.29; found: C 54.91, H 7.18, N 4.04; MS (FAB): m/z=573, 574 [M-Br]⁺; 491, 492, 493 [*M*–2Br]⁺; 434, 435, 436 [ligand]⁺.

Crystal-structure determination

The crystals were mounted on glass fibers and transferred to a Bruker SMART 1000 CCD diffractometer, and data were collected

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2

1244 1384 0.44×0.31×0.24 $0.22 \times 0.20 \times 0.15$ $0.41 \times 0.35 \times 0.10$ 1.89-26.42 1.23-27.09 $-12 \le h \le 12$ $-15 \le h \le 15$ $-21 \le k \le 21$ $-26 \le k \le 26$ -11 < l < 12-24 < l < 2421 225/2935 26674/13483 0.0311 0.0780 99.1% 97.0% 0.5307/0.3497 0.618/0.509 0.7423/0.3566 2935/0/165 13483/0/709 1.186 1.059 $R_1 = 0.0754, wR_2 = 0.1512$ $R_1 = 0.0384, wR_2 = 0.0930$ $R_1 = 0.0377, wR_2 = 0.0942$ $R_1 = 0.0619, wR_2 = 0.1033$ $R_1 = 0.1099, wR_2 = 0.1617$ $R_1 = 0.0695, wR_2 = 0.1090$ 0.950/-0.378 0.850/-1.592 1.378/-0.506 in the ω -2 θ scan mode with graphite-monochromated Mo_{Ka} radiation ($\lambda = 0.71073$ Å) at 293 K. The structures were solved by direct

methods, and further refinement by full-matrix least-squares methods on F^2 was performed with the SHELXTL program package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in calculated positions with the displacement factors of the host carbon atoms. Crystal data and structure-refinement parameters are listed in Table 3. CCDC 961650 (4), 961651 (5) and 961652 (7) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data request/cif.

Acknowledgements

Table 3. Crystal data and structure refinement for nickel complexes 4, 5, and 7.

 $C_{34}H_{46}Br_2N_2Ni$

monoclinic

12.753(2)

24.757(4)

90.413(3)

3311.5(10)

1.60-27.06

 $-16 \le h \le 12$

 $-13 \le k \le 9$

-31 < l < 31

16448/7146

7146/0/377

0.0301

98.1%

1.046

90

90

4

1.407

1448

10.4887(18)

701.26

P2₁/c

4

empirical formula

formula weight

crystal system

space group

a [Å]

b [Å]

c [Å]

 α [°]

β[°]

 γ [°]

V [ų]

F(000)

Rint

 $ho_{
m calcd}\,[
m g\,cm^{-3}]$

 θ range [°]

index ranges

crystal size [mm]

reflns collected/unique

Transmission (max./min.)

data/restraints/parameters

largest diff. peak/hole [e Å⁻³]

data completeness

goodness of fit on F²

R indices $[l > 2\sigma(l)]$

R indices (all data)

Ζ

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Keywords: N ligands · nickel · polymerization · polymers · substituent effects

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 $\mathsf{C}_{31}\mathsf{H}_{48}\mathsf{Br}_2\mathsf{N}_2\mathsf{Ni}$

667.24

triclinic

9.9228(13)

16.740(2)

19.513(3)

83.465(2)

79.838(2)

83.492(2)

3155.3(7)

4

1.405

ΡĪ

7

 $C_{27}H_{37}Br_2N_2Ni$

orthorhombic

608.12

Pnma

12.587(5)

21.541(9)

10.380(5)

90

90

90

4

2815(2)

1.435

32	32

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