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Thermostable α-Diimine Nickel(II) Catalyst for Ethylene Polymerization: Effects of the Substituted Backbone Structure on Catalytic Properties and Branching Structure of Polyethylene

Feng-Shou Liu,[†,‡] Hai-Bin Hu,[†] Ying Xu,[†] Li-Hua Guo,[†] Shao-Bo Zai,[†] Ke-Ming Song,[†] Hai-Yang Gao,*[†] Ling Zhang,[†] Fang-Ming Zhu,[†] and Qing Wu*[†,‡]

[†] *DSAPM Lab, Institute of Polymer Science, School of Chemistry and Chemical Engineering, Sun Yat-Sen (Zhongshan) University, Guangzhou, 510275, China, and* [‡] *PCFM Lab, OFCM Institute, Sun Yat-Sen (Zhongshan) University, Guangzhou, 510275, China*

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ABSTRACT: On the basis of the strategy of promoting thermostability of α-diimine nickel catalyst by ligand backbone framework, a series of α-diimine nickel(II) complexes with bulky camphyl or diaryl-substituted backbones, $[2,6\text{-}(R^2)_2C_6H_3{-}N{=}C(R^1){-}C(R^1){=}N{-}2,6\text{-}(R^2)_2C_6H_3]NiBr_2$ (**1a**, R^1 = Ph, R^2 = CH_3; **2a**, R^1 = 4-methylphenyl, R^2 = CH_3; **3a**, R^1 = 4-fluorophenyl, R^2 = CH_3; **4a**, R^1 = camphyl, R^2 = CH_3; **4b**, R^1 = camphyl, R^2 = *i*-Pr), were synthesized and used as catalyst precursors for ethylene polymerization. Crystallographic analysis revealed that the bulky camphyl backbone has a valid steric-effect on the nickel center by blocking the axial site for the metal center and suppressing the potential rotation of the $C_{Ar}{-}N$ bond. Ethylene polymerizations catalyzed by these nickel α-diimine complexes activated by MAO were systematically investigated and the influences of the substituted backbones as well as reaction temperature on the catalytic activity, molecular weight and branching structure of the polymers were evaluated. It was found that the catalysts containing a camphyl backbone have excellent thermal stability and polymer structure control for ethylene polymerizations. Even at 80 °C, the **4b**/MAO system still kept high activity and relatively stable kinetics and produced high molecular weight polyethylene. Moreover, the branching degrees and branched chain distribution of the polyethylenes obtained by the complex could also be controlled by tuning the reaction temperature.

Introduction

Since Brookhart and co-workers discovered nickel and palladium(II) aryl-substituted α-diimine catalysts for olefin polymerization,[1] late transition metal catalysts have been a topic of significant interest because they can produce polymers with various types of branches and have good tolerance toward functional groups.[2] As to nickel α-diimine catalysts, it was found that the alkyl substituents on *o*-aniline moieties show important influences on the polymerization activities and polymer microstructures.[3,4] For instance, olefinic oligomers and high molecular weight of branched polyethylenes can be obtained by tuning alkyl substituents. Moreover, living polymerization has been achieved by a delicate design on ligand structures, and even the sequence length and regioregular block of copolymers could be controlled under a 1-fold monomer by changing the polymerization temperature.[5] Though these catalysts mentioned above exhibited excellent catalytic properties, one drawback is their relatively low thermal stability.[6] It has been reported that nickel α-diimine catalysts tend to decay rapidly over 60 °C because aniline moieties may freely rotate away from the perpendicular orientation, resulting in increased associative chain transfer and C−H activation.[6] Moreover, the molecular weight of the obtained polyethylene also dropped rapidly as the reaction temperature increased.

Recently, some approaches have been applied in improving the thermal stability of the catalyst. Modification in substituents on the *ortho*-position of the aniline has been an important method for improving thermal stability (Scheme 1). Reiger developed a series of bulky 2,6-diaryl-substituted diimine catalysts, which exhibited high activities for ethylene polymerization at high temperature in the presence of hydrogen.[7a,b] Subsequently, Ionkin reported *o*-benzofuran-substitued diimine catalysts which produced ultrahigh molecular weight polyethylene at 70 °C.[7c] A novel cyclophane-based α-diimine catalyst synthesized by Guan, in which the cyclophane framework shields all directions of the metal center except two coordination sites, showed high activities and significantly higher thermostable properties for olefin polymerization than the acyclic analogues.[8]

On the other hand, it is worth noting that the backbone groups (derived from diketone) behind the metal center also played an important role in catalytic olefin polymerization.[3c,d,6,9] Okuda[9a] and Zhu[9c] revealed that catalysts bearing 1,4-diazadiene ligands derived from glyoxal produced low molecular weight and linear polyethylene. Comparatively, catalysts with backbones of methyl (alkyl group) and acenaphthyl substituents obtained higher molecular weight and branched polyethylene. Furthermore, alkyl substituents on backbones tended to give higher molecular weight polymers with more narrow molecular distributions than the planar acenaphthyl backbones.[6] Despite all this, the modification in backbone group for improving thermal stability of catalyst remains to be explored.

As for ethylene polymerization, our interest lies in systematic observation of substituted bulky backbones along with electronic effect. Considering that substituted bulky backbone may enhance the stability of nickel α-diimine complexes by hindering the rotation of aniline moieties and protecting the metal center effectively, 1,2-diarylethanediimine and camphyldiimine were

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*Corresponding authors. E-mail: (Q.W.) ceswuq@mail.sysu.edu.cn; (H.-Y.G.) gaohy@mail.sysu.edu.cn.

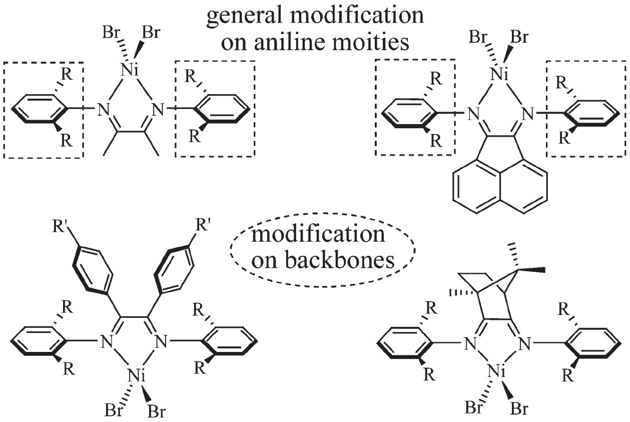
designed as ligands. Herein, we report the syntheses of a series of new nickel α-diimine complexes and the influence of the substituted backbone on catalytic properties in ethylene polymerization.

Results and Discussion

Synthesis of α-Diimine Ligands and Corresponding Nickel(II) Complexes. The procedures in preparation of ligands **L1a**, **L2a**, **L3a** and **L4a-b** and corresponding nickel(II) complexes **1a**, **2a**, **3a**, and **4a**,**b** are shown in Scheme 2. α-Diimine ligands used to be prepared by acid-catalyzed condensation between primary anilines and diketone in ethanol or toluene solution.[3,4] However, an attempt to synthesize the α-diimines containing bulky backbones was unsuccessful under similar conditions. Therefore, the primary aniline was first treated with trimethylaluminum (TMA) to form aminoalane dimer.[10] Because of the fact that Al−O bond is significantly stronger than Al−N bond, aminoalanes are effective reagent for converting bulky ketones into imines. As a result, the α-diimine ligands were produced in good yields. The α-diimine nickel(II) dibromide complexes were readily obtained from the reaction of the corresponding ligands with (DME)$NiBr_2$ in high yields.

All of the nickel complexes were confirmed by elemental analysis and FAB^+−MS. High resolution NMR spectroscopic analysis of these complexes is impossible because of their paramagnetism. Fortunately, single crystal of **4a** with camphyl backbone suitable for X-ray diffraction analysis was obtained from a dichloromethane solution layered with hexane. As shown in Figure 1, the crystal structure of **4a** with a camphyl backbone displays a distorted tetrahedral geometry. Similar to the related structures,[4b,1] the aryl rings on aniline moieties are approximately perpendicular to the chelate ring. As to the camphyl backbone framework, it is significant to note that the *gem*-dimethyl substituents (C(16) and C(17)) are oriented toward the axial position indicating a steric effect on the metal center, and another methyl C(18) lies behind one of the aryl rings, which could suppress the potential rotation or fluctuation of the C_{Ar}−N bond in solution.

Scheme 1. Structure of Nickel α-Diimine Complexes



Ethylene Polymerization. *1. Influences of Ligand Structure.* On treatment with MAO, all the nickel complexes were highly active for ethylene polymerization. To evaluate the effect of catalyst structure on ethylene polymerization, all catalysts were screened under similar conditions and compared with the typical α-diimine nickel catalysts **5a** and **5b** containing acenaphthyl backbone.[6] The polymerization data from experiments carried out at 40 °C and 0.5 atm of ethylene are listed in Table 1 (entries 3, 6, 9, 12, 15, 18, and 25).

Similar to previous observations,[6] the catalysts with 2,6-diisopropyl substituent on aniline moieties (**4b**, **5b**) showed higher turnover frequencies (TOF) and yielded higher molecular weight of polymer than their analogues with 2,6-dimeth-

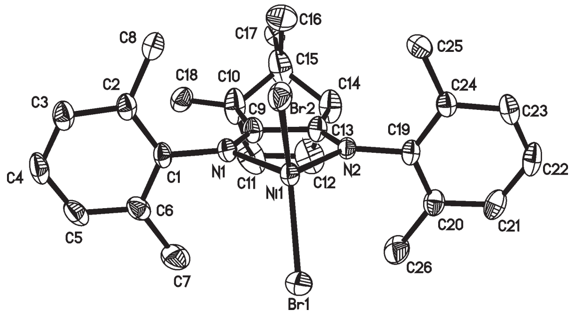


Figure 1. Molecular structure of **4a** depicted with 30% thermal ellipsoids and with hydrogen atoms omitted. Selected bond distances (Å) and angles (deg): Ni(1)−N(1) 2.021(5), Ni(1)−N(2) 2.027(6), Ni(1)−Br(1) 2.3415(14), Ni(1)−Br(2) 2.3063(13); N(1)−Ni(1)−N(2) 83.3(2), N(1)−Ni(1)−Br(1) 111.04(17), N(1)−Ni(1)−Br(2) 109.89(17), N(2)−Ni(1)−Br(1) 103.3(2), N(2)−Ni(1)−Br(2) 119.2(2), Br(1)−Ni(1)−Br(2) 123.08(5).

Scheme 2. Syntheses of α-Diimine Ligands and Corresponding Nickel Complexes

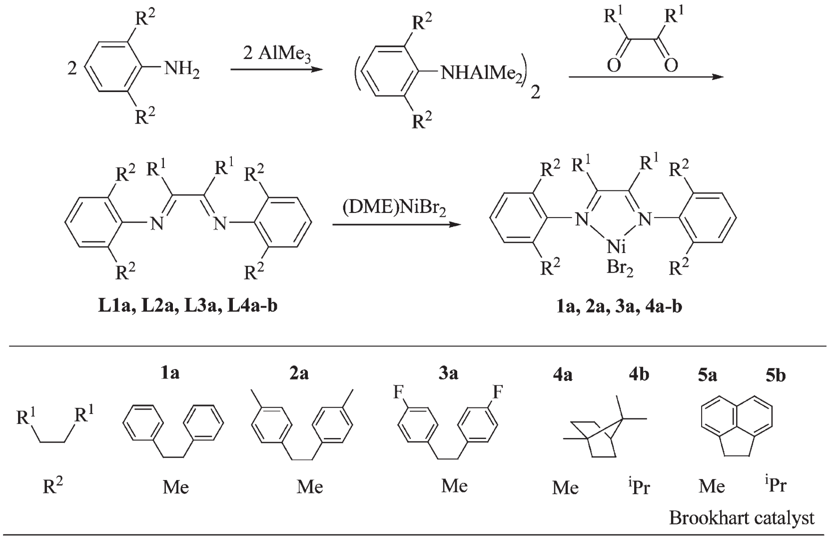


Table 1. Ethylene Polymerizations with Different Complex/MAO Systems[a]

								thermal transitions (°C)	
entry	catalyst	temp (°C)	yield (g)	TOF ($\times 10^{-4}$/h)	M_n (kg/mol)	PDI	branching degrees (per 1000C)	T_g	T_m
1	**la**	0	0.83	1.19	150.7	2.2	15.0		78, 131
2		20	1.24	1.77	92.4	2.3	35.2	−18	92, 102
3		40	0.85	1.21	41.0	2.0	69.6	−48	
4	**2a**	0	0.80	1.14	177.2	2.0	22.9		80, 110
5		20	1.29	1.84	103.0	2.2	41.8	−18	83, 102
6		40	0.85	1.21	35.1	2.1	81.8	−50	
7	**3a**	0	0.94	1.34	119.9	2.5	13.1		126
8		20	1.81	2.59	68.8	2.2	20.7	−21	120
9		40	1.22	1.74	27.6	2.0	62.5	−49	
10	**4a**	0	1.36	1.94	152.8	2.4	20.2		66, 125
11		20	1.80	2.57	94.0	2.3	63.2	−45	34, 65
12		40	1.02	1.46	61.3	2.3	88.5	−51	
13	**5a**	0	0.97	1.39	48.1	2.5	11.8		126
14		20	0.81	1.16	23.8	2.5	15.6		117
15		40	0.54	0.77	12.7	2.7	23.4		110
16	**4b**	0	1.19	1.70	209.4	2.5	89.3	−39	44, 58
17		20	1.23	1.76	199.2	2.6	125.5	−46	
18		40	1.37	1.96	156.0	2.7	133.3	−49	
19		60	1.34	1.91	154.9	2.7	135.5	−52	
20		80	0.88	1.26	122.9	2.0	129.4	−53	
21[b]		40	6.46	9.23	309.3	2.8	119.1		
22[b]		80	6.29	8.99	233.2	2.7	125.7		
23	**5b**	0	2.40	3.43	224.9	2.9	58.1	−19	81
24		20	1.92	2.74	135.6	2.7	102.4	−24	
25		40	1.54	2.20	109.5	2.5	209.6	−45	
26		60	1.17	1.67	56.7	2.4	229.2	−61	
27		80	0.26	0.37	34.2	2.7	219.2	−63	

[a] Reaction conditions: Ni=5 μmol; Al/Ni = 600; t_p = 0.5 h; toluene 20 mL; 0.5 atm of ethylene. [b] Reaction conditions: Ni=5 μmol; Al/Ni=600; t_p=0.5 h; toluene 100 mL; 5 atm of ethylene.

yl substituent (**4a**, **5a**). The results can be ascribed to the increase in steric hindrance of the *ortho*-substituents, leading to an increase in the rate of chain propagation relative to chain transfer and a stabilization of the insertion transition state relative to the resting state.[6,11] On the other hand, a significant comparison between these two sets of catalysts shows that there are great differences to the extent of increasing TOF and molecular weight of polymer when bulkier *ortho*-substituents are introduced into the aniline moieties. For the catalysts containing camphyl backbone, replacement of 2,6-dimethyl-substituent (**4a**) by 2,6-diisopropyl-substituent (**4b**) led to an increase of 34% in TOF from 1.46×10^4 to 1.96×10^4 h^{-1} and an increase of 160% in molecular weight of polyethylene from 61.3 to 156.0 kg/mol. It was much less than the catalysts containing acenaphthyl backbone for replacement of **5a** by **5b**, which showed an increase of 190% in TOF from 0.77×10^4 to 2.20×10^4 h^{-1} and an increase of 760% in molecular weight of polyethylene from 12.7 to 109.5 kg/mol. Although the TOF value of **5b** was roughly similar to that of **4b**, the molecular weight of polyethylene produced by **5b** was lower than that of **4b**. The less fluctuations in the TOF and polymer molecular weight with altering *ortho*-substituents on aniline moieties for the catalysts containing camphyl backbone can be ascribed to an effective steric effect of the backbone group on metal center, so that the catalytic center even containing less bulky *ortho*-substituents can be stabilized. These facts suggest that the bulky backbone-substituent can play an important role in improving catalytic behaviors.

As shown in Table 1, among the catalysts with the same 2,6-dimethyl-substituent on aniline moieties but different backbones (**1**−**5a**), **4a** with a bicyclic-substituted backbone yielded the highest molecular weight of polyethylene (61.3 kg/mol), catalysts **1**−**3a** with diaryl-substituted backbone came second (27.6−41.0 kg/mol), and **5a** with acenaphthyl backbone produced the lowest one (12.7 kg/mol). On account of bearing the same aniline substitution, the observed discrimination of catalytic properties can be ascribed to the efficiency of steric hindrance of the backbone groups. Even though **5a** contains a large acenaphthyl group, it is a planar substituent in a coplanar fashion with the chelating ring, which lies far away from the nickel atom and has less effect on protecting the metal center.[4a,b,l] As compared with **5a**, **1**−**3a** bearing two aryl groups on the backbone could exhibit a certain steric effect on retarding the rotation of aniline moieties. Especially, **4a** with a bicyclic-substituted backbone shows a superior steric hindrance on the nickel center.

Besides the steric effect, we have also investigated the electronic effect of the backbone framework on ethylene polymerization by using catalysts **1**−**3a** containing phenyl, 4-methylphenyl, and 4-fluorophenyl, respectively. Catalyst **3a** bearing the electron-withdrawing nature of the 4-fluorophenyl substituents on the backbone showed the highest TOF and yielded the lowest molecular weight of polyethylene among these three catalysts. The observation on backbone was not all in accord with that of *para*-substituent on aniline moieties, which showed an overall trend of lower catalytic TOF and lower molecular weight polyethylene produced with catalysts bearing more electronic-withdrawing ligands.[12] The reason for the different electronic-effects of the substituent on different part of α-diimine on TOF is unclear.

Backbone structure also influenced the branching degrees of the obtained polyethylene. With the catalysts containing the same 2,6-dimethyl-substituent on aniline moieties (**1**−**5a**), the dependence of branching degrees upon backbone structure followed a similar trend shown in molecular weight of polyethylene, i.e., polyethylene obtained with **4a** had the highest branching degrees (88.5 branches/1000C) and that of polyethylene obtained with **5a** showed the lowest (23.4 branches/1000C) under the same condition (40 °C). In addition, the branching degrees were also observed to increase with more steric bulk on aniline moieties. For example, the branching degrees of polyethylene prepared by using

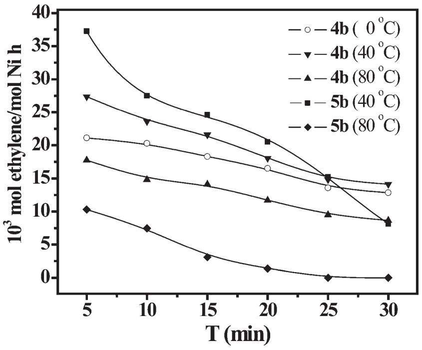


Figure 2. Plots of polymerization rate vs time in ethylene polymerization reactions.

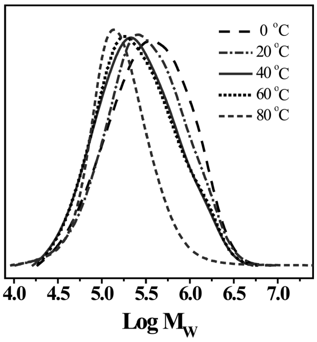


Figure 3. GPC curves of polyethylene samples prepared by **4b**/MAO at different temperature.

catalyst **4a** were 88.5 branches/1000C, whereas 133.3 branches/1000C were found when bulkier **4b** was employed. These observations suggest that the relative rates of monomer insertion and chain walking ($K_{\text{ins}}/K_{\text{w}}$) are affected dually by steric bulks of both aniline moiety and backbone structure.

2. Influences of Polymerization Temperature. In general, traditional α-diimine late-transition-metal catalysts are highly sensitive to temperature, and show the maximum activities at room temperature or below and decompose rapidly at 50−70 °C.[1,6,8] Herein, ethylene polymerizations carried out at different temperatures with catalysts containing different backbones and *ortho*-substituted anilines and the effect of temperature on catalytic properties are reported.

As shown in Table 1, all catalysts **1**−**4a** containing 2,6-dimethylaniline exhibited the highest TOF for ethylene polymerization at 20 °C; however, the TOF of **5a** with acenaphthyl backbone decreased continuously with increasing temperature from 0 to 40 °C. In addition, at an elevated temperature, the molecular weight of the polyethylene produced by each catalyst was found to decrease dramatically, along with the corresponding increase in branching degrees. For example, when **4a** was employed, the M_{n} dropped from 152.8 kg/mol at 0 °C to 94.0 kg/mol at 20 °C and then to 61.3 kg/mol at 40 °C, and the branching degrees increased from 20.2 branches/1000C at 0 °C to 63.2 branches/1000C at 20 °C and then to 88.5 branches/1000C at 40 °C. These results suggest that both the relative rate of chain transfer and monomer insertion ($K_{\text{tr}}/K_{\text{ins}}$) and that of chain walking and monomer insertion ($K_{\text{w}}/K_{\text{ins}}$) increase with increasing temperature. It is worth noting that catalyst **4b** containing camphyl backbone and 2,6-diisopropylaniline showed a fine thermostability over the temperature range of 0−80 °C for ethylene polymerization. Its catalytic TOF reached a maximum value at 40 °C and then decreased slowly with rising temperature. The TOF value decreased from $1.96 \times 10^4\ \text{h}^{-1}$ at 40 °C to $1.26 \times 10^4\ \text{h}^{-1}$ at 80 °C only by 35%. The slight reduction of TOF with increasing temperature can be solely attributed to a decrease in ethylene solubility in toluene.[13] Raising the ethylene pressure to 5 atm, TOF values of **4b** increased to $9.23 \times 10^4\ \text{h}^{-1}$ at 40 °C and $8.99 \times 10^4\ \text{h}^{-1}$ at 80 °C, respectively, which further demonstrates the thermostability of **4b** catalyst and the dependence of TOF on ethylene solubility in toluene. In contrast, the polymerizations with **5b** containing acenaphthyl backbone showed a continuous decrease in TOF by a bigger margin as temperature increased from 0 to 60 °C and then dropped rapidly over 60 °C. In order to gain further information concerning catalyst stability, the rates of ethylene consumption over a period of 30 min at different temperatures were measured. As shown in Figure 2, at temperatures of 0−80 °C, relatively slow activity decay was observed for **4b**, while **5b** showed a sufficiently rapid decline of the activity. In the setting time of 30 min with catalyst **4b**, the rate of ethylene consumption decreases only by 48% at 40 °C and by 51% at 80 °C. However, with **5b,** the rate decreased by 78% at 40 °C over 30 min, and even no ethylene consumption was observed after 20 min at 80 °C which implied an entire decomposition of the catalyst. As reported in the literature,[14] mass transfer limitation can be affected greatly by the amount of polymer in solution, and it is only minor effect when polymer content is less than 15 mass % and sharply severe when polymer content is above 30 mass %. In general, the polyethylene contents in toluene were in a range of 2−14 mass % in the ethylene polymerizations reported herein. Therefore, the mass transfer limitations were not serious under the conditions though there might exist mass transfer limitations to some extent for the polymerizations by **5b** at temperatures ≤40 °C due to the fast polymerization rate in the early stage. The results suggest that the more steric bulky backbone can effectively prolong catalyst lifetime, especially at high temperatures.

Furthermore, the M_{n} value of polyethylene produced by **4b** did not drop as fast as the temperature rose, and the polydispersities (PDI) were close to 2 and appeared as a single modal in GPC chromatograms, which indicated that the polymerizations occur at the single active site (see Table 1 and Figure 3). Even at 80 °C, the M_{n} value was still as high as 122.9 kg/mol, and decreased only by 41% as compared with the M_{n} (209.4 kg/mol) obtained at 0 °C. In contrast, the M_{n} value was reduced by a factor of 7 as increasing temperature from 0 to 80 °C with **5b**. The result once again demonstrated the excellent thermostability of **4b** complex and the valid suppression of chain transfer at high temperature.

For deactivation in α-diimine metal polymerization catalysts, a possible reason has been proposed that the metal center reacts with the C−H bonds of the *o*-aryl substituents on aniline moiety (C−H activation) to give a six-membered metallacycle.[15] At elevated temperature, the aryl rings on the aniline moieties may freely rotate into the square plane of the complex, resulting in an increase in the C−H activation. Therefore, increasing the steric bulk of the ligand is expected to make this process less favorable. Recently, a successful cyclophane-based catalyst was reported that connected two aniline groups through a macrocycle could prohibit free rotation of the aryl−N bond and showed high thermal stability.[8a] As mentioned above, the *gem*-dimethyl groups of the camphyl backbone are oriented to the axial sites and partially block the axial face of the metal, and another methyl substituent lies behind one of the aniline moieties. As a result, the bulky backbone can prohibit free C_{Ar}−N bond rotation or fluctuation and decrease associative chain

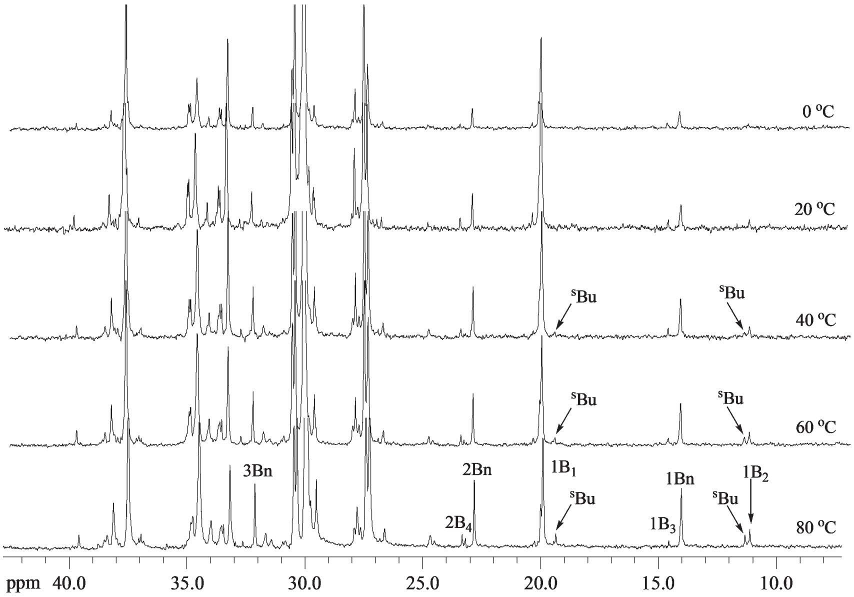


Figure 4. ^{13}C NMR spectra of polyethylene samples synthesized by **4b**/MAO at different temperature.

Table 2. Branched Chain Distributions of Polyethylenes Obtained with 4b and 5b/MAO

			branched chain (%)						
entry	catalyst	T (°C)	Me	Et	Pr	Bu	Pe	Lg	branches (per 1000C)
16	**4b**	0	82.5	2.2	1.5	0.9	0	12.9	89.3
17		20	79.6	4.3	2.8	2.2	0	11.1	125.5
18		40	69.9	6.1	3.0	1.6	0.9	18.5	133.3
19		60	63.5	8.4	2.8	2.4	2.1	20.8	135.5
20		80	58.2	11.4	1.5	5.1	0.8	23.0	129.4
23	**5b**	0	74.6	5.9	4.1	2.8	2.8	9.8	58.1
24		20	73.2	6.1	4.0	2.9	2.5	11.3	102.4
25		40	73.4	6.6	3.5	3.1	3	10.4	209.6
26		60	60.1	16.4	2.1	5.5	2.1	13.8	229.2
27		80	59.8	20.3	1.0	5.3	1.5	12.1	219.2

transfer. Consequently, the catalyst showed high activity and thermal stability for ethylene polymerization and could produce high molecular weight polymer at high temperature. Besides, the bulky backbone can also retard the decomposition of the catalyst.[6]

In general, the branching degrees of the obtained polyethylenes prepared by all catalysts were observed to increase with more steric bulky ligands and increasing temperature when polymerization temperatures were limited to below 40 °C (see Table 1). At the elevated temperature range of 40−80 °C, the branching degrees, however, were kept in a basically unchanged level. For example, the branching degrees of the polyethylenes prepared by **4b** at 40, 60, and 80 °C are 133.3, 135.5, and 129.4 branches/1000C, respectively. A similar trend in the dependence of branching degrees on temperature was observed for **5b**, but it produced lower branching degree polyethylenes at temperatures below 40 °C and higher branching degree polyethylenes at temperatures above 40 °C than those produced by **4b** under the same conditions. The observation also indicated a relatively low sensitivity of the branching degrees to temperature for **4b**, which may be ascribed to an inapparent discrimination of energy barriers between ethylene insertion and chain walking in the process of polymerization. The bulky camphyl-backbone of **4b** is likely to partially retard the monomer coordination to the active species, leading to an increased energy for ethylene insertion into growing chain relative to chain walking.[16]

Besides, it is noteworthy that though the total number of branches per 1000 carbons of polyethylenes remains essentially constant at the polymerization temperatures of 20−80 °C, the topology of the polyethylene prepared by **4b** varies significantly. The branching distributions of the polyethylenes were detected by ^{13}C NMR spectroscopy (Figure 4) and the data are listed in Table 2. As shown in Table 2, the methyl branch decreased and meanwhile the long branched chains (≥C6) increased as the increase of reaction temperature, implying that the Ni species can migrate over a larger number of carbons prior to insertion at elevated temperatures. Most significantly, at the reaction temperatures of 40−80 °C, *sec*-butyl branches, the shortest branch-on-branch structure generated via chain walking through tertiary carbons can be seen from the methyl and ethyl resonances centered at 19.44 and 11.72 ppm,[17] respectively. By comparison, the branched chain distributions of the polyethylenes obtained with **5b** are less sensitive to temperature.

The thermal properties of these branched polyethylenes were detected by differential scanning calorimetry (DSC), and the melting point (T_m) and glass-transition temperature (T_g) are shown in Table 1. In general, with the increasing of the branching degrees, the melting point moves to a lower temperature, and the glass-transition temperature becomes more observable. The polyethylenes with a branching degrees more than 100 branches/1000C did not show any melting point and appeared as an elastomer.

Conclusions

In summary, a series of α-diimine nickel complexes containing bulky backbones were successfully synthesized and used as catalyst precursors to investigate the steric effects of the bulky backbone on ethylene polymerization in the presence of MAO. In the case of camphyl backbone, the solid structure shows that the *gem*-dimethyl substituents (C(16) and C(17)) are oriented toward the axial position and another methyl C(18) lies behind one of the aryl rings, which can take a steric-effect on metal center and suppress the potential rotation or fluctuation of C_{Ar}−N bond. As a result, the bulky backbone catalysts show significantly higher thermal stability and produce higher molecular weight polyethylene as compared with the acenaphthyl backbone analogues. By using **4b** catalyst containing camphyl backbone and

2,6-diisopropyl-substituted aniline groups, the catalytic activity, molecular weight and branching degrees of the obtained polyethylene remain essentially constant with the increase of polymerization temperature from 20 to 80 °C. Furthermore, the catalyst can remain active for a long period of time even at 80 °C. The contrast in both the catalyst thermal stability and polymer molecular weight between the camphyl backbone complexes and tranditional α-diimine complexes suggests that the bulky camphyl backbone environment significantly influences catalytic properties of the complexes and promoting thermostability of α-diimine nickel catalyst.

Experimental Section

Materials. 2,6-Dimethylaniline and 2,6-diisopropylaniline were purchased from Aldrich Chemical and were distilled under reduced pressure before being used. TMA (1 M, hexane) was purchased from Aldrich Chemical. 2-Diarylaniline, acenaphthenequinone, benzil, 4,4′-dimethylbenzil, 4,4′-difluorobenzil and (D,L)-camphorquinone were purchased from Alfa Aesar Chemical and used as received. Toluene and hexane were refluxed over metallic sodium for 24 h before being used. Dichloromethane was dried over phosphorus pentoxide for 8 h, and distilled under nitrogen atmosphere. Methylaluminoxane (MAO) was prepared by partial hydrolysis of trimethylaluminum (TMA) in toluene at 0−60 °C with $Al_2(SO_4)_3 \cdot 18H_2O$ as the water source. The initial $[H_2O]/[Al]$ in molar ratio was 1.3. Polymerization-grade ethylene and extra-pure-grade nitrogen were further purified before feeding into the reactor by passing them through a DC-IB gas purification instrument.

Ethylene Polymerization. Polymerizations were carried out in 50 mL glass flasks equipped with a magnetic stirrer. The MAO and toluene (19 mL) were added into the reactor. Ethylene was introduced under 0.5 atm until the solution was saturated and the pressure was maintained during the full runs. Polymerization was started by injecting the catalyst solution (5 μmol, 1 mL toluene) into the reactor. The reaction temperatures were controlled with a thermostatic circulation bath, and the inner temperature of the reactor was measured by a mercury thermometer. It was shown that in the early stage of polymerization, the inner temperature could be raised up 2−3 °C from the setting temperature, especially for highly active catalysts. The polymerizations were terminated by adding 200 mL of the acidic ethanol (ethanol−HCl, 95:5). The precipitated polymer was collected and treated by filtering, washing with ethanol several times, and then drying in vacuum at 60 °C to a constant weight.

Characterization. Elemental analyses were performed with a Vario EL series elemental analyzer from Elementar. The NMR data of ligands were obtained on a Varian Mercury-Plus 300 MHz spectrometer at ambient temperature, using $CDCl_3$ as solvent and referenced versus TMS as standard. The NMR data of polyethylene samples were obtained on a Varian Mercury-Plus 500 MHz spectrometer at 110 °C, using o-$C_6D_4Cl_2$ as solvent. The molecular weight and the molecular weight distribution of the polyethylenes were determined on Water GPC 2000 at 135 °C, and 1,2,4-trichlorobenzene was employed as the eluent at a flow rate of 1.0 mL/min. Differential scanning calorimetry (DSC) analysis was conducted with a Perkin-Elmer DSC-7 system in a heating rate of 10 °C/min and was recorded at second heating curves. The X-ray diffraction data of single crystals were obtained with the ω-2θ scan mode on a Bruker SMART 1000 CCD diffractiometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 173K. The structure was solved using direct methods, and further refinement with full-matrix least-squares on F^2 was obtained 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.

Synthesis of 2,6-$(CH_3)_2C_6H_3$−N=C(Ph)−C(Ph)=N−2,6-$(CH_3)_2C_6H_3$ (L1a). Under a nitrogen atmosphere, 2,6-dimethylphenylaniline (1.5 mL, 12 mmol) in toluene (20 mL) solution was injected into a Schlenk flask, and trimethylaluminum (12 mL, 1.0 M in hexane) was added slowly through a syringe at room temperature, and then the reaction was heated to reflux for 2 h. After the solution was cooled to ambient temperature, benzil (1.05 g, 5 mmol) was added. The mixture was stirred for another 6 h at refluxed temperature. When having reached the determined time, the solution was cooled to 0 °C, and the reaction mixture was carefully hydrolyzed with 5% aqueous NaOH solution. The organic product was extracted with ethyl acetate and dried over $MgSO_4$, and the solvent was evaporated off. The desired product obtained as viscous, slowly solidifying oil. It was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (15:1) as eluent, and was crystallized from ethanol as orange crystal in 69.2% yield. A mixture of two geometrical isomers was detected by NMR, which is consistent with previous investigation.[18] ^1H NMR (300 MHz, $CDCl_3$), δ (ppm) [an isomer ratio of 2.1:1]: major isomer: 7.96−6.51 (m, 16H, Ar−H), 1.33 (s, 12H, CH_3). Minor isomer: many peaks obscured by major isomer. Observed: 7.96−6.51 (m, 16H, Ar−H), 1.60 (s, 12H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): major isomer: 164.92 (C=N), 147.03 (C−N), 137.73 (CC=N), 134.72 (C_{Ar}−Me), 129.55, 128.34, 127.74, 127.25, 126.36, 123.04, 18.57 (*Me*). Minor isomer: 165.19 (C=N), 147.44 (C−N), 137.73 (CC=N), 134.72 (C_{Ar}−Me), 130.68, 128.42, 127.91, 127.33, 126.23, 123.15, 18.85 (*Me*). Anal. Calcd for $C_{30}H_{28}N_2$: C, 86.50; H, 6.78; N, 6.72. Found: C, 86.33; H, 6.79; N, 6.51.

Synthesis of 2,6-$(CH_3)_2C_6H_3$−N=C(4′-CH_3−Ph)−C(4′-CH_3−Ph)=N−2,6-$(CH_3)_2C_6H_3$ (L2a). Following the above procedure, **L2a** was isolated as orange viscous slowly solidifying oil in 74.1% yield. ^1H NMR (300 MHz, $CDCl_3$), δ (ppm) [an isomer ratio of 2.5:1]: major isomer: 8.12−6.82 (m, 14H, Ar−H), 2.46 (s, 12H, CH_3 at aniline phenyl), 1.79 (s, 6H, CH_3 at benzil backbone). Minor isomer: 8.12−6.82 (m, 14H, Ar−H), 2.22 (s, 12H, CH_3 at aniline phenyl), 1.59 (s, 6H, CH_3 at benzil backbone). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): major isomer: 164.49 (C=N), 147.60 (C-N), 140.91 (CC=N), 131.77(C_{Ar}−Me), 128.49, 127.30, 126.32 125.25, 122.80, 21.46, 18.67. Minor isomer: 165.00 (C=N), 147.33 (C−N), 139.88 (CC=N), 132.59 (C_{Ar}−Me), 129.12, 127.50, 126.78, 124.91, 122.93, 21.31, 18.50. Anal. Calcd for $C_{32}H_{32}N_2$: C, 86.44; H, 7.25; N, 6.30. Found: C, 86.53; H, 7.14; N, 6.05.

Synthesis of 2,6-$(CH_3)_2C_6H_3$−N=C(4′-F-Ph)−C(4′-F-Ph)-=N−2,6-$(CH_3)_2C_6H_3$ (L3a). Following the above procedure, **L3a** was isolated as orange viscous oil in 56.2% yield. ^1H NMR (300 MHz, $CDCl_3$), δ (ppm): [an isomer ratio of 2.2:1]: major isomer: 8.18−6.63 (m, 14H, Ar−H), 1.83 (s, 12H, CH_3). Minor isomer: 8.18−6.63 (m, 14H, Ar−H), 1.70 (s, 12H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): major isomer: 165.96 (C−F), 164.34 (C=N), 161.84 (C−N), 147.52 (CC=N), 133.98 (C_{Ar}−Me), 131.05, 129.79, 128.33, 127.69, 125.48, 123.70, 115.97, 115.41, 18.82 (*Me*). Minor isomer: 165.71 (C−F), 164.02 (C=N), 161.84 (C−N), 146.99 (CC=N), 133.98 (C_{Ar}−Me), 130.71, 129.12, 128.09, 126.40, 124.91, 123.50, 115.75, 115.20, 18.64 (*Me*). Elemental analysis calculated for $C_{30}H_{26}F_2N_2$: C, 79.62; H, 5.79; N, 6.19. Found: C, 79.41; H, 5.62; N, 6.05.

Synthesis of 2,6-$(CH_3)_2C_6H_3$−N=C(R)−C(R)=N−2,6-$(CH_3)_2C_6H_3$ (R = Camphyl) (L4a). Following the above procedure, **L4a** was isolated as yellow crystal in 84.7% yield. ^1H NMR (300 MHz, $CDCl_3$), δ (ppm) [an isomer ratio of 1.2:1]: major isomer: 6.86−6.70 (m, 6H, Ar−H), 2.07 (s, 12H, C_{Ar}−CH_3), 1.79 (m, 4H, CH_2 at camphyl), 1.39 (m, 1H, tertiary hydrogen at camphyl), 1.26 (s, 3H, CH_3 at camphyl), 1.07 (s, 6H, CH_3 at camphyl). Minor isomer: 6.86−6.70 (m, 6H, Ar−H), 2.04 (s, 12H, C_{Ar}−CH_3), 1.86 (m, 4H, CH_2 at camphyl), 1.42 (m, 1H, tertiary hydrogen at camphyl), 1.26 (s, 3H, CH_3 at camphyl), 0.93 (s, 6H, CH_3 at camphyl). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): major isomer: 170.87 (C=N), 149.37 (C−N), 127.53 (C_{Ar}−Me), 123.96, 122.71, 55.30, 51.18, 45.46, 32.59, 23.38, 21.68, 18.42, 11.20. Minor isomer: 168.56 (C=N), 148.11 (C−N), 127.07, 124.88, 123.17, 55.30, 51.18, 45.46, 32.59, 23.38, 21.68, 18.26 ($C_{Ar}-CH_3$), 11.20. Anal. Calcd for $C_{26}H_{32}N_2$: C, 83.82; H, 8.66; N, 7.52. Found: C, 83.70; H, 8.74; N, 7.46.

Synthesis of 2,6-(i-Pr)$_2$C$_6$H$_3$−N=C(R)−C(R)=N−2,6-(i-Pr)$_2$C$_6$H$_3$ (R = Camphyl) (L4b). Following the above procedure, **L4b** was isolated as yellow crystal in 38.0% yield. ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) [an isomer ratio of 1.8:1]: major isomer: 7.06−6.81 (m, 6H, Ar−H), 2.88 (m, 4H, CH(CH$_3$)$_2$), 2.36 (m, 1H, tertiary hydrogen at camphyl), 1.86 (m, 4H, CH_2 at camphyl), 1.24 (d, 24H, CH(CH_3)$_2$), 0.96 (s, 6H, CH_3 at camphyl), 0.77 (s, 3H, CH_3 at camphyl). Minor isomer: 7.06−6.81 (m, 6H, Ar−H), 2.69 (m, 4H, CH(CH$_3$)$_2$), 2.36 (m, 1H, tertiary hydrogen at camphyl), 1.86 (m, 4H, CH_2 at camphyl), 1.12 (d, 24H, CH(CH_3)$_2$), 0.94 (s, 6H, CH_3 at camphyl), 0.77 (s, 3H, CH_3 at camphyl). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): major isomer: 168.57 (C=N), 144.89 (C−N), 136.10 ($C_{Ar}-{}^{i}$Pr), 122.53, 121.78, 55.92, 50.68, 45.43, 32.27, 28.41, 24.64, 22.44, 17.97, 11.30. Minor isomer: 168.57 (C=N), 144.89 (C−N), 134.71 ($C_{Ar}-{}^{i}$Pr), 123.42, 121.46, 55.92, 50.68, 45.43, 32.27, 28.70, 24.73, 22.96, 17.97, 11.30. Anal. Calcd for $C_{34}H_{48}N_2$: C, 84.24; H, 9.98; N, 5.78. Found: C, 84.13; H, 9.87; N, 5.69.

Synthesis of [2,6-(CH$_3$)$_2$C$_6$ H$_3$−N=C(Ph)−C(Ph)=N−2,6-(CH$_3$)$_2$C$_6$H$_3$]NiBr$_2$ (1a). L1a (416 mg, 1.0 mmol) and (DME)-NiBr$_2$ (308 mg, 1.0 mmol) were combined in 20 mL of dichloromethane at room temperature, and stirred for 12 h under nitrogen atmosphere. The solution was filtered through Celite, and the solvent of the filtrate was evaporated, and the residue was washed 3×10 mL hexane and dried in vacuum. The product was isolated as a red-brown solid in 85.4% yield. FAB$^+$−MS: m/z: 553, 554, 555, 556, [M − Br]$^+$; 474, 475, 476, 477, [M − 2Br]$^+$; 416, 417, 418, [M − NiBr$_2$]$^+$. Anal. Calcd for $C_{30}H_{28}Br_2N_2Ni$: C, 56.74; H, 4.44; N, 4.41. Found: C, 56.42; H, 4.81; N, 4.28.

Synthesis of [2,6-(CH$_3$)$_2$C$_6$H$_3$−N=C(4′-CH$_3$−Ph)−C(4′-CH$_3$−Ph)=N−2,6-(CH$_3$)$_2$C$_6$H$_3$]NiBr$_2$ (2a). Following the above procedure, **2a** was isolated in 93.1% yield. FAB$^+$−MS: m/z: 582, 583, 584, 585, [M − Br]$^+$; 502, 503, 504, [M − 2Br]$^+$; 444, 445, 446, 447, [M − NiBr$_2$]$^+$. Anal. Calcd for $C_{32}H_{32}Br_2N_2Ni$: C, 57.96; H, 4.86; N, 4.22. Found: C, 57.81; H, 4.94; N, 4.03.

Synthesis of [2,6-(CH$_3$)$_2$C$_6$H$_3$−N=C(4′-F−Ph)−C(4′-F−Ph)=N−2,6-(CH$_3$)$_2$C$_6$H$_3$]NiBr$_2$ (3a). Following the above procedure, **3a** was isolated in 87.1% yield. FAB$^+$−MS: m/z: 589, 591, 592, [M − Br]$^+$; 510, 511, 512, 513, [M − 2Br]$^+$; 452, 453, 454, [M − NiBr$_2$]$^+$. Anal. Calcd for $C_{30}H_{26}Br_2F_2N_2Ni$: C, 53.70; H, 3.91; N, 4.17. Found: C, 53.44; H, 3.87; N, 4.02.

Synthesis of [2,6-(CH$_3$)$_2$C$_6$H$_3$−N=C(R)−C(R)=N−2,6-(CH$_3$)$_2$C$_6$H$_3$]NiBr$_2$ (R = Camphyl) (4a). Following the above procedure, **4a** was isolated in 86.7% yield. FAB$^+$−MS: m/z: 510, 511, 512, 513, [M − Br]$^+$; 430, 431, 432, 433, 434, [M − 2Br]$^+$; 372, 373, 374, [M − NiBr$_2$]$^+$. Anal. Calcd for $C_{26}H_{32}Br_2N_2Ni$: C, 52.83; H, 5.46; N, 4.74. Found: C, 51.67; H, 5.32; N, 4.59.

Synthesis of [2,6-(i-Pr)$_2$C$_6$H$_3$−N=C(R)−C(R)=N-2,6-(i-Pr)$_2$C$_6$H$_3$]NiBr$_2$ (R = Camphyl) (4b). Following the above procedure, **4b** was isolated in 94.2% yield. FAB$^+$−MS: m/z: 622, 623, 624, 625, [M − Br]$^+$; 542, 543, 544, 545, 546, [M − 2Br]$^+$; 484, 485, 486, [M − NiBr$_2$]$^+$. Anal. Calcd for $C_{34}H_{48}Br_2N_2Ni$: C, 58.07; H, 6.88; N, 3.98. Found: C, 56.86; H, 6.73; N, 3.75.

[2,6-(CH$_3$)$_2$C$_6$H$_3$−N=C(An)−C(An)=N−2,6-(CH$_3$)$_2$-C$_6$H$_3$]NiBr$_2$ (**5a**) and [2,6-(i-Pr)$_2$C$_6$H$_3$−N=C(An)−C-(An)=N−2,6-(i-Pr)$_2$C$_6$H$_3$]NiBr$_2$ (**5b**) were prepared according to literature procedures.[6]

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Supporting Information Available: A cif file containing the details of the crystallographic study of **4a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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