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Systematic Investigations of Ligand Steric Effects on α-Diimine Nickel Catalyzed Olefin Polymerization and Copolymerization

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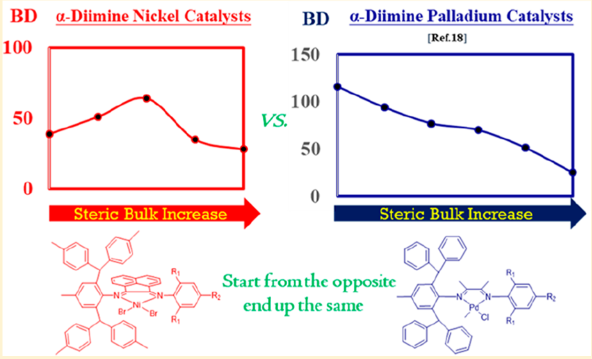
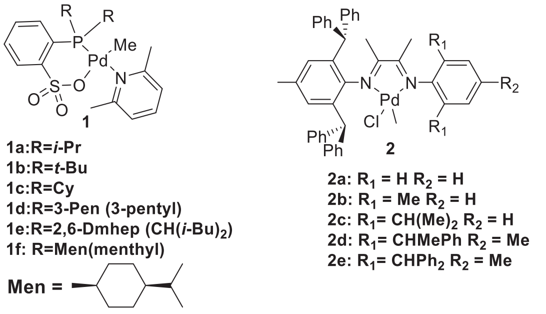
Supporting Information

ABSTRACT: So far, ligand steric effects of the α-diimine nickel catalysts on the polyolefin branching densities are not systematically investigated. Generally, in contrast to the α-diimine palladium systems, the branching densities of the polyethylene obtained by the α-diimine nickel catalysts increased when the more sterically encumbering substituent was employed. In this contribution, we described the synthesis and characterization of a series of α-diimine ligands and the corresponding nickel catalysts bearing the diarylmethyl moiety and varied steric ligands. In ethylene polymerization, the catalytic activities [(2.82−15.68) × 10^6 g/(mol Ni·h)], polymer molecular weights [M_n: (0.37−131.51) × 10^4 g mol^{-1}], branching densities [(28−81)/1000 C], and polymer melting temperatures (−4.7−122.9 °C) can be tuned over a very wide range. To our surprise, the polymer branching density first rose and then fell when we systematically increased the steric bulk of α-diimine nickel catalysts, like a downward parabola, not in line with previous conclusions. In ethylene-methyl 10-undecenoate (E-UA) copolymerization, the catalytic activities [(1.0 × 10^3) − (104.8 × 10^4) g/(mol Ni·h)], copolymer molecular weights [(1.2 × 10^3) − (242.4 × 10^3) g mol^{-1}], branching densities [(42−70)/1000 C], and UA incorporation ratio (0.17−2.12%) can also be controlled over a very wide range. The tuning in steric ligands enables the tuning of the polymer microstructures such as molecular weight and branching density. In this way, the best polyethylene elastomer catalysts are screened out.



INTRODUCTION

Scheme 1. Two Examples of Systematic Investigations of Ligand Steric Effects on Late Transition Metal Catalyzed Ethylene Polymerization and Copolymerization



Ligand steric and electronic effects are two of the most important factors in late transition metal catalyzed ethylene polymerization and copolymerization.[1] Systematic investigations of ligand electronic effects in late transition metal catalyzed ethylene polymerization and copolymerization have been widely explored in different catalytic systems.[2−8] However, systematic investigations of ligand steric effects are rarely reported since the substituents' change is tedious work. One of the famous examples is the quantification of the steric influence of palladium/alkylphosphine−sulfonate catalysts on ethylene polymerization[9] (Scheme 1, **1**). Good correlation between the steric bulk of the ligands and the molecular weight of the (co)polymers was observed. Consequently, bulky alkylphosphine−sulfonate Pd complexes bearing menthyl groups (Scheme 1, **1f**) was used to obtain high-molecular-weight polymers and copolymers. Notably, in the α-diimine Pd(II) and Ni(II) catalyst system,[10−16] steric effects on the ortho-aryl substituents in the ligand could slow the chain transfer process and thus is the key factor to produce high polymer molecular weight polyethylene. The slow rate of chain transfer was ascribed to a slow associative displacement of the unsaturated polymer chain since the bulky ortho substituents can block the axial approach of the monomer.[17] Chen's group reported a series of systematically varied steric ligands of α-diimine palladium catalysts (Scheme 1, **2**) and further

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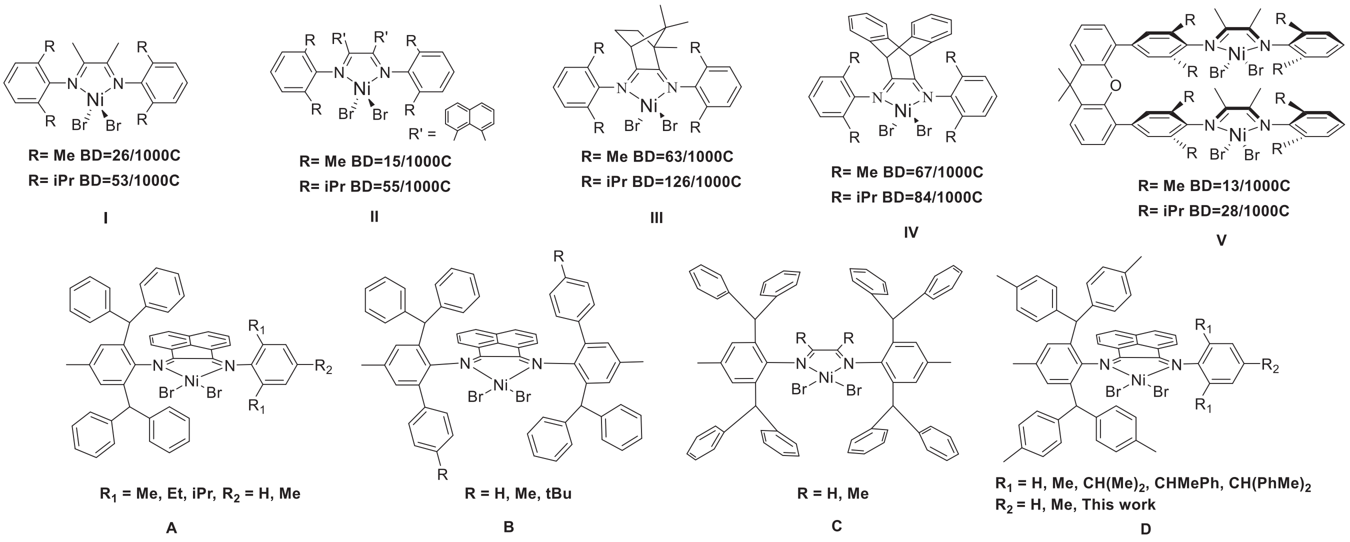
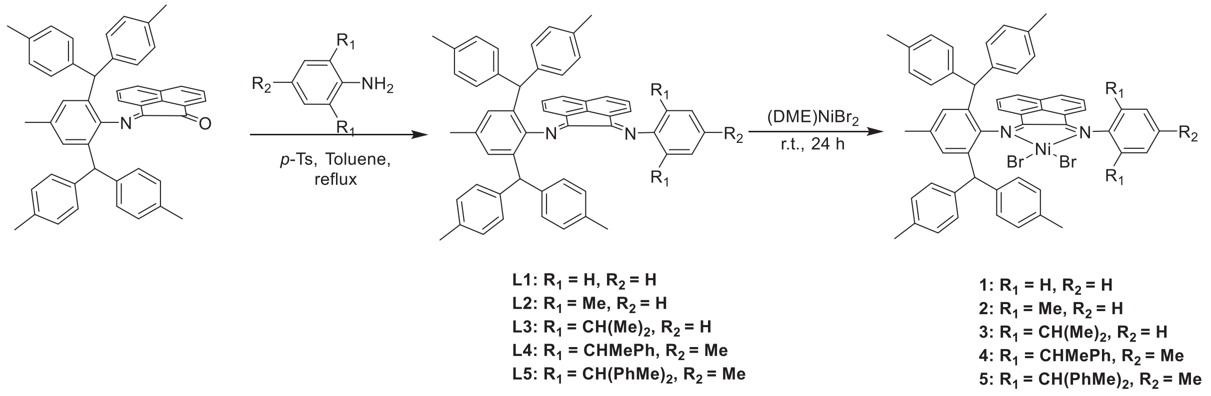
Scheme 2. Previously Reported α-Diimine Nickel Catalysts



Scheme 3. Synthesis of Nickel Complexes



confirmed the conclusions above.[18] It is normal that the more sterically encumbering substituents lead to higher catalytic activities, higher polymer molecular weights, and lower branching densities. In ethylene polymerization, the catalytic activities [(0.77−8.85) × 10^5 g/(mol Pd·h)], polymer molecular weights [M_n: (0.2−164.7) × 10^4], branching densities [(25−116)/1000 C], and polymer melting temperatures (amorphous to 98 °C) of this system can be tuned over a very wide range when we systematically improved the steric bulk effects. Similar results were found in ethylene-methyl acrylate (E-MA) copolymerization.

The α-diimine nickel catalysts with simply steric ligands increased are reported extensively (Scheme 2, **I**−**V**). A series of α-diimine Ni(II) with various backbone structures such as butane (Scheme 2, **I**),[19] acenaphthene (Scheme 2, **II**),[19] camphyl (Scheme 2, **III**),[20] and dibenzobarrelene (Scheme 2, **IV**)[21] were investigated previously; the polyethylene obtained by these catalysts showed similar regularity, i.e., the molecular weights of the polyethylene increased when the more sterically encumbering substituent was added. This is consistent with the α-diimine palladium systems. However, in contrast to the α-diimine palladium systems, the branching densities of the polyethylene obtained by the α-diimine nickel catalysts increased when the more sterically encumbering substituent was employed. The xanthene bridged dinuclear α-diimine Ni(II) system (Scheme 2, **V**) also showed the same trend.[19]

The branching densities of the polyethylene or copolymers are among the most important factors in determining the macroscopic physical and chemical properties of a polymer.[14] Therefore, it is very meaningful to systematically investigate the ligand steric effects of the α-diimine nickel catalysts.

In this contribution, a series of acenaphthene-based α-diimine nickel complexes bearing both diarylmethyl moiety and systematically varied ligand steric environments were designed to address this issue (Scheme 2, **D**). Catalysts with similar structures and polymerization results have previously been reported (Scheme 2, **A**−**C**).[22−24] Very interestingly, the ligand steric effect was found to be different from that of the corresponding α-diimine palladium systems. The correlation between the branching densities of the obtained polyethylene and the steric hindrance seems to be like a parabola. In addition, the mechanical properties of the generated polyethylene also followed the same trend.

■ RESULTS AND DISCUSSIONS

Catalyst Synthesis. The monoimine ligand 2-((2,6-bis(di-*p*-tolylmethyl)-4-methylphenyl)imino) acenaphthylen-1-one was prepared from the reaction of 2,6-bis(diphenylmethyl)-4-methylaniline with 1 equiv of acenaphthylen-1,2-dione at 70% yield on the multigram scale (Scheme 3). Subsequently, the reaction with 2 equiv of the corresponding anilines catalyzed

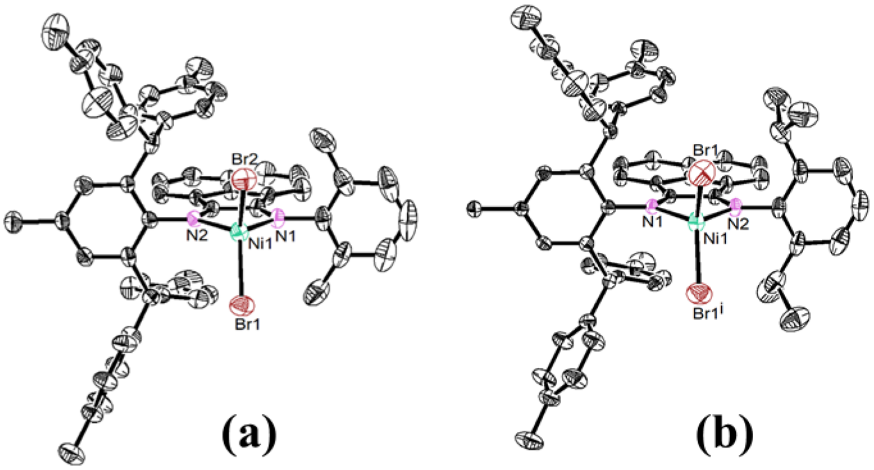


Figure 1. Molecular structures of the nickel complexes **2** and **3** with 30% probability level, and H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg) for (a) complex **2**: Ni(1)−N(1), 2.009(6); Ni(1)−N(2), 2.044(5); Ni(1)−Br(1), 2.3466(15); Ni(1)−Br(2), 2.3363(15); N(1)−Ni(1)−N(2), 82.5(3); Br(2)−Ni(1)−Br(1), 120.89(6); (b) complex **3**: Ni(1)−N(1), 2.059(4); Ni(1)−N(2), 2.017(5); Ni(1)−Br(1), 2.3283(7); N(1)−Ni(1)−N(2), 82.65(19); Br(i1)−Ni(1)−Br(1), 116.60(4).

Table 1. Effect of Catalyst and Temperature on Ethylene Polymerization[a]

Entry	Precat.	T (°C)	Yield/g	Actual[b]	M_n[c]	M_w/M_n[c]	B[d]	T_m/(°C)[a]
1	**1**	20	7.84	15.68	0.65	2.20	39	115.1, 122.9
2	**1**	40	5.77	11.54	0.86	2.49	55	122.1
3	**1**	60	4.26	8.52	0.58	2.27	62	119.8
4	**1**	80	2.05	4.10	0.37	1.92	74	wax
5	**2**	20	2.98	5.96	51.24	2.19	51	73.6
6	**2**	40	2.66	5.32	31.28	2.37	74	46.0
7	**2**	60	2.69	5.38	21.78	2.70	76	31.0
8	**2**	80	2.64	5.28	12.02	2.67	80	10.1
9	**3**	20	2.50	5.00	71.55	1.79	64	47.2
10	**3**	40	3.91	7.82	68.53	2.07	64	40.2
11	**3**	60	3.14	6.28	43.46	2.39	81	−3.2
12	**3**	80	2.48	4.96	38.44	2.30	81	−4.7
13	**4**	20	3.24	6.48	100.25	1.97	35	81.7
14	**4**	40	3.42	6.84	103.76	1.86	48	73.4
15	**4**	60	3.12	6.24	67.55	2.05	52	58.5
16	**4**	80	2.18	4.36	54.56	2.35	61	51.6
17	**5**	20	1.41	2.82	131.51	1.46	28	107.3
18	**5**	40	1.52	3.04	104.84	1.58	38	81.6
19	**5**	60	1.86	3.72	95.22	1.74	45	72. 0
20	**5**	80	2.01	4.02	86.34	1.95	46	71.0

[a] General conditions: Ni = 1.0 μmol, Al/Ni = 600, CH_2Cl_2 = 2 mL, toluene = 40 mL, ethylene = 8 atm, time = 30 min. [b] Activity = 10^6 g of PE (mol of Ni)$^{-1}$ h^{-1}. [c] M_n: 10^4 g mol^{-1}, M_n and M_w/M_n determined by GPC. [d] Branching numbers per 1000 C were determined by ^{1}H NMR. Branching numbers for low molecular weight samples (M_n < 10 000) were corrected for end groups. [e] Melting temperature determined by DSC.

by *p*-Ts (*p*-toluene sulfonic acid) led to the formation of the acenaphthene-based α-diimine ligands **L1**−**L4** at 31−53% yields. Symmetric acenaphthene-based α-diimine bearing the bulky diarylmethyl moiety **L5** was prepared with no chromatography involved in 48.2% yields by an efficient method we previously reported.[25]

The nickel complexes **1**, **2**, **3**, **4**, and **5** were readily prepared in 86−93% yields from the reaction of the corresponding ligands with 1 equiv of (DME)$NiBr_2$ (DME = 1,2-dimethoxyethane). These nickel complexes were characterized by mass spectrometric and elemental analysis as well as X-ray crystallography. The molecular structures of complexes **2** and **3** are shown in Figure 1. The bond distances and bond angles are typical, compared with some previously reported α-diimine nickel complexes.[22,23,26] The effective blockage of the axial positions of the metal center from the N-aryl moiety was observed. The steric properties of nickel complexes **1**−**5** bearing a diarylmethyl moiety and varied steric ligands were evaluated using the percentage of buried volume (%V_{Bur}) as a molecular descriptor.[27,28] The steric maps of the five complexes are shown in Figure S2. The %V_{Bur} of **1**−**5** was calculated to be 77.9%, 82.3%, 83.7%, 86.4%, and 87.6%, respectively, indicating that the steric bulk of the α-diimine nickel catalysts increased from **1** to **5**.

Ethylene Polymerization. Nickel complexes **1**−**5** were screened for ethylene polymerization with MAO (methylaluminoxane) as cocatalyst under 8 atm of ethylene pressure at different temperatures, and the polymerization results are summarized in Table 1. These nickel complexes are all highly active (well above 10^6 g of PE (mol of Ni)$^{-1}$ h^{-1}) in ethylene

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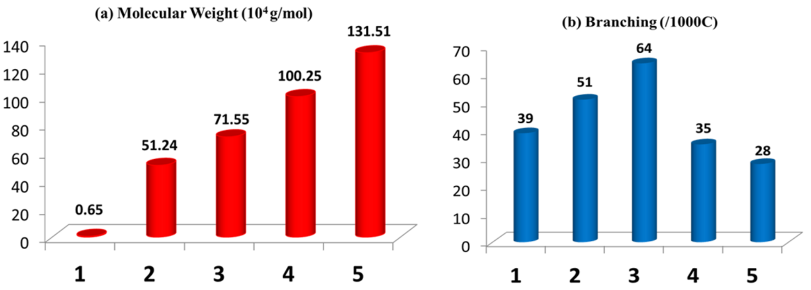

Figure 2. (a) Molecular weight (M_n) of the polyethylene obtained by catalysts **1**−**5** (Table 1, entries 1, 5, 9, 13, 17). (b) Branching density of the polyethylene generated using catalysts **1**−**5** (Table 1, entries 1, 5, 9, 13, 17).

polymerization (Table 1). Complex **1** showed the highest activity at 1.6 × 10^7 g·mol^{-1}·h^{-1} at 20 °C and 8 atm of ethylene, which was comparable to those of metallocene catalysts.[29] In view of the mass transfer-limited rates caused by the high polymerization activities and the highly branched PEs produced by complexes **2**−**4**, the polymerizations were conducted at short times to minimize the effects from mass transport (Table S2, Supporting Information). It was indicated that the polymerization activity decreased with steric ligands increasing from complex **1** to complex **5**. In the α-diimine nickel catalysts, the rate-determining step in ethylene polymerization is the coordination of ethylene monomers to metal centers; therefore, the higher the steric resistance of catalyst, the lower the activity of ethylene polymerization. At the same time, the molecular weight (M_n) of polyethylene were increased gradually from 6.5 × 10^3 to 1.31 × 10^6 g/mol (Table 1, Figure 2a) due to the bulkier substituents slowing the chain transfer efficiency. This is consistent with previous reports and theories.[9,17,18]

Most interestingly, the polymer branching density increased from 39 to 64/1000 C and decreased later from 64 to 28/1000 C (Table 1, Figure 2b) along with the increasing steric bulk of α-diimine nickel catalysts, indicating a different relationship between the polymer branching density and the steric bulk.[17,19−21] The branching degree of polyethylene is determined by two factors: the chain walking speed and the chain growth rate. When the ortho-aryl substituents in the ligand, or the axial substituents of the metal center, become bulkier, the chain walking speed and the chain growth rate both become slower, but the ratio of the two factors changes with the increase of the steric hindrance. From complexes **1** to **3**, the bulky substituents can slow chain growth rate more than the rate of chain walking, thus more chain walking and branching can occur in the catalysts from complexes **1** to **3**. In contrast, from **3** to **5**, the highly bulky substituents could make the rate of chain walking slower than the rate of chain growth. The previously reported α-diimine palladium systems showed that the insertion of ethylene into a primary metal alkyl species is easier than the insertion into a secondary metal alkyl species.[18] Similarly, the highly bulky α-diimine nickel systems might have similar behavior. Consequently, the relatively greater preference of insertion of ethylene into a primary metal alkyl species versus insertion into a secondary metal alkyl species may also contribute; thus less chain walking and branching can occur in the catalysts from complexes **3** to **5**. Correspondingly, the melting points of polyethylene products follow the contrasting trend, first falling from 123 to 47 °C and then rising from 47 to 107 °C, like an upward parabola.

The polymerization activity of complex **1** with the lowest steric hindrance decreases rapidly from 1.6 × 10^7 g·mol^{-1}·h^{-1} at 20 °C to 4.1 × 10^6 g·mol^{-1}·h^{-1} at 80 °C. In contrast, complexes **2**−**4** with moderate steric hindrance exhibited similar activities at 20−80 °C. Furthermore, complex **5** with the bulkiest substituents diarylmethyl displayed higher activity at higher temperatures. Complex **5** has a good thermal stability at 100 °C (Table 2, Figure 3). At 80 °C, almost constant activity [(3.04−4.02) × 10^6 g·mol^{-1}·h^{-1}] was found over 60 min (Figure 3a). Moreover, the molecular weight increased with polymerization time and reached over 1.21 × 10^6 g·mol^{-1} (Figure 3b). Further, polymerizations conducted at 100 °C showed a slight decrease of activity (from 4.68 × 10^6 g·mol^{-1}·h^{-1} to 2.52 × 10^6 g·mol^{-1}·h^{-1}) (Figure 3a) as well as molecular weight (from 57.30 × 10^4 g·mol^{-1} to 30.28 × 10^4 g·mol^{-1}) (Figure 3b) with time. These results indicated that the chain transfer and catalyst deactivation of complex **5** were suppressed by the bulkiest ligand.

Table 2. Effect of Reaction Time on Ethylene Polymerizations Using Catalyst 5 at Elevated Temperatures[a]

Entry	T (°C)	Time (min)	Yield/g[b]	Act.[b]	M_n[c]	M_w/M_n[c]
1	80	5	0.31	3.72	35.15	1.61
2	80	10	0.61	3.66	53.98	1.71
3	80	15	0.95	3.80	60.33	1.88
4	80	30	2.01	4.02	86.34	1.95
5	80	60	3.04	3.04	120.94	1.52
6	100	5	0.39	4.68	52.15	1.53
7	100	10	0.78	4.68	50.78	1.83
8	100	15	1.12	4.48	57.30	1.87
9	100	30	1.57	3.14	54.50	2.02
10	100	60	2.52	2.52	30.28	3.51

[a] General conditions: Ni = 1.0 μmol, Al/Ni = 600, CH_2Cl_2 = 2 mL, toluene = 40 mL, ethylene = 8 atm. [b] Activity = 10^6 g of PE (mol of Ni)$^{-1}$ h^{-1}. [c] M_n: 10^4 g mol^{-1}, M_n and M_w/M_n determined by GPC.

Ethylene-Methyl 10-Undecenoate (UA) Copolymerization.

Recently, the nickel-catalyzed ethylene copolymerization with polar functionalized comonomers have been widely studied;[30−39] the investigations of ligand steric effects on the nickel-catalyzed ethylene copolymerization with polar functionalized comonomers are rarely reported. Here we use the nickel complexes **1**−**5** to catalyze the copolymerization of ethylene with methyl 10-undecenoate in the presence of 1000 equiv of Et_2AlCl (Table 3). The activities and polymer molecular weights were largely reduced in ethylene copolymerization, except complex **3** with moderate steric hindrance showed the highest activities at 1.0 × 10^6 g·mol^{-1}·h^{-1} at 20 °C (Table 3, entry 3), and complex **4** showed the highest molecular weight at 24.2 × 10^4 g/mol at 20 °C (Table 3, entry

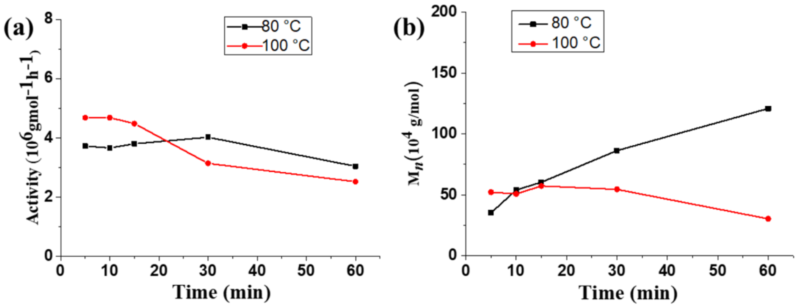

Figure 3. Plots of (a) activity versus time and (b) M_n versus time for **5** at 80 °C (black) and 100 °C (red).

Table 3. Ethylene-Methyl 10-Undecenoate (UA) Copolymerization[a]

Entry	Catalyst	T (°C)	[UA](M)	Yield (g)	Actual[b]	X_{UA}[c] (%)	M_n[d] ($\times 10^{-3}$)	PDI	B[e]
1	**1**	20	0.08	0.05	1.0	0.32	1.2	3.05	59
2	**2**	20	0.08	2.86	57.2	0.53	22.1	3.01	61
3	**3**	20	0.08	5.24	104.8	0.43	85.8	2.99	70
4	**4**	20	0.08	1.62	32.4	0.23	242.4	4.21	45
5	**5**	20	0.08	1.46	29.2	0.17	10.4	1.80	42
6	**5**	40	0.08	1.36	27.2	0.23	3.3	3.53	51
7	**5**	60	0.08	1.52	30.4	0.51	2.7	2.36	54
8	**5**	80	0.08	1.03	20.6	0.59	3.0	5.10	57
9	**5**	80	0.16	1.58	31.6	1.03	2.2	2.36	64
10	**5**	80	0.32	0.13	2.6	1.54	1.6	2.45	58
11	**2**	20	0.16	2.51	50.2	1.04	18.9	2.83	61
12	**3**	20	0.16	1.15	23.0	1.02	40.3	2.85	59
13	**4**	20	0.16	1.30	26.0	0.59	65.7	6.95	45
14	**2**	20	0.32	0.98	19.6	2.03	7.8	3.40	55
15	**3**	20	0.32	0.58	11.6	2.12	18.8	2.78	66
16	**4**	20	0.32	1.02	20.4	0.99	17.7	3.31	47

[a]General conditions: Ni = 5.0 μmol, Al/Ni = 1000, CH_2Cl_2 = 2 mL, total volume of toluene and UA: 20 mL, ethylene = 2 atm, time = 60 min. [b]Activity = 10^4 g of PE (mol of Ni)$^{-1}$ h^{-1}. [c]X_{UA} = UA incorp. (mol %). [d]M_n: 10^4 g mol^{-1}, M_n and M_w/M_n determined by GPC. [e]B = branches per 1000 carbons, branching numbers were determined using ^{1}H NMR spectroscopy, the branches ending with functional groups are added to the total branches.

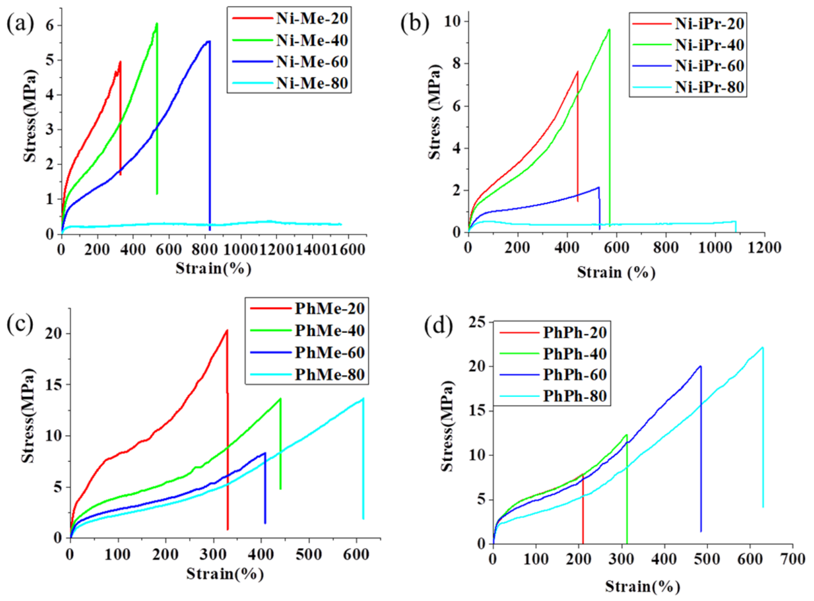

Figure 4. Stress–strain curves for polyethylene generated by (a) **2**, (b) **3**, (c) **4**, and (d) **5** at 20, 40, 60, and 80 °C.

4). Complex **1** with the lowest steric hindrance showed the lowest activity and molecular weight, revealing that it is easily poisoned by the polar comonomer. The comonomer incorporation ratio decreased with steric ligand increasing from complex **2** to complex **5** (Table 3, entries 2–5). This is consistent with previous reports and theories.[9,18] For

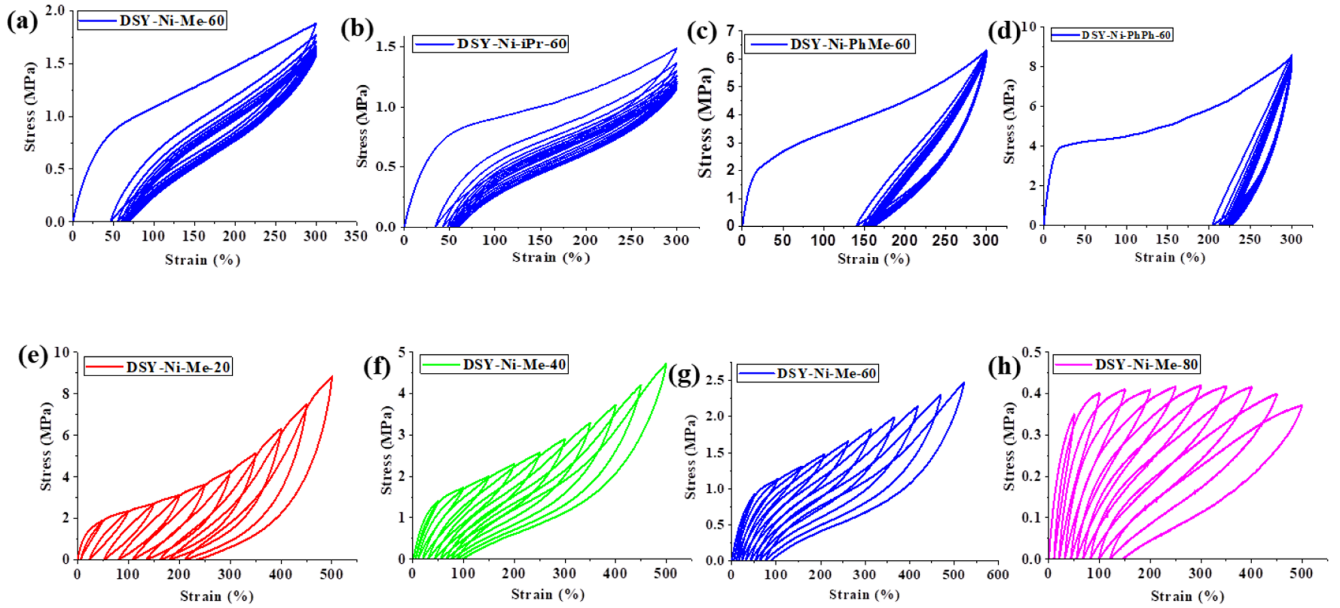

Figure 5. Plots of hysteresis experiments of ten cycles at a strain of 300% for samples generated by **2** at 60 °C (a), **3** at 60 °C (b), **4** at 60 °C (c), and **5** at 60 °C (d). Stress−strain curves during step-cycle tensile deformation at different strains of the polyethylene samples generated using catalysts **2** at 20 °C (e), 40 °C (f), 60 °C (g), and 80 °C (h).

complexes **2**−**5**, an increase in comonomer concentration led to decreases in both activity and copolymer molecular weight and an increase in the comonomer incorporation ratio (Table 3, entries 8−16). The copolymers with molecular weights of between 1.2 × 10^3 and 24.2 × 10^4 g/mol and comonomer incorporation ratios 0.17−2.12% were generated (Table 3). As complex **5** has great thermal stability at high temperatures, the copolymerization using complex **5** was conducted at 40, 60, and 80 °C, the comonomer incorporation ratios went up when the temperature rose, and the activity almost remained the same (Table 3, entries 5−8). This shows that complex **5** is also thermally stable in the copolymerization. However, the copolymer molecular weights obtained by complex **5** at high temperatures are very low. The probable reason is that the chain transfer may accelerate with the comonomer at high temperatures. It should be pointed out that the amount of Et_2AlCl is much larger than that of polar comonomers. As such, the protecting effect of the aluminum cocatalyst on the polar comonomers helps in avoiding their poisoning toward the nickel catalysts.

Properties of the Polymer Products. The steric bulk of the ligand has a significant influence on the degree of branching density of the generated PEs (Table 1, Figure 2b). This translates into tuning of the properties of the resulting polymeric products such as melting temperatures and mechanical properties. The polyethylene products generated using catalyst **1** are low molecular weight wax which cannot be tested in the tensile tests. To examine the mechanical properties of these branched PEs, tensile tests were carried out for all the polyethylene samples prepared by using **2**, **3**, **4**, and **5** catalysts at different polymerization temperatures (Figure 4 and Table S1, Supporting Information). These samples showed stress at break values in the range from 0.3 to 22.1 MPa and exhibited typical features of elastomers with high strain at break values ranging from 208% to 1558%. In general, the higher the reaction temperature, the higher the branching density of the obtained polyethylene, the lower the melting point of the obtained polyethylene, and the greater the strain at break of the obtained polyethylene. Furthermore, polyethylene obtained by the catalysts **2** and **3** with moderate steric hindrance displayed lower stress at break values (0.3−9.6 MPa) than those obtained by catalysts **4** and **5** with larger steric hindrance (7.8−22.1 MPa) at the same polymerization conditions. Clearly, the polyethylene microstructures including molecular weights and branching densities, which can be modulated by catalyst steric bulk and polymerization conditions, have a significant influence on the mechanical properties of these polyethylene.

In order to study the elastic recovery of the obtained polyethylene, that is, the ability to return to the initial state once the force is removed, the polyethylene samples were also used in a hysteresis experiment in which each sample was extended to 300% strain in 10 cycles. (Figure 5 and Table S1, Supporting Information). The strain recovery values (SR) can be calculated by SR = $100\ (\varepsilon_a - \varepsilon_r)/\varepsilon_a$ (ε_a = the applied strain, ε_r = the strain in the cycle at zero load after the 10th cycle). These polyethylene samples exhibit a certain amount of unrecovered strain after the first cycle, followed by minimal deformation in each subsequent cycle. A permanent structural change occurs during the first cycle, after which a better elastomeric property is produced. Overall, these samples exhibit SR values ranging from 22% to 80%, which are comparable with previously reported elastic polyolefin materials obtained by late transition metal catalysts.[40−43] The high molecular weight and highly branched microstructure of the polyethylene appear to contribute to their unique elastic properties. Therefore, the current catalytic system uses only ethylene as the feedstock to synthesize thermoplastic elastomers in only one step, which has been reported recently.[26,41−43] The steric bulk of the catalyst plays an important role in the elastic properties of these polyethylene samples. The strain recovery values (SR) for the polyethylene sample produced using **2**, **3**, **4**, and **5** at 60 °C are 77%, 80%, 46%, and 22%, respectively (Figure 5a−d). Catalysts **2** and **3** with moderate steric hindrance clearly stand out, displaying excellent elastic properties, maintaining SR values of >75%. This result can be attributed to the highest branching density of polyethylene samples produced using catalysts **2** and **3** with moderate steric hindrance. In addition, the samples generated by **2** at different temperatures (20, 40, 60, and 80 °C) were tested during step-cycle tensile deformation at different strains (Figure 5e−h). The sample generated by **2** at 60 °C has the best elastic properties, maintaining SR values of >80% throughout the cyclic tensile deformation. Curiously, the polymer sample generated by **2** at 80 °C showed the much lower SR value (SR = 45%) and stress values (0.3 MPa) at 300% (Figure S1, Supporting Information) than that generated at 60 °C. Since these two samples have similar branching densities, the higher molecular weight of the polyethylene sample generated by **2** at 60 °C (21.78×10^4 g·mol^{-1}) than that at 80 °C (12.02×10^4 g·mol^{-1}) seems to enhance the elastic property. ^{13}C NMR analysis showed that the polyethylene prepared by complexes **2** composed of various alkyl branches from C1 to C ≥ 5, even *sec*-butyl (branch on branch structure), the highly branched microstructures, and the presence of various alkyl branches in these samples probably contribute to their unique properties (Figure S3, Supporting Information).

CONCLUSIONS

In summary, a series of acenaphthene-based α-diimine nickel complexes bearing bulky diarylmethyl moiety and with systematically varied steric ligands have been synthesized and characterized. Activated by MAO, these nickel catalysts showed high activities (up to 1.6×10^7 g·mol^{-1}·h^{-1}) and great thermal stability (quite stable at up to 100 °C) and generated branched polyethylene (M_n up to 1.31×10^6 g·mol^{-1}) with branching density in a wide range of (28−81)/1000 C in ethylene polymerization. The systematically varied steric ligands in these complexes and polymerization temperature exert great influence on the catalytic properties of these nickel catalysts as well as the mechanical properties of the generated polyethylene. Specifically, the moderate steric hindrance catalysts **2** and **3** with much higher branching density and elastic strain recovery value than other catalysts at the same polymerization temperature. These branched polyethylene materials displayed properties characteristic of thermoplastic elastomers. As a result, this work may provide an alternative and effective strategy to screen out the best polyethylene elastomer catalyst. Activated by Et_2AlCl, the investigations of the steric ligand effects on the nickel-catalyzed ethylene copolymerization with methyl 10-undecenoate have been studied; the moderate steric hindrance catalysts **2** and **3** also showed the best copolymerization properties by both the comonomer incorporation ratio and copolymer molecular weight.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.9b00267.

Full experimental details for the synthesis of nickel complexes and polymers (PDF)

CIF data files (TXT)

Accession Codes

CCDC 1886683−1886685 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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