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Neutral nickel complexes chelating monoamidinate ligands: Syntheses, characterizations and catalytic properties toward ethylene oligomerization and norbornene polymerization

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1. Introduction

Amidinates of the type $[R^1C(NR^2)(NR^3)]$ $(R^1, R^2, R^3 = H, alkyl, aryl or SiMe_3)$ have been widely used in recent years to form a multitude of complexes with main group and transition metals [1–3]. Due to the fact that they can be modified by tuning the substituents R^1 , R^2 , and R^3 , different steric and electronic properties are achieved easily. Amidinates are considered as a steric equivalent of the cyclopentadienyl (Cp) moiety, and its anionic ligand $[R^1C(NR^2)(NR^3)]^-$ can provide four electrons, which promote higher electrophilicity at the metal center compared to six-electron of $[Cp]^-$. Therefore, various group IV and rare earth metal complexes bearing amidinate ligands have been developed as non-Cp olefin polymerization catalysts [4–20].

Besides, it has been found that the amidinate ligands are very useful in the preparation of new late transition metal complexes [2]. This type of ligands are extremely flexible in bonding mode (shown in Scheme 1), thus various well-characterized complexes, such as iron, cobalt, nickel, palladium, platinum and so on, have been reported [21–25]. In comparison with early transition complexes, late transition metal complexes bearing chelating amidinate ligands were less applied in olefin polymerization field due

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ABSTRACT

Three new neutral monoamidinate nickel complexes $[(2,6^{-i}Pr-C_6H_3)N=C(Ar^1)-N(Ar^2)]Ni(Ph)(PPh_3)$ (1, $Ar^1 = phenyl$, $Ar^2 = 2,6$ -diispropyphenyl; 2, $Ar^1 = p$ -tolyl, $Ar^2 = 2,6$ -diimethylphenyl; 3, $Ar^1 = p$ -tolyl, $Ar^2 = p$ -tolyl,

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to their instability and small bite angle (62–69°). Eisen and co-workers synthesized nickel complexes with chelating monobenzamidinate or bisbenzamidinate ligands, and found that the reaction of nickel metal compounds with amidinate ligands is complicated [26–28]. In the presence of methylaluminoxane (MAO), these nickel complexes showed high activity for the addition polymerization of norbornene and also efficiently oligomerized ethylene and propylene.

Recently, much attention has been focused on neutral nickel catalysts such as salicylaldiminato Ni(II) complexes because they are less oxophilic and therefore able to tolerate polar functional-containing monomers [29–32]. In an effort to develop bulky neutral monoamindinate nickel complexes as olefins polymerization catalysts, we synthesized and characterized a series of bulky monoamindinate nickel complexes with triphenylphosphine ancillary ligand. Furthermore, ethylene oligomerization and norbornene polymerization catalyzed by neutral monoamindinate nickel complexes after activation with MAO were also investigated.

2. Experimental

2.1. General procedures

All manipulations were performed under nitrogen atmosphere using glove box and Schlenk techniques. Polymerization-grade ethylene and extra-pure-grade nitrogen were further purified



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before feeding into the reactor by passing through a DC-IB gas purification instrument. Norbornene was purified by distillation over potassium and used as a solution (0.4 g/ml) in toluene. Toluene and hexane were refluxed over metallic sodium for 24 h before use. Dichloromethane was dried over phosphorus pentoxide for 8 h, and distilled under nitrogen atmosphere. 2,6-Diisopropylaniline and 2,6-dimethylaniline were purchased from Aldrich Chemical Co. and distilled under reduced pressure before use. Pentafluoroaniline, *p*-toluoyl chloride and *n*-butyllithium (2.6 M) in hexane were purchased from Aldrich Chemical Co. and used as received. Benzoyl chloride was purchased from Guangzhou Chemical Reagent Co. and used without further purification. Transchloro(phenyl)bis(triphenylphosphine) nickel(II) was synthesized according to the procedure in the literature [33]. Methylaluminoxane (MAO) was prepared by partial hydrolysis of trimethylaluminum (TMA) in toluene at 0-60 °C with Al₂(SO₄)₃ · 18H₂O as the water source. The initial [H₂O]/[Al] in molar ratio was 1.3.

2.2. Characterization

NMR spectra were recorded on a Varian Mercury-Plus 300 MHz NMR spectrometer and referenced versus TMS as standard. Elemental analyses were determined with a Vario EL series elemental analyzer from Elementar. MS-FAB spectra were obtained with a VG ZAB-HS scan instrument, using *m*-nitrobenzylalcohol as matrix. The GC-MS data were recorded with a Finnigan Voyager GC-8000 Top series GC-MS system with DB-5MS GC column. Gel permeation chromatography (GPC) analyses of the molecular weight and molecular weight distribution of the polymers were performed on a Waters Alliance GPC-2000 instrument using standard polystyrene as the reference and with 1,2,4-trichlorobenzene as the eluent at 135 °C. The polymer samples were processed into KBr thin films for IR measurements. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet NEXUS-670 FTIR spectrometer. The X-ray diffraction data of single crystal of complex 2 was obtained with the ω -2 θ scan mode on a Bruker SMART 1000 CCD diffractiometer with graphite-monochromated Mo K α radiation $(\lambda = 0.71073 \text{ Å})$ at 173 K. 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 nonhydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in calculated positions with the displacement factors of the host carbon atoms except disordered hexane molecule.

2.3. Ethylene oligomerization

Ethylene oligomerization reactions were performed in a 50 ml glass flask equipped with magnetic stirrer, oil control of tempera-

ture, and continuous feed of ethylene was used. A typical reaction was performed by adding proper amount of MAO solid and introducing toluene (19 ml) into the reactor under ethylene atmosphere. The toluene catalyst solution (1 ml, [Ni] = 5 μ mol) was injected into the reactor *via* syringe. Ethylene was continuously fed in order to maintain the ethylene pressure at 0.5 atm. After 30 min, the reaction was stopped by cooling the system to 0 °C, and terminated by addition of cold acidic ethanol (ethanol–HCl, 95:5). The organic layer was analyzed quickly by gas chromatography (GC) for determining the composition and mass distribution of oligomers.

2.4. Norbornene polymerization

Norbornene polymerization reactions were performed in a 50 ml glass flask equipped with magnetic stirrer, oil control of temperature. A typical reaction was performed by adding proper amount of MAO solid and introducing toluene (14 ml) into the reactor under nitrogen atmosphere. Toluene solution of norbornene (10 ml, 0.4 g/ml) and the toluene catalyst solution (1 ml, [Ni] = 1 μ mol) was injected into the reactor *via* syringe. After 10 min, the reaction was 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.

2.5. Synthesis of bis(2,6-diisopropylphenyl)benzamidine (L1)

Benzoyl chloride (1.1 ml, 10 mmol) and triethylamine (1.6 ml, 11 mmol) were added to a vigorously stirred solution of 2,6-diisopropylaniline (1.9 ml, 10 mmol) in CH₂Cl₂ (45 ml). After 3 h, the precipitate of $(C_2H_5)_3N \cdot HCl$ was filtrated, and white solid benzamide was obtained by evaporating the solvent. Then, an excess of thionyl chloride (2.0 ml, 28 mmol) was added to the benzamide, and the reaction mixtures were stirred for 2 h at 80 °C. The remainder thionyl chloride was distilled off under reduced pressure, to obtain the imidovl chloride as vellow, slowly solidifying oil. Successively, toluene (50 ml), triethylamine (1.6 ml, 11 mmol) and 2,6-diisopropylaniline (1.9 ml, 10 mmol) were added to the reaction system. The mixtures were heated to reflux for 12 h under the protection of nitrogen atmosphere. (C₂H₅)₃N · HCl was removed by filtration, and toluene was evaporated from the filtrate. After recrystallization of the product from ethanol/water, bis(2,6diisopropylphenyl)benzamidine (L1) as a colorless crystal was obtained in 60% yield (2.65 g, 6.02 mmol). EI-MS (m/z): 441 [M]⁺. ¹H NMR (300 MHz, CDCl₃), δ (ppm): 7.35–6.85 (m, 11H, Ar–H), 5.65 (s, 1H, NH), 3.25 (m, 4H, CH(CH₃)₂), 1.31 (d, 12H, CH(CH₃)₂), 0.94 (d, 12H, CH(CH₃)₂). ¹³C NMR (300 MHz, CDCl₃), δ (ppm): 153.43 (C=N), 145.19, 143.81, 139.27, 135.05, 134.02, 129.11, 128.78, 127.66, 127.47, 123.61, 123.42, 123.22, 28.57, 25.15 (CH(CH₃)₂), 22.45, 22.30 (CH(CH₃)₂). Anal. Calc. for C₃₁H₄₀N₂: C, 84.49; H, 9.15; N, 6.36. Found: C, 84.07; H, 9.20; N, 6.28%.

2.6. Synthesis of 2,6-diisopropylphenyl-4-methyl-N-(2,6-dimethylphenyl) benzamidine (**L2**)

L2 was prepared according to the method described above in 72% yield. EI-MS (*m*/*z*): 400 [M]⁺. ¹H NMR (300 MHz, CDCl₃), δ (ppm): 7.36–6.90 (m, 10H, Ar–*H*), 5.73 (s, 1H, N*H*), 3.24 (m, 2H, CH(CH₃)₂), 2.38 (s, 3H, 4-CH₃C₆H₂), 1.38 (s, 6H, CH₃), 1.04 (d, 12H, CH(CH₃)₂). ¹³C NMR (300 MHz, CDCl₃), δ (ppm): 154.20 (C=N), 145.18, 143.68, 139.44, 134.77, 131.75, 129.10, 128.40, 128.05, 127.48, 126.33, 123.55, 122.89, 28.53 (CH(CH₃)₂), 24.52 (CH₃–Ph), 22.08 (CH₃–Ph), 18.98 (CH(CH₃)₂). Anal. *Calc.* for C₂₈H₃₄N₂: C, 84.37; H, 8.60; N, 7.03. Found: C, 84.18; H, 8.51; N, 6.92%.

2.7. Synthesis of 2,6-diisopropylphenyl-4-methyl-N-(pentafluorophenyl)benzamidine (**L3**)

L3 was prepared according to the method described above. The resulting product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (10/1) as eluent, and then recrystallized from ethanol in 49% yield. EI-MS (*m*/*z*): 461 [M]⁺. ¹H NMR (300 MHz, CDCl₃), δ (ppm): 7.35–7.17 (m, 7H, Ar-*H*), 6.16 (s, 1H, N*H*), 3.43 (m, 2H, C*H*(CH₃)₂), 2.35 (s, 3H, 4-CH₃C₆H₂), 1.37 (d, 12H, CH(CH₃)₂). ¹³C NMR (300 MHz, CDCl₃), δ (ppm): 162.26 (*C*=N), 146.80, 140.73, 138.73, 138.63, 136.33, 132.00, 131.71, 129.59, 128.79, 127.17, 126.58, 123.69, 28.93 (CH(CH₃)₂), 24.21 (CH₃–Ph), 21.36 (CH(CH₃)₂). Anal. *Calc.* for C₂₆H₂₅F₅N₂: C, 67.82; H, 5.47; N, 6.08. Found: C, 67.93; H, 5.32; N, 6.02%.

2.8. Synthesis of $[(2,6^{-i}PrC_6H_3)N=C(ph)-N(2,6^{-i}PrC_6H_3)]Ni(PPh_3)(Ph)$ (1)

n-BuLi (0.43 ml, 2.6 M, 1.1 mmol) in hexane was added dropwise to a solution of **L1** (0.44 g, 1 mmol) in toluene (20 ml) at -78 °C. The mixtures were warmed up to room temperature and stirred overnight. *Trans*-chloro(phenyl)bis(triphenylphosphine) nickel(II) (0.69 g, 1.0 mmol) in toluene (20 ml) was added and continuously stirred overnight at room temperature. After filtration, the filtrate was concentrated to a volume of *ca*. 5 ml under reduced pressure, and then *n*-hexane (20 ml) was added. Solvent was removed from the precipitate via cannula filtration, and the residual orange powder was washed with *n*-hexane (3 × 5 ml). Drying in vacuo produces the desired nickel complex in 45% yield. FAB⁺-MS: *m/z*: 836, 837, 838, [M]⁺; 574, 575, 576, 577, [M–PPh₃]⁺; 497, 498, [M–PPh₃–Ph]⁺; 440, 441, 442, [L1]⁺; 262, 263, 264, [PPh₃]⁺. Anal. *Calc.* for C₅₅H₅₉N₂NiP: C, 78.85; H, 7.10; N, 3.34. Found: C, 78.32; H, 7.00; N, 3.15%.

2.9. Synthesis of $[(2,6^{-i}PrC_6H_3)N=C(4-CH_3C_6H_4)-N(2,6-MeC_6H_3)]Ni(PPh_3)(Ph)$ (2)

Complex **2** was prepared according to the same method described for **1**. Because of the good solubility in hexane, **2** was obtained in 26% yield. FAB⁺-MS: *m/z*: 794, 795, 796, $[M]^+$; 532, 533, 534, $[M-PPh_3]^+$; 455, 456, 457, $[M-PPh_3-Ph]^+$; 398, 399, 400, $[L2]^+$; 262, 263, 264, $[PPh_3]^+$. Anal. *Calc.* for C₅₂H₅₃N₂NiP: C, 78.50; H, 6.71; N, 3.52. Found: C, 78.39; H, 6.70; N, 3.25%.

2.10. Synthesis of $[(2,6^{-i}PrC_6H_3)N=C(4-CH_3C_6H_4)-N(pentafluorophenyl)]Ni(PPh_3)(Ph) ($ **3**)

Complex **3** was prepared according to the same method described for **1** in 52% yield. FAB⁺-MS: m/z: 836, 837, 838, [M]⁺; 556, 557, 558, 559, 860, [M–PPh₃]⁺; 594, 595, 596, 597, [M–PPh₃–Ph]⁺; 460, 461, 462, [L3]⁺; 262, 263, 264, [PPh₃]⁺. Anal. *Calc.* for C₅₀H₄₄F₅N₂NiP: C, 70.03; H, 5.17; N, 3.27. Found: C, 70.55; H, 5.05; N, 3.04%.

3. Results and discussion

3.1. Synthesis and characterizations of complexes

As shown in Scheme 2, the ligands were prepared according to a modified literature procedure in high yield [16]. Among these ligands, **L1** has been reported [17,34]. Benzamides were easily available from 2,6-diisopropylaniline and benzoyl chloride. Imidoyl chloride could be produced by the dehydration reaction between benzamide and the excess of thionyl chloride. After distilling the residue of thionyl chloride off, the crude products were obtained by the reaction between the quantitative anilines and imidoyl chlorides in refluxing toluene. Pure ligands **L1** and **L2** were recrystallized from ethanol/water solution, while **L3** was purified using silica chromatography and then recrystallized from ethanol. All of these ligands had been characterized by EI-MS, NMR and elemental analysis.

After the amidinate ligands were treated with *n*-butyllithium in toluene, an equimolar amount of *trans*-chloro(phenyl)bis(triphen-ylphosphine) nickel(II) was added to the solution and nickel complexes **1–3** were obtained as orange solids in a moderate yield.

Single crystal of complex **3** suitable for X-ray diffraction was grown from toluene/hexane solution under nitrogen atmosphere at ambient temperature. The diagram of the single-crystal structure is presented in Fig. 1 along with selected bond lengths and bond angles. Besides, the data collection and structure refinement parameters are summarized in Table 1.

Complex **3** in the solid state cocrystallizes with half a hexane molecule, which does not interact with the metal center and is omitted for clarity. As seen in Fig. 1, complex **3** contains one chelating amidinate, one phenyl, and one triphenylphosphine ancillary ligand around the nickel metal center, adopting a slightly distorted square planar coordination geometry (the sum of the angles around the nickel atom is near 360°). The aryl rings in aniline



L1, 1: Ar^1 =Phenyl, Ar^2 =2,6-diispropyphenyl; L2, 2: Ar^1 = *p*-tolyl, Ar^2 =2,6-dimethylphenyl; L3, 3: Ar^1 = *p*-tolyl, Ar^2 = pentafluorophenyl;

Scheme 2. Synthesis route of nickel complexes 1-3.



Fig. 1. Molecular structure of complex **3** depicted with 30% thermal ellipsoids. Hydrogen atoms and the uncoordinated hexane molecule have been omitted for clarity. Selected bond distances (Å) and angles (°): C(7)-N(1) 1.350(4), C(7)-N(2) 1.317(4), Ni(1)-C(27) 1.883(3), Ni(1)-N(1) 2.012(3), Ni(1)-N(2) 1.936(2), Ni(1)-P(1) 2.139 (1), C(27)-Ni(1)-N(2) 97.5(1), C(27)-Ni(1)-N(1) 164.2(1), N(1)-Ni(1)-N(2) 66.9(1), C(27)-Ni(1)-P(1) 92.6(1), N(2)-Ni(1)-P(1) 166.8(1), N(1)-Ni(1)-P(1) 103.2(1).

Table 1

Crystallographic data for complexes 3 1/2 hexane.

	3 1/2 hexane
Formula	C ₅₃ H ₅₁ F ₅ N ₂ PNi
Formula weight	900.64
Crystal color, form	red block
Crystal size (mm)	0.48 imes 0.28 imes 0.26
Crystal system	triclinic
Space group	ΡĪ
T (K)	173(2)
a (Å)	11.6755(12)
b (Å)	11.7115(12)
<i>c</i> (Å)	19.168(2)
α (°)	96.642(2)
β (°)	98.991(2)
γ (°)	115.716(2)
V (Å ³)	2282.3(4)
$D_{\text{calc}} (\text{g cm}^{-3})$	1.300
F(000)	928
Ζ	2
$\mu (\mathrm{mm}^{-1})$	0.518
Reflections collected	17993
R _{int}	0.0286
Data/parameters	8852/554
Goodness-of-fit	1.054
$R_1/wR_2 \left[I > 2\sigma(I)\right]^*$	0.0503/0.1319
R_1/wR_2 (all data)	0.0783/0.1521
Largest difference peak and hole (e $Å^{-3}$)	1.363/-0.508

* $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|, \ wR_2 = [\sum w(F_0^2 - F_c^2)^2 / \sum w(F_0^2)^2]^{1/2}.$

moieties are tilted to the chelate ring, the dihedral angles being 65° for the ring bonded to N(1), and 75° for the ring bonded to N(2), respectively. The C(7)–N(1) and C(7)–N(2) bond length are 1.350(4) and 1.317(4) Å, respectively. It is similar to typical C(sp²)–N(sp²) single and double bonds length, which indicate rather significant delocalization in the amidinate complex. The C_{ph}–Ni bond length (1.883(3) Å) in **3** is similar to that of neutral salicylaldiminato Ni(II), while P–Ni bond length (2.139(1) Å) in **3** is slightly shorter than that of neutral salicylaldiminato Ni(II) (2.172(2) Å) [29], suggesting there is a stronger interaction between nickel metal center and the triphenylphosphine. The N(1)–Ni–N(2) bite angle in **3** is 66.9(1)°, smaller than that of Ni(II) mono-

amidinate acetylacetonate complexes $(69.7(1)^\circ)$ and bisamidinate nickel complex $(68.6(1)^\circ)$ [28,35].

3.2. Ethylene oligomerization

As reported in the literature, for neutral salicylaldiminato Ni(II) complexes, Ni(COD)₂ usually was used as phosphine scavenger in ethylene polymerization [29–32]. The phosphine scavenger bound PPh₃ more strongly than the nickel(II) center, effectively removing phosphine from the salicylaldiminato nickel catalysts. However, in attempts to polymerize ethylene with **1** or **3** combined with two or 20-fold Ni(COD)₂, neither polymers nor oligomers of ethylene were obtained. The similar phenomenon was also found in neutral iminophosphonamide (PN₂) nickel complex [36,37]. In contrast, these neutral nickel complexes could be activated for ethylene oligomerization upon the addition of MAO. **1–3**/MAO showed moderate turnover frequency (TOF) of *ca*. 5×10^3 mol ethylene/(mol Ni h) for ethylene oligomerization at 0.5 atm of ethylene pressure (see Table 2).

The structure of the nickel complexes slightly influences their catalytic activities. Bulky nickel complex **1** showed a higher TOF than **2**, while **3** with an electron-withdrawing pentafluorophenyl group exhibited the highest TOF for ethylene oligomerization. A reasonable explanation for the TOF enhancement is that the introducing of an electron-withdrawing group would generate a more electrophilic nickel center, thus reducing activation energy for ethylene insertion, and favoring the olefin coordination and insertion [38,39].

GC–MS analysis (Fig. 2) confirmed that the oligomer obtained at 20 °C mainly contained dimers (*ca.* 65%) and trimers (*ca.* 35%) of ethylene. In addition, with an increase in the reaction temperature from 20 to 40 °C, the TOF and selectivity of products were also enhanced. At 40 °C, **3** showed a high selectivity of dimerization of ethylene, up to 94%.

Even though **1** has two bulky 2,6-diisopropylphenyl substituents, only low-molecular-weight oligomers were obtained from the catalysis reaction. Obviously, the results can be attributed to the unique structure of the complex. Recent DFT-based stochastic simulation on amidinate nickel complexes in ethylene polymerization indicated that the insertion barrier versus chain transfer is lower than 0.8 kcal/mol, suggesting there is a relatively rapid rate of chain transfer in ethylene oligomerization [37]. Moreover, as shown in X-ray single-crystal structure of **3**, the coordinated bite angle of four-membered ring complex is $66.9(1)^{\circ}$, resulting in the steric substituents in axial location being far away from the nickel center. The unshielded metal center easily leads to rapid β -H elimination or chain transfer in the process of polymerization. Therefore, low-molecular-weight oligomers rather than high-molecular-weight polymers were obtained.

Table 2The results of ethylene oligomerzation with 1-3/MAO.

Entry	Complex	T (°C)	Oligomers (mol%)			TOF ^c
			C ₄	C ₆	C ₈ -C ₁₂	
1 ^a	1 or 3	20	-	-	-	inactive
2	1	20	63.4	36.0	0.6	4.6
3	2	20	68.5	31.5	-	4.3
4	3	20	63.9	36.1	-	5.7
5 ^b	3	40	94.3	5.7	-	7.5

Reaction conditions: Ni complex, 15 μ mol; Al/Ni = 600; t_p , 0.5 h; toluene, 20 ml; ethylene pressure, 0.5 atm.

^a Two or 20-fold Ni(COD)₂ instead of MAO.

^b Ni, 5 μmol.

^c 10³ mol ethylene/(mol Ni h).



Fig. 2. GC spectrum of oligomer obtained by 1/MAO at 20 °C (entry 2 in Table 2).

3.3. Norbornene polymerization

The monoamidinate nickel complexes were also tested for norbornene (NBE) polymerization with MAO as cocatalyst and the polymerization results are summarized in Table 3. These three complexes showed very high activities (*ca.* 10^7 g PNBE/mol Ni h) for norbornene polymerization. As shown in Table 3, the reaction temperature strongly affected the catalytic activities. With an increase in reaction temperature, the catalytic activity for norbornene polymerizations increased and then decreased. All of the complexes showed the highest activities for norbornene polymerization at 60 °C. Polymerization temperature also affected the molecular weights of the polymers. The M_n values of the obtained

Table 3 The results of norbornene polymerization with 1–3/MAO.

Entry	Complex	T (°C)	Yield (g)	Activity ^a	$M_{\rm n}$ (kg/mol)	MWD
1	1	0	0.96	0.58	375.8	2.31
2	1	40	1.59	0.95	335.0	2.55
3	1	60	2.47	1.48	304.0	2.44
4	1	80	2.38	1.43	265.3	2.63
5	2	0	1.08	0.65	311.1	2.70
6	2	40	1.62	0.97	284.3	2.52
7	2	60	2.34	1.40	209.4	2.47
8	2	80	1.76	1.06	146.2	2.58
9	3	0	2.01	1.21	282.8	2.67
10	3	40	2.58	1.55	195.8	2.66
11	3	60	3.24	1.94	123.6	2.71
12	3	80	2.94	1.76	82.5	2.46

Reaction conditions: Ni complex, 1 μ mol; norbornene, 4 g; Al/Ni = 600; t_p , 10 min; total solution volume, 25 ml toluene.

^a In unit of 10⁷ g PNBE/(mol Ni h).

polymers decreased with an increase in polymerization temperature, suggesting that chain transfer or termination began to accelerate at a high temperature. The molecular weight distributions (MWDs) were close to 2 and appeared as a single modal in GPC chromatograms, which indicated that the polymerizations occur at the single active site.

Moreover, a comparison between the polymerization results of three catalytic systems at 60 °C showed that the structure of the nickel complex played effects on the polymerization. Through the comparison between **1** and **2**, it is found that the steric hindrance of complex did not clearly affect the catalytic activity, but obviously affected the molecular weight of the polymer. The M_n values of the obtained polynorbornenes by different catalysts were in the order of 1 > 2 > 3, which is well consistent with the steric bulk of these complexes. Additionally, complex **3** with an electron-withdrawing pentafluorophenyl group exhibited the highest catalytic activity for norbornene polymerization, which might result from a more electrophilic nickel center allowing the rapid olefin insertion.

All of the obtained polynorbornenes are soluble in chlorobenzene, *o*-dichlorobenzene and cyclohexane at room temperature, and show similar IR and ¹H NMR spectra. The IR spectrum revealed no traces of double bond which often appeared at 1620–1680, 966 and 735 cm⁻¹, while the existence of vibration bands of bicyclics of norbornene units was at 941 cm⁻¹. The ¹H NMR spectrum (0.86– 2.38 ppm) (Fig. 3) also proved no traces of any double bond, ensuring the occurrence of vinyl-type polymerization rather than ringopening metathesis polymerization [40–43]. TGA curves of the obtained polynorbornenes showed that the polymer samples were stable up to 450 °C. Attempts to measure glass transition temperature (T_g) of the polynorbornenes by DSC were unsuccessful



Fig. 3. ¹H NMR spectrum of polynorbornene prepared by 1/MAO at 60 °C.

because T_g was close to the decomposition temperature [44]. The wide-angle X-ray diffraction analysis of the obtained polynorbornene showed two major broad peaks ($2\theta = 9-11^{\circ}$ and $17-19^{\circ}$), which indicated that the obtained polymer was non-crystalline and had low stereoregularity [45,46].

4. Conclusion

Three monoamidinate nickel complexes have been synthesized and characterized. The solid-state structure of complex **3** reveals four-coordination and a rough planar geometry with nickel center. Though monoamidinate nickel complexes had bulky steric hindrance, the small bite angle of four-membered ring complex led to ethylene oligomerization in the presence of MAO, and the obtained products were mainly dimers and trimers. However, complexes **1–3** activated with MAO showed very high catalytic activities for vinyl-addition polymerization of norbornene. Complex **1** with the most steric hindrance groups produced the highest molecular-weight polynorbornene, while complex **3** with an electron-withdrawing group exhibited the highest catalytic activity for norbornene polymerization.

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Appendix A. Supplementary data

CCDC 700699 contains the supplementary crystallographic data for complex **1**. These data can be obtained free of charge via http:// www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2008.12.019.

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