

Nickel(II) α -Diimine Catalysts with Carboxyl Groups for Ethylene Oligomerization and Polymerization*

Bing Liu, Meng-zhe Fang, Su-yun Jie**, Zhi-yang Bu and Bo-Geng Li
*State Key Laboratory of Chemical Engineering, College of Chemical and Biological Engineering,
Zhejiang University, Hangzhou 310027, China*

Abstract A series of nickel(II) α -diimine complexes with strong electron-withdrawing carboxyl groups, having reactive hydrogen atoms, were prepared and used as precatalysts for ethylene oligomerization and/or polymerization. The influence of metal halides and ligand structure on the catalytic activity and properties of products was investigated. The results showed that nickel bromide was much more active than nickel chloride, and the substituents at the *ortho*-position of aryl ring had large influence on the properties of products. Therefore, the products ranging from liquid oligomers to polymers could be readily obtained by the variation of the substituents on the ligands and reaction conditions.

Keywords: α -Diimine; Nickel; Ethylene; Oligomerization; Polymerization.

INTRODUCTION

Olefin polymerization and oligomerization catalyzed by transition metal complexes have attracted great attention in both academic and industrial research^[1–4]. Thereinto, late transition metal catalysts play an important role since Brookhart and co-workers discovered nickel and palladium(II) α -diimine catalysts for olefin polymerization^[5–7]. Currently, the access of branched polyethylenes mostly relies on the copolymerization of ethylene and short-chain α -olefin comonomers or radical polymerization under extreme conditions. Compared with the Ziegler-Natta and metallocene catalysts^[8–12], the α -diimine nickel catalysts are providing new approaches to branched polyethylenes *via* the homopolymerization of ethylene through a chain isomerization mechanism. Furthermore, one of the most unique aspects of these α -diimine nickel catalysts is that it is easy to customize the microstructures of polymers by varying the catalyst structure. Namely, the catalytic activity and properties of the resulting polymers are greatly dependent on the ligand structure^[13–16]. With the modification of ligand structure, including the steric and electronic effects of substituents, ligand backbone, and the chelating heteroatoms, the molecular weights of products could vary from the order of 10^2 (oligomers) to that of 10^5 (polymers), and the branching degree of polymers could be also changed from low to high, which may yield a new family of advanced polyethylenes. In addition, the reaction conditions, such as ethylene pressure and reaction temperature, can be also used to control the catalytic activity and the properties of polymers^[17, 18]. The increase in reaction temperature commonly results in the higher degree of branching and the decrease in molecular weight of polymers. The degree of branching rapidly decreases and the catalyst activity is improved significantly under higher ethylene pressure^[7, 19]. What's more important, the stronger tolerance to polar functional groups of late transition metal catalysts has been recognized as another key advantage over early transition metal catalysts^[20–23].

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** Corresponding author: Su-yun Jie (介素云), E-mail: jiesy@zju.edu.cn

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Although the various electron-withdrawing substituents have been studied for the α -diimine late transition metal catalysts^[24–26], no any information about the groups with reactive hydrogen atoms was found in the literatures. Therefore, a series of nickel(II) α -diimine catalysts with a carboxyl group at the *para*-position of the aryl ring were synthesized and characterized in this work. Because of the existence of reactive hydrogen atoms and the strong electron-withdrawing nature, the carboxyl groups could affect the catalytic performance of nickel complexes. Herein, the influence of carboxyl groups, ligand structure and reaction conditions on the ethylene oligomerization and/or polymerization was also investigated.

EXPERIMENTAL

General Considerations

All manipulations of air- and/or moisture-sensitive compounds were performed under nitrogen using standard Schlenk and glove-box techniques. The solvents for synthesis and polymerization, THF and toluene were refined through solvent purification system. 2,3-Butanedione, 4-aminobenzoic acid, 4-amino-3-methylbenzoic acid, 4-amino-3,5-dimethylbenzoic acid, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, and NiBr_2 were obtained from J&K Scientific Ltd and used as received. Methylaluminoxane (MAO, 1.44 mol/L in toluene) and diethylaluminum chloride (Et_2AlCl , 1.1 mol/L in toluene) were purchased from Acros Chemicals. Polymerization-grade ethylene (TOPGRAND Petrification Industry Gas. Ltd) was purified by passing through ethylene purification equipment comprised by CuO catalyst and 3 Å molecular sieves columns. All other chemicals were obtained commercially and used without further purification unless otherwise stated.

The FTIR spectra were recorded on a Nicolet 5700 spectrometer using KBr disks in the range of 4000–400 cm^{-1} . ^1H -NMR and ^{13}C -NMR spectra of ligands were recorded on a Bruker DMX-400 instrument in DMSO-d_6 with TMS as the internal standard. Elemental analysis was performed on a Flash EA1112 microanalyzer. The molecular weight and molecular weight distribution of polymers were measured at 150 °C in 1,2,4-trichlorobenzene with a PL-GPC220 coupled with an in-line capillary viscometer. The melting temperatures of polymers were measured with a Perkin-Elmer DSC 7 instrument in a standard mode. The samples were first heated to 150 °C at 20 $\text{K} \cdot \text{min}^{-1}$ to eliminate thermal history and held for 2 min at 150 °C. The samples were then cooled to 30 °C at 10 $\text{K} \cdot \text{min}^{-1}$ and held for 2 min at 30 °C, before heating to 150 °C at 10 $\text{K} \cdot \text{min}^{-1}$. The ^{13}C -NMR spectra of polymers were conducted at 120 °C with a Varian Merourey 300 pulsed NMR Spectrometer in *o*-dichlorobenzene- d_4 .

Synthesis of α -Diimine Ligands L1–L3

To a solution of the corresponding aminobenzoic acid derivative (21 mmol) in dry methanol (100 mL), 2,3-butanedione (10 mmol) and a catalytic amount of *p*-toluene sulfonic acid were added. The reaction solution was stirred at 60 °C for 18 h. The pale yellow precipitate was filtered, washed with cold methanol, and dried in vacuo to give the pure product.

L1: Pale yellow solid in 36% yield. FTIR (KBr disk, cm^{-1}): 2980, 2836, 2667, 1682 ($\nu_{\text{C=O}}$), 1635 ($\nu_{\text{C=N}}$), 1599, 1567, 1422, 1361, 1315, 1283, 1213, 1172, 1119, 867, 831, 789, 709, 660. ^1H -NMR (400 MHz, DMSO-d_6 , δ): 12.82 (s, 2 H, COOH), 7.98 (d, 4 H, $J = 8.4 \text{ Hz}$, Ar–H), 6.93 (d, 4 H, $J = 8.4 \text{ Hz}$, Ar–H), 2.08 (s, 6 H, CH_3). ^{13}C -NMR (100 MHz, DMSO-d_6 , δ): 167.6 (C=O), 166.9 (C=N), 154.4, 130.6, 126.1, and 118.5 (aromatic–C), 15.3 (CH_3). Anal. Calcd. for $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_4$ (324.34): C, 66.66; H, 4.97; N, 8.64. Found: C, 66.77; H, 4.89; N, 8.58.

L2: Pale yellow solid in 43% yield. FTIR (KBr disk, cm^{-1}): 2992, 2853, 2647, 1686 ($\nu_{\text{C=O}}$), 1650 ($\nu_{\text{C=N}}$), 1600, 1567, 1430, 1365, 1308, 1288, 1262, 1225, 1189, 1122, 1105, 945, 911, 847, 792, 758, 658. ^1H -NMR (400 MHz, DMSO-d_6 , δ): 12.72 (s, 2 H, COOH), 7.86 (s, 2 H, Ar–H), 7.80 (dd, 2 H, $J_1 = 8.0 \text{ Hz}$, $J_2 = 1.6 \text{ Hz}$, Ar–H), 6.81 (d, 2 H, $J = 8.4 \text{ Hz}$, Ar–H), 2.11 (s, 6 H, Ar– CH_3), 2.08 (s, 6 H, $\text{N}=\text{CCH}_3$). ^{13}C -NMR (100 MHz, DMSO-d_6 , δ): 167.12 (C=O), 167.10 (C=N), 153.0, 131.5, 128.0, 126.3, 126.1, and 117.5 (aromatic–C), 17.2 (Ar– CH_3), 15.6 ($\text{N}=\text{CCH}_3$). Anal. Calcd. for $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_4$ (352.39): C, 68.17; H, 5.72; N, 7.95. Found: C, 68.08; H, 5.66; N, 7.62.

L3: Pale yellow solid in 24% yield. FTIR (KBr disk, cm^{-1}): 2976, 2855, 2603, 1677 ($\nu_{\text{C=O}}$), 1655 ($\nu_{\text{C=N}}$), 1601, 1571, 1436, 1407, 1367, 1313, 1246, 1202, 1126, 951, 909, 791, 694. $^1\text{H-NMR}$ (400 MHz, DMSO-d_6 , δ): 12.62 (s, 2 H, COOH), 7.71 (s, 4 H, Ar-H), 2.04 (s, 12 H, Ar-CH_3), 1.99 (s, 6 H, N=CCH_3). $^{13}\text{C-NMR}$ (100 MHz, DMSO-d_6 , δ): 167.38 (C=O), 167.22 (C=N), 151.9, 129.1, 125.4, and 124.4 (aromatic-C), 17.2 (Ar-CH_3), 15.9 (N=CCH_3). Anal. Calcd. for $\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_4$ (380.44): C, 69.46; H, 6.36; N, 7.36. Found: C, 69.30; H, 6.37; N, 7.19.

Synthesis of the (α -Diimine)nickel(II) Complexes 1a, 1b, 2a, 2b

The α -diimine ligand (30 mmol) was dispersed in anhydrous methanol (40 mL) and 0.95 equiv. of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ or NiBr_2 was added under N_2 atmosphere. The mixture was stirred at 60 °C for 24 h. For purification, the resulting solution was concentrated under reduced pressure and then filtered through a plug of celite. The filtrate was evacuated and the residue was then washed twice with dried THF to give the desired product in good yield and purity.

1a: Brown solid in 85% yield. FTIR (KBr disk, cm^{-1}): 3399, 3248, 2977, 1692, 1655, 1603, 1419, 1393, 1377, 1315, 1285, 1243, 1175, 1031, 822, 760. Anal. Calcd. for $\text{C}_{18}\text{H}_{16}\text{Cl}_2\text{N}_2\text{NiO}_4$ (453.93): C, 47.63; H, 3.55; N, 6.17. Found: C, 47.50; H, 3.47; N, 6.14.

1b: Brown solid in 90% yield. FTIR (KBr disk, cm^{-1}): 3346, 3216, 2972, 1670, 1661, 1603, 1412, 1378, 1314, 1241, 1172, 1112, 1020, 878, 761. Anal. Calcd. for $\text{C}_{18}\text{H}_{16}\text{Br}_2\text{N}_2\text{NiO}_4$ (542.84): C, 39.83; H, 2.97; N, 5.16. Found: C, 39.91; H, 3.10; N, 5.01.

2a: Brown solid in 93% yield. FTIR (KBr disk, cm^{-1}): 3385, 3236, 2973, 1688, 1656, 1605, 1418, 1381, 1303, 1244, 1194, 1150, 1040, 773. Anal. Calcd. for $\text{C}_{20}\text{H}_{20}\text{Cl}_2\text{N}_2\text{NiO}_4$ (481.98): C, 49.84; H, 4.18; N, 5.81. Found: C, 49.69; H, 4.12; N, 5.73.

2b: Brown solid in 92% yield. FTIR (KBr disk, cm^{-1}): 3349, 2960, 2924, 2854, 1679, 1649, 1603, 1563, 1422, 1378, 1311, 1293, 1261, 1188, 1114, 1031, 755. Anal. Calcd. for $\text{C}_{20}\text{H}_{20}\text{Br}_2\text{N}_2\text{NiO}_4$ (570.89): C, 42.08; H, 3.53; N, 4.91. Found: C, 42.23; H, 3.64; N, 4.66.

Ethylene Oligomerization and Polymerization

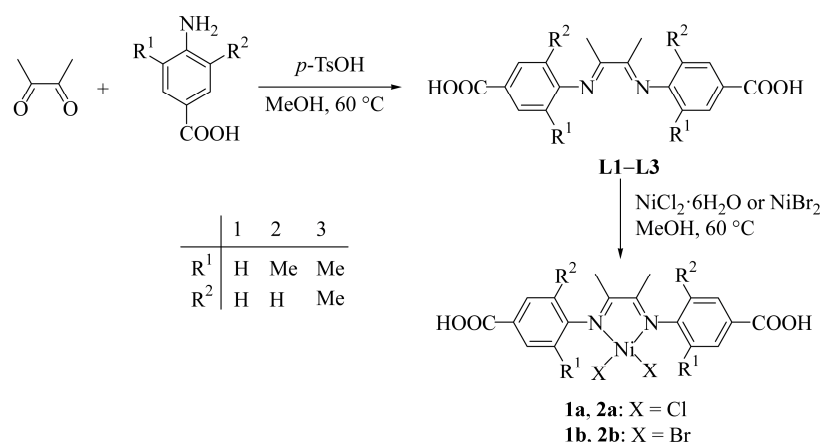
Ethylene polymerization was carried out in a 250 mL glass reactor with a mechanical stirrer under atmospheric pressure. After it was dried under vacuum, purged 3 times with nitrogen and replaced twice with ethylene, the reactor was full of ethylene, and then placed into a water bath set at the operating temperature. Toluene (100 mL) and the required amount of co-catalyst were introduced to the reactor. Subsequently a prescribed amount of catalyst was added through a connected ampoule to start the polymerization. After the desired time, the acidified ethanol (10 wt% HCl) was injected into the reactor to terminate the polymerization. A sample of liquid mixture was taken out and analyzed by gas chromatography. The large amount of acidified ethanol was added to the mixture and stirred overnight. The polymers were collected, washed with ethanol, and dried in vacuo overnight at 60 °C.

The polymerization reactions under high pressure of ethylene were carried out in a 500 mL stainless steel autoclave with a mechanical stirrer and a temperature controller. Except for 150 mL of toluene used, the same procedure was employed as that under atmospheric pressure.

RESULTS AND DISCUSSION

Synthesis and Characterization

The α -diimine ligands (**L1–L3**) with carboxyl groups (Scheme 1) were readily synthesized by the condensation reaction of 2,3-butanedione with two equivalents of the corresponding 4-aminobenzoic acid in anhydrous methanol according to the reported procedure^[27, 28]. All the ligands were characterized by FTIR, ^1H - and ^{13}C -NMR spectra, as well as elemental analysis.



Scheme 1 Synthesis of ligands and nickel complexes with carboxyl groups

The nickel(II) complexes (**1a**, **1b**, **2a**, **2b**) were prepared by the coordination reaction between the corresponding α -diimine ligand (**L1** or **L2**) and nickel halides ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ or NiBr_2) in anhydrous methanol. However, the reaction between ligand **L3** and nickel halides didn't occur because of the insolubility of **L3** in organic solvents. The comparison of FTIR spectra between nickel complexes and free ligands indicated the successful occurrence of coordination reactions. Moreover, the elemental analysis data were consistent with the formula LNiCl_2 of nickel chloride complexes (**1a**, **2a**) and LNiBr_2 of nickel bromide complexes (**1b**, **2b**). Due to the paramagnetic nature of these (α -diimine)nickel(II) complexes, the NMR studies were not feasible.

Ethylene Oligomerization and Polymerization

According to the previous results^[29, 30], the Al-containing co-catalysts, such as methylaluminoxane (MAO) or diethylaluminum chloride (Et_2AlCl), are commonly employed to activate the nickel-based pre-catalysts. Therefore, upon activation with MAO or Et_2AlCl , the catalytic properties of nickel complexes **1a**, **1b**, **2a**, **2b** for ethylene oligomerization and/or polymerization were investigated, and the results are summarized in Tables 1 and 2. The carboxyl group in the catalyst structure is not only a strong electron-withdrawing group, but also has a reactive hydrogen atom. Therefore, an induction time of several minutes were observed in each case due to the reaction between carboxyl groups and co-catalysts.

Table 1. Ethylene oligomerization and polymerization with nickel complexes at 0.1 MPa^a

Entry	Cat.	<i>T</i> (°C)	Activity ^b	Oligomers ^c (wt%)	Distribution ^d			Polymers		
					C ₄	C ₆	C ₈₊	<i>T</i> _m ^e (°C)	<i>M</i> _w ^f (g·mol ⁻¹)	<i>M</i> _w / <i>M</i> _n ^f
1	1a	25	2.48	100	52	16	32	—	—	—
2	1b	25	7.27	100	67	15	18	—	—	—
3 ^g	1b	25	1.75	100	34	12	54	—	—	—
4	1b	0	1.51	100	100	0	0	—	—	—
5	1b	50	3.63	100	78	16	6	—	—	—
6	2a	25	20.57	13	47	12	41	117.4	2940	3.55
7	2b	25	80.77	44	58	21	21	116.4	4230	4.39
8 ^g	2b	25	39.35	31	26	19	55	114.4	2470	2.82
9	2b	0	8.14	72	86	5	9	—	—	—
10	2b	50	38.52	67	69	19	12	wax	—	—
11 ^h	4b	25	104.8	25	32	18	50	—	—	—
12 ^h	5b	25	786.2	100	8	11	81	—	—	—

^a Polymerization conditions: 30 μmol of Ni, 100 mL of toluene, co-catalyst: MAO, Al/Ni = 500, 30 min, 400 $\text{r} \cdot \text{min}^{-1}$;

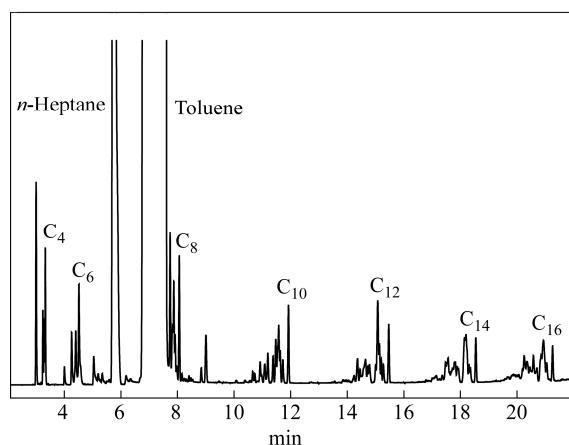
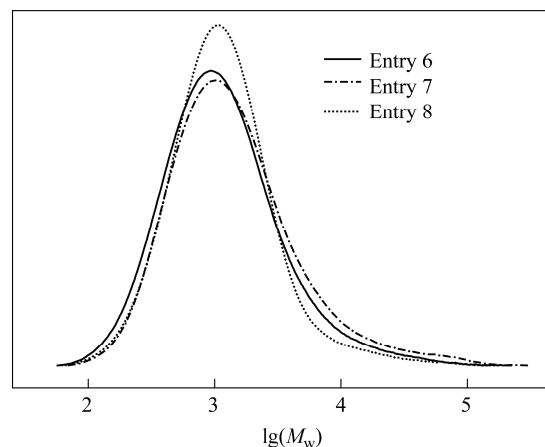
^b Activity: in unit of $10^3 \text{ g} \cdot \text{mol}^{-1} \cdot \text{h}^{-1}$; ^c Mass percentage of oligomers in total products; ^d Mass percentage of C_x in total oligomers, determined by GC; ^e Determined by DSC with the second heat curves; ^f Determined by GPC; ^g Co-catalyst: AlEt_2Cl , Al/Ni = 200; ^h Experiments for comparison

Table 2. Ethylene oligomerization and polymerization with nickel complexes at 3.0 MPa^a

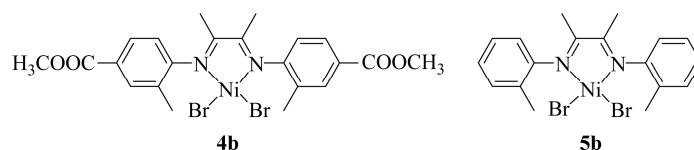
Entry	Cat.	Activity ^b	Oligomers ^c (wt%)	Distribution ^d			Polymers		
				C ₄	C ₆	C ₈₊	<i>T</i> _m ^e (°C)	<i>M</i> _w ^f (g·mol ⁻¹)	<i>M</i> _w / <i>M</i> _n ^f
13	1a	1.54	96	99	0	1	122.2	18980	17.00
14	1b	2.02	98	74	2	24	127.9	55280	20.64
15	2a	7.37	10	34	5	61	123.4	14680	11.44
16	2b	29.42	14	22	10	68	114.2	4530	5.38

^a Polymerization conditions: 30 μmol of Ni, 150 mL of toluene, co-catalyst: MAO, Al/Ni = 500, 25 °C, 30 min, 400 r·min⁻¹;^b Activity: in unit of 10⁵ g·mol⁻¹·h⁻¹; ^c Mass percentage of polymers in total products; ^d Mass percentage of C_x in total oligomers, determined by GC; ^e Determined by DSC with the second heat curves; ^f Determined by GPC

Upon activation with MAO, the catalytic activity of nickel complexes (**2a**, **2b**) bearing *o*-methyl group on the aryl ring was much higher than that of nickel complexes (**1a**, **1b**) without any other substituents under the same conditions (entries 1, 2, 6 and 7 in Table 1). On the other hand, the nickel bromide complexes produced higher catalytic activity than the corresponding nickel chloride complexes bearing the same ligand (**1b** > **1a**, **2b** > **2a**) due to the easier formation of active species after the activation with MAO^[31]. Furthermore, similar to the results reported in the literature^[32], the products obtained by nickel complexes (**1a**, **1b**) without any other substituents were totally liquid oligomers, which were branched olefins distributed from C₄ to C₁₆, with butenes as the major product. However, the products obtained by nickel complexes (**2a**, **2b**) bearing *o*-methyl group consisted of liquid oligomers (Fig. 1) and solid polyethylenes although the molecular weight of polyethylenes was relatively low with a little broader PDI^[33] (Fig. 2). The melting point at about 117 °C of polymers demonstrated that the polyethylenes obtained were also branched.

**Fig. 1** GC traces of the oligomers obtained at 0.1 MPa (entry 7 in Table 1)**Fig. 2** GPC curves of the polyethylenes obtained at 0.1 MPa (entries 6–8 in Table 1)

In order to compare the influence of carboxyl group on the catalytic performance, the nickel α -diimine catalysts **4b** with carbomethoxy group and **5b** without any substituent at *para*-position (Scheme 2) have been also synthesized and used in ethylene oligomerization and/or polymerization. The catalytic activity of nickel complex **2b** with carboxyl group was slightly lower than that of **4b** with carbomethoxy group, whereas both of them produced oligomers and polymers (entries 7 and 11 in Table 1). Although **5b** without any substituent at *para*-position was much more active, only liquid oligomers were obtained (entry 12 in Table 1).



Scheme 2 Structures of nickel α -diimine catalysts **4b** and **5b** for comparison

Reaction temperature commonly had great influence on the polymerization of ethylene. For the current catalytic systems, when reaction temperature increased from 0 °C to 50 °C, the catalytic activity increased firstly and then decreased because both the reaction rate constant (K_p) and the deactivation rate constant (K_d) increased as reaction temperature was raised. For the **2b**/MAO system, the large amount of polymers was obtained at 25 °C, whereas the small amount of polymers at 0 °C was not enough to be measured. Because of the low molecular weight, some wax was observed and adhered on the container expect for the liquid oligomers (entry 10 in Table 1). The Cl-containing co-catalyst (Et_2AlCl) was also used to activate nickel complexes **1b** and **2b** at 25 °C. Compared with MAO systems, the Et_2AlCl catalytic systems gave much lower activity for both **1b** and **2b**. Polyethylenes with lower molecular weight and melting point were obtained by the **2b**/ Et_2AlCl system (entry 8 in Table 1).

In order to clarify the influence of ethylene pressure, the reactions were conducted with nickel complexes/MAO catalytic systems at 3.0 MPa of ethylene pressure (Table 2). Based on the increase in ethylene concentration, the catalytic activity obtained by each complex was improved greatly. Meanwhile, complexes **1a** and **1b** produced a small amount of polymer and the amount of liquid oligomers produced by complexes **2a** and **2b** also decreased. The reason is that higher ethylene concentration is favorable for the coordination and insertion of ethylene, meanwhile it also suppresses chain transfer, yielding higher molecular weight of polymers. Nickel complexes **2a** and **2b** bearing *o*-methyl group on the aryl ring produced much more polymers than **1a** and **1b** without any substituent. The same influencing regularity of substituents and halides on the catalytic activity was observed as the results at 0.1 MPa. The influence of metal halide on the properties of polyethylenes was more obvious under high pressure. Both melting point and molecular weight of polyethylenes obtained by complex **1b** were higher than those by complex **1a**; however, an inverse result was observed for **2a** and **2b** bearing ligand **L2**, namely, the molecular weight and melting point of polyethylenes obtained by **2b** decreased. High pressure usually resulted in the broader molecular weight distribution (Fig. 3) and the decrease in the degree of branching. In comparison with the GC traces of oligomers obtained by the **2b**/MAO system at 0.1 MPa and 3.0 MPa (Figs. 1 and 4), it is obvious that the degree of branching of products significantly decreased under high pressure.

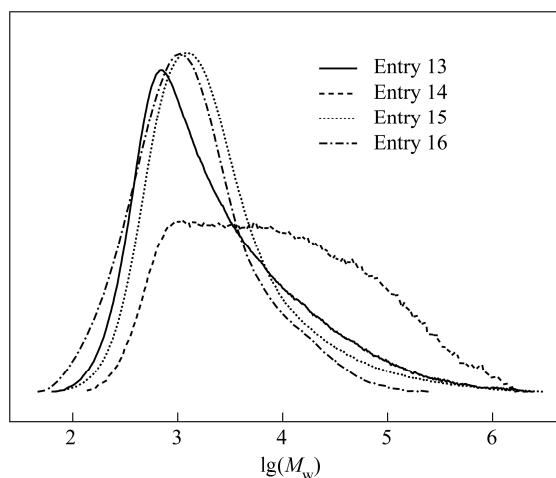


Fig. 3 GPC curves of the polyethylenes obtained by entries 13–16 in Table 2

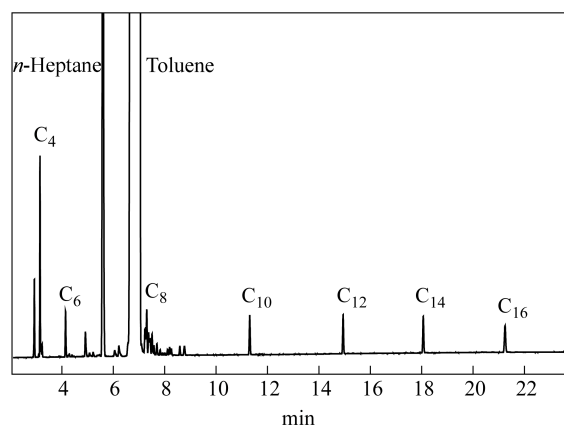


Fig. 4 GC traces of oligomers obtained by entry 14 in Table 2

In this work, all the polymers exhibited low melting points and low crystallinities, which illustrated that the polyethylenes formed possessed branches. This commonly occurred with nickel systems due to the chain migration during the polymerization. To further understand the microstructure of polyethylenes, a representative sample (entry 7 in Table 1) was characterized by ^{13}C -NMR spectra (Fig. 5). The single peaks at $\delta = 114.2$ and 139.1 showed the property of vinyl unsaturated chain end and the other assignments were determined according to the literatures^[34, 35]. The analysis indicated that the branches consisted of methyl (27.82%), butyl (16.94%), and long branches (55.24%) and the extent of branching was counted ~ 47 branches per 1000 carbon atoms according to the calculation method reported^[34].

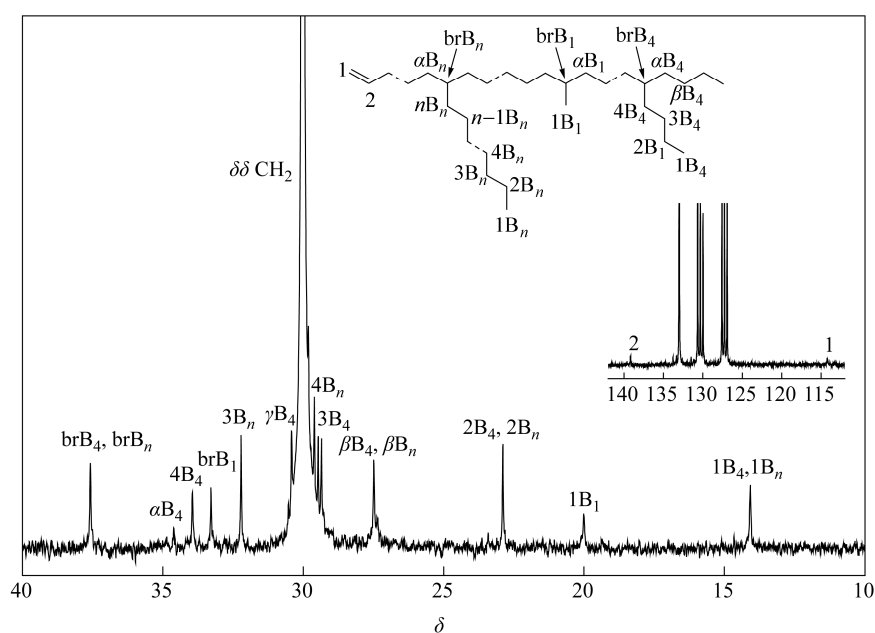


Fig. 5 ^{13}C -NMR spectrum of the polyethylene (entry 7 in Table 1)

CONCLUSIONS

A series of α -diimine Ni(II) complexes with carboxyl groups has been synthesized and characterized. Upon activation with MAO or AlEt_2Cl , these nickel complexes exhibited moderate catalytic activity for ethylene oligomerization and/or polymerization at 0.1 MPa of ethylene pressure in spite of the reactive hydrogen in the

catalyst structure. High pressure of ethylene enhanced the catalytic activity greatly and led to the formation of more polymers. The products ranging from liquid oligomers to polymers could be obtained by varying the catalyst structures and reaction conditions. Nickel bromide complex with *o*-methyl substituent (**2b**) gave the highest activity and produced more solid polymers. The polyethylenes exhibited low melting points due to the branches.

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