ORIGINAL PAPER

Novel dendrimer-based nickel catalyst: synthesis, characterization and performance in ethylene oligomerization

[a]Jun Wang*, [a]Guang Yang, [a]Cui-Qin Li, [a]Wei-Guang Shi, [b]Si-Han Wang

[a]*Key Laboratory of Oil Gas & Chemical Technology, College of Chemistry & Chemical Engineering, Northeast Petroleum University, [b]Daqing Petrochemical Research Center Daqing 163318, Heilongjiang Province, China*

A novel nickel metallodendrimer was synthesized with poly(amidoamine), 3,5-di-tert-butyl-2-hydroxy-benzaldehyde and nickel chloride via the Schiff's base and the complexation reactions. Structures of the dendritic ligand and its nickel complex were characterized by IR, NMR, UV, ESI-MS and elemental analyses. This new nickel metallodendrimer as a catalyst precursor, together with methylaluminoxane as an activator, was evaluated in the ethylene oligomerization. Under the conditions of 0.5 h, 0.5 MPa, 25 ℃ and Al/Ni mole ratio 500 : 1 employed for the nickel complex, the catalytic activity showed a maximum value of 4.93×10^5 grams per mole of Ni catalyst per hour. Substituents on the benzene ring seem to have a negative influence on the catalytic activity of the complex.

Introduction

The concept of dendrimers was first introduced in the late 1970s and it was developed during 1980s by Newkome et al. (1986) and other researchers. Dendrimers are a class of three-dimensional macro-molecules with a central core and branches expanding to peripheral units. Their potential applications, such as catalysts (van Koten & Jastrzebski, 1999), drug delivery agents (Svenson & Tomalia, 2005), adhesives (Mezzenga et al., 2001) and high performance polymers have made them to one of the most exciting areas of science. Issberner et al. (1995) incorporated transition metals into dendrimer frameworks which act as newborn and promising dendrimers, metallodendrimers. In addition, some metallodendrimers can be employed as catalysts or catalyst precursors (van Koten & Jastrzebski, 1999), providing the advantage of the combination of the best properties of homogeneous and heterogeneous systems catalyzing polymerization in the processes of ethylene oligomerization (Benito et al., 2006, 2005).

Müller et al. (2004) reported nickel catalyst systems for the ethylene oligomerization with the catalyst embedded within a dendrimer template. So, it becomes more popular to incorporate functionalities into commercially available dendrimers, and subsequently synthesize new dendritic ligands of nickel. Multinuclear nickel complexes were applied as catalyst precursors in ethylene oligomerization (Malgas-Enus et al., 2008, 2009; Malgas et al., 2008) due to their biocompatibility, high water solubility and lack of immunogenicity. The terminal-modifiable amine functional groups can be used to bind various targeting or guest molecules (Malgas & Mapolie, 2012, 2014) with the same function of poly(amidoamine) (PAMAM) dendrimers appearing particularly well suited for such an application. On basis of our previous work (Wang et al., 2013), a substitute dendritic-salicylaldehyde imine ligand and its nickel complex were synthesized and characterized in this paper. At the same time, this novel nickel metallodendrimer was employed in the ethylene oligomerization, and the effect of substituents on the peripheral salicylaldimine units as well as on the cat-

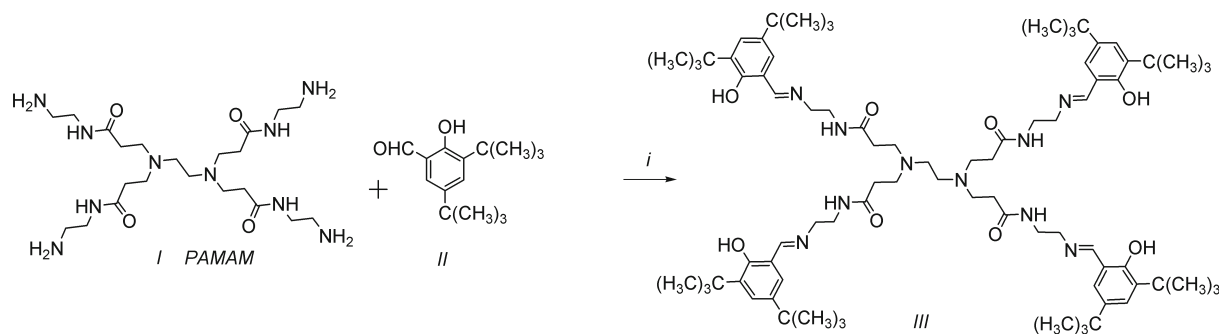*Corresponding author, e-mail: wangjun1965@yeah.net

Fig. 1. Synthetic route of ligand *III*; *i*) sodium sulfate, etanol, 78 °C, 12 h.
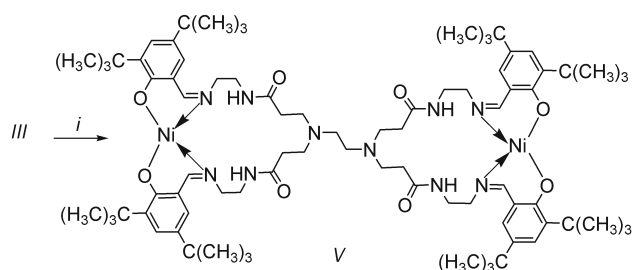

Fig. 2. Synthetic route of complex *V*; *i*) *IV*, methanol, 25 °C, 24 h.

alytic activity and selectivity of the nickel complex was investigated.

Experimental

General

All procedures were performed under nitrogen atmosphere by standard Schlenk techniques. Toluene, ethanol and methanol were provided by Tianjin Jinbei Fine Chemical Industry (China). Toluene was dried by refluxing over sodium/benzophenone. 1.0G PAMAM (*I*) was synthesized and reported in our former work (Wang et al., 2013). 3,5-ditertbutylsalicylal (*II*) was provided by Hubei KangbaoTai Fine Chemical Industry (China) and used without any further purification. Nickel chloride (AR) was purchased from Tianjin Zong Hengxing Industrial and Trading Chemical Reagent Branch (China). Methylaluminoxane (MAO), 10 mass % solution in toluene was obtained from Sigma–Aldrich (USA).

Synthesis of the ligands

Ligand *III* was prepared in the following steps: *I* (2.299 g, 4.455 mmol) was added to purified ethanol (10 mL) in a flask under nitrogen atmosphere. Anhydrous sodium sulfate (3 g) was added to the solution and stirred at 78 °C for 10 min; *II* (8.540 g, 35.64 mmol) was dissolved in ethanol (60 mL) and the solution was added to the stirred mixture (Fig. 1).

The mixture was stirred at 78 °C for 12 h and filtered, the pale yellow precipitate was collected and purified. The precipitate, ligand *III*, was then dried at 78 °C.

Dehydrated nickel chloride (*IV*) (0.159 g, 1.23 mmol) was dissolved in methanol (25 mL) and transferred to a recovery flask (Fig. 2). The mixture was stirred at 25 °C for 24 h, a light brown precipitate was formed and the solid was collected at 4 °C by vacuum filtration, and washed extensively with cold methanol. The residue was dried in vacuum to afford a light brown complex *V*.

Oligomerization reaction

Ethylene oligomerization reactions were carried out in a 250 mL stainless steel autoclave which was charged three times with dry nitrogen and then purged by ethylene. The catalyst (5 mL) was injected in dry toluene (50 mL) in a stainless steel reactor. Then, MAO was added to the reaction solution by a glass syringe. The ethylene pressure was set as a constant value throughout the oligomerization process by constantly pumping in ethylene. Different parameters were investigated in parallel experiments. A sample was taken to investigate the distribution of the products by gas chromatography (GC). In the end of the experiments, the remaining reaction mixture was quenched by adding 10 mL of acidified ethanol.
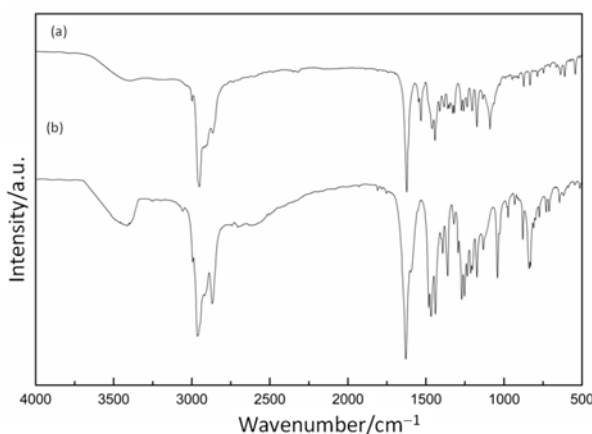
Test statistics

Infrared spectra were recorded on a Nicolet FT-IR750 (USA) infrared spectrometer using the KBr pellets method. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were obtained on a Varian VN-MRS 400 MHz (USA) and a Varian Unity Inova 400 MHz spectrometers, using MeOD and CDCl3 as the solvents and tetramethylsilane (TMS) as the internal standard. Chemical shift is given in δ relative to TMS. Absorbency of the ligand and its complex were determined using a UV-1700 UV-VIS (Shenzhen Kemeijia Instrument Company, China) spectrophotometer. Liquid chromatography-mass spectrometry (LC-MS) data were collected on an Apex Ultra 70

Table 1. Characterization data of newly prepared compounds

| Compound | Formula | M_r | w_i(calc.)/% w_i(found)/% | | | Yield |
			C	H	N	%
III	$C_{82}H_{128}N_{10}O_8$	1380.0	71.27	9.34	10.14	78
			71.18	9.30	10.18	
V	$C_{82}H_{124}N_{10}O_8Ni_2$	1493.4	65.86	8.36	9.37	82
			65.82	8.35	9.33	

Table 2. Spectral data of newly prepared compounds

Compound	Spectral data
III	IR, $\tilde{\nu}$/cm^{-1}: 1628 (C=N), 3409 (–OH), 3307 (CONH), 1041 (Ar—O) ^{1}H NMR (MeOD), δ: 1.33 (s, 36H, –^{t}Bu), 1.46 (s, 36H, –^{t}Bu), 3.25 (t, J = 3.4 Hz, 8H, –CH$_2$CO–), 3.34 (t, J = 3.59 Hz, 4H, –CH$_2$N–), 3.59 (t, J = 3.4 Hz, 8H, –CH$_2$N–), 3.62–3.71 (m, 8H, –NHCH$_2$–), 4.02 (t, J = 3.7 Hz, 8H, –CH$_2$N=), 7.18 (s, 4H, –Ar—H), 7.42 (s, 4H, –Ar—H), 8.49 (s, 4H, –N=CH—Ar), 4.87 (bs, 8H, –NH–, –OH) D$_2$O exchangeable ^{13}C NMR (CDCl$_3$), δ: 29.4 (–CH$_3$), 31.5 (–CH$_2$N–), 34.1 (–CH$_2$N=), 35.0 (–$\underline{C}$H$_2$—CONH–), 38.4 (–CONH—$\underline{C}$H$_2$–), 59.6 (–$\underline{C}$(CH$_3$)$_3$), 117.8 (Ar—C), 126.0 (Ar—C), 127.0 (Ar—C), 136.6 (Ar—C), 140.1 (Ar—C), 145.3 (Ar—C), 158.0 (C—imine), 167.6 (–CONH–) ESI-MS, m/z: 1403.8 [M + Na]$^+$ UV (ethanol, λ/nm): 233, 264, 331
V	IR, $\tilde{\nu}$/cm^{-1}: 1622 (C=N), 3233 (CONH), 1089 (Ar—O) ESI-MS, m/z: 1516.9 [M + Na]$^+$ UV (ethanol, λ/nm): 196, 253

Fig. 3. FTIR spectra of the nickel complex *V* (a) and ligand *III* (b).

FTMS (Bruker, Germany) mass spectrometer. Elemental analysis was carried out on a Heraeus element analyzer (Germany). Sampling of ethylene oligomerization products was done by flame ionization detector (FID) gas chromatography using a Shimadzu GC-14C-60 column (Japan). Characterization data of newly prepared compounds are shown in Tables 1 and 2.

Results and discussion

IR spectra for the ligand and the nickel complex are shown in Fig. 3. Two strong bands at 3409 cm^{-1} and 1628 cm^{-1} that belong to –OH vibration and C=N vibration, respectively, are apparent in ligand *III*. Characteristic peaks in the C=N vibration stretching frequency region indicate that *I* had reacted with the amino groups on the peripheries of the ligand. The band at 3409 cm^{-1} was due to the –OH group of the salicylaldimine units. However, compared with the ligand spectra, the IR spectra of the nickel complex showed a shift of the bands at the C=N stretching frequencies caused by the effect of the metal on the ligand system. The band at 3409 cm^{-1} in the ligand spectra indicates that the metal had coordinated with the O atom in the ligand, which is no longer present in the complex spectra.

^{1}H NMR spectra of the ligand showed proton signals for the internal branches of the dendrimer, where the proton is attached to the imine group and to the protons of the aryl rings, respectively. The ligand showed two proton signals at around δ 1.33, which indicate the presence of two *tert*-Bu substituents on the aryl ring of the ligand. When many kinds of active hydrogen atoms are present in the system, such as sample molecules containing amino and hydroxyl groups, the ^{1}H NMR spectra only show an average hydrogen signal (Ning, 2005). Due to water sorption of the samples, the ligand showed a proton signal at δ 4.87 representing all the active hydrogen atoms (Figs. 4 and 5).
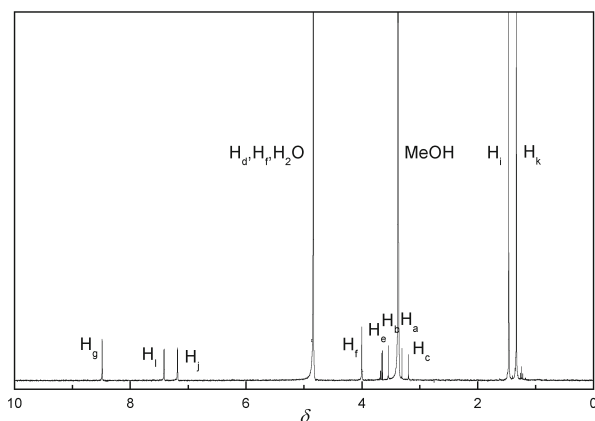
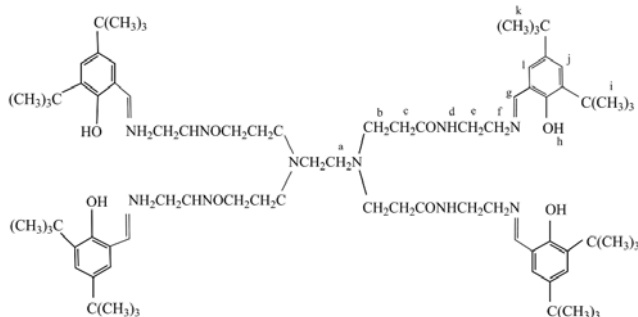**Fig. 4.** ^{1}H NMR spectra of ligand *III* (for atom numbering see Fig. 5).

Fig. 5. Structure of ligand *III*.

Fig. 6. Ethylene oligomerization proceeding by a chain growth mechanism.

McGuinness et al., 2007), the use of MAO as a co-catalyst in olefin oligomerization is normally thought to provide a cationic active nickel center. Thus, the Ni-complex catalyst need be activated by MAO in the ethylene oligomerization. In order to investigate the parameters (including the co-catalyst concentration (Al/Ni ratio), reaction temperature, ethylene pressure, reaction time as well as the structure of the complex) influencing the catalytic performance and olefin product distribution, a series of catalyst evaluations for complex *V* was carried out under different catalytic conditions.

Complex *V* was first activated in toluene by the addition of MAO with the Al/Ni mole ratio from 100 : 1 to 1200 : 1. All oligomerizations of complex *V* were done at the ethylene pressure of 0.5 MPa at 25 °C for 0.5 h, and the ethylene oligomerization results are shown in Table 3 (catalytic activity and product distribution).

As shown in Table 3, the increase of the Al/Ni ratio from 100 to 500 can lead to enhanced catalytic activity. A further increase of the Al/Ni ratio to 1200 results in a decrease in the catalytic activity, which reaches the maximum at Al/Ni ratio 500, in accordance with the results reported by Chen et al. (2006). However, the prepared complex *V* displays higher catalytic activity than that of a binuclear nickel complex (Malgas-Enus et al., 2008), which may lead to the activation of the metal center at higher co-catalyst mole ratio and the elimination of the impurities present in the solutions, causing an increase in the number of active sites. But, excess MAO addition might hinder the accessibility of the active sites to ethylene. Moreover, the increasing amount of impurities (such as trimethylaluminum) in MAO can react with the active metal center, which leads to the "consumption" of active sites and the decrease of the catalytic activity (Chen et al., 2006).

As shown in Table 3 for catalyst *V*, with the increasing Al/Ni ratio, the shorter chain oligomers were obtained with at first increasing and then decreasing

UV spectra of the ligand showed three absorption bands. Two of the bands viz. those at 233 nm and 264 nm can be assigned to band E$_2$ of the benzene ring and band K consisting of the conjugation of the benzene ring and the C=N bond. The band observed at 331 nm was assigned to the $n{\rightarrow}\pi^*$ transition of C=N. After nickel coordinated with the ligand, and band K showed a blue shift in the UV spectrum illustrating that the nickel complex was generated as the hyperchrome –OH group had disappeared. Moreover, the nickel coordination with C=N led to the disappearance of the lone pair electrons of the N atom. Hence, no $n{\rightarrow}\pi^*$ transition of the C=N bond was observed.

Based on the results above, the novel dendritic ligand *III* and its complex *V* have been identified.

Recently, dendritic complexes have gained increasing attention and they are widely studied in catalytic processes including the processes of ethylene oligomerization. The existing technologies for olefin production are mostly based on ethylene oligomerization by the ethylene insertion/β-elimination mechanism (Fig. 6.) (Peitz et al., 2010). The complex exhibited remarkable catalytic activity for ethylene oligomerization in the presence of MAO. While a great deal of work on more well-defined oligomerization systems based on cation-anion pairs has been done (de Souza et al., 2007;
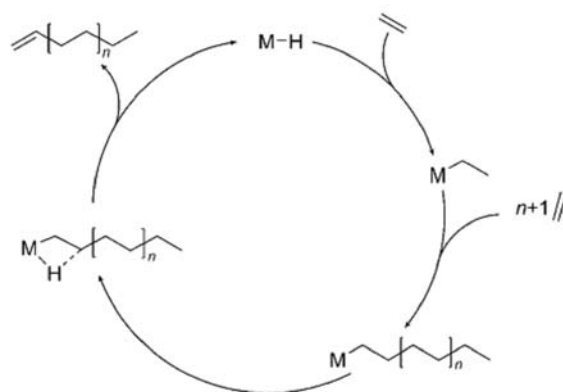
Table 3. Effect of Al/Ni ratio on the catalytic activity and the product distribution for catalyst V

Entry	Al/Ni	$10^5 \cdot \text{TOF}^a$	Selectivity/%									
			C_4	C_6	C_8	$\leq C_8^b$	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}	$> C_{10}^c$
1	100	0.80	13.60	9.08	0.62	23.30	0.03	23.10	17.79	25.40	10.38	76.70
2	300	3.75	26.78	7.36	8.33	42.47	0.41	20.37	12.52	18.18	6.05	57.53
3	500	4.93	34.54	4.53	6.76	45.83	1.26	17.04	14.07	20.74	1.06	54.17
4	800	3.09	18.40	8.61	3.73	30.74	0.06	30.67	14.10	17.90	6.53	69.26
5	1200	3.87	17.92	8.28	2.67	28.87	0.39	34.24	13.15	17.20	6.15	71.13

a) In gram of oligomer produced per mole of nickel complex per hour; *b*) less than 8 carbon atoms in oligomers, shorter chain oligomers; *c*) more than 10 carbon atoms in oligomers, longer chain oligomers.

Table 4. Effect of reaction time on the catalytic activity and product distribution for catalyst V

Entry	Time/min	$10^5 \cdot \text{TOF}^a$	Selectivity/%									
			C_4	C_6	C_8	$\leq C_8^b$	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}	$> C_{10}^c$
1	20	6.84	26.37	5.67	2.13	34.17	0.74	33.25	11.49	15.34	5.30	65.83
2	30	4.93	34.54	4.53	6.76	45.83	1.26	17.04	14.07	20.74	1.06	54.17
3	50	2.90	41.67	8.44	6.42	56.53	0.70	18.15	7.89	12.42	4.31	43.47
4	80	2.54	42.07	8.57	0.28	50.92	1.02	25.00	9.02	11.24	2.80	49.08
5	100	1.92	30.68	4.05	1.62	36.35	0.72	31.45	11.10	14.05	6.33	63.65

a) In gram of oligomer produced per mole of nickel complex per hour; *b*) less than 8 carbon atoms in oligomers, shorter chain oligomers; *c*) more than 10 carbon atoms in oligomers, longer chain oligomers.

Table 5. Effect of ethylene pressure on the catalytic activity and product distribution for catalyst V

Entry	Pressure/MPa	$10^5 \cdot \text{TOF}^a$	Selectivity/%									
			C_4	C_6	C_8	$\leq C_8^b$	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}	$> C_{10}^c$
1	0.1	2.69	48.00	10.10	5.41	63.51	1.04	4.05	12.55	15.14	3.71	36.49
2	0.2	3.34	42.96	9.30	5.90	58.16	0.56	13.14	10.15	16.58	1.41	41.84
3	0.3	3.53	40.00	7.06	4.95	52.01	5.78	3.75	10.84	20.66	6.96	47.99
4	0.4	4.15	39.22	6.05	2.26	47.53	1.11	18.86	12.41	13.44	6.65	52.47
5	0.5	4.93	34.54	4.53	6.76	45.83	1.26	17.04	14.07	20.74	1.06	54.17

a) In gram of oligomer produced per mole of nickel complex per hour; *b*) less than 8 carbon atoms in oligomers, shorter chain oligomers; *c*) more than 10 carbon atoms in oligomers, longer chain oligomers.

tendency, and a maximum value of 45.83 % at Al/Ni ratio 500. This is caused by the lower rate of the chain transferring process from an active nickel center to Al compared to the chain growth considering low or high MAO concentration. Moreover, longer chain oligomers are formed in greater proportions in all cases for catalyst V. Therefore, the amount of MAO has a significant effect on the catalytic activity and product distribution when using catalyst V.

The effect of reaction time on the catalytic activity and the product distribution is shown in Table 4. With the increasing reaction time, a decrease of the ethylene oligomerization activity of catalyst V was observed. Since the ethylene oligomerization mainly takes place at the beginning of the reaction, comparatively less ethylene was oligomerized with the reaction time, leading to a decrease of the TOF value. In addition, the reducing activity of the catalyst can be

assigned to the deactivation effect of the active sites, but the reason is not clear at this stage and it needs to be explored in a future study. The obtained results are in good agreement with those of Doherty et al. (2007). For catalyst V, the amount of products of shorter chain oligomers increases at first and then decreases with the reaction time in Table 4, the maximum value was obtained at the reaction time of 50 min. However, under these conditions, not the highest activity was achieved.

In Table 5, the effect of pressure on the catalytic activity, product distribution and the range of oligomerization is shown at 25 °C, reaction time of 0.5 h and Al/Ni ratio 500. With the increasing pressure, the ethylene oligomerization activity and selectivity (for high carbon olefins) increase for catalyst V. This is understandable for the increase of the ethylene pressure results in higher solubility of ethylene in toluene.

Table 6. Effect of temperature on the catalytic activity and product distribution for catalyst *V*

| Entry	Temperature/°C	$10^5 \cdot \text{TOF}^a$	Selectivity/%									
			C_4	C_6	C_8	$\leq C_8^b$	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}	$> C_{10}^c$
1	10	3.91	37.79	26.05	12.71	76.55	0.49	3.90	4.47	9.55	5.04	23.45
2	25	4.93	34.54	4.53	6.76	45.83	1.26	17.04	14.07	20.74	1.06	54.17
3	35	6.13	18.64	33.91	1.44	53.99	0.96	7.61	9.85	4.81	22.78	46.01
4	45	4.63	17.77	15.93	0.42	34.12	1.00	15.81	29.76	12.96	6.35	65.88
5	55	3.18	31.49	21.04	13.20	65.73	0.95	6.85	16.41	6.78	3.28	34.27

a) In gram of oligomer produced per mole of nickel complex per hour; *b*) less than 8 carbon atoms in oligomers, shorter chain oligomers; *c*) more than 10 carbon atoms in oligomers, longer chain oligomers.

Therefore, the catalytic activity reached the maximum value at 0.5 MPa for catalyst *V*. This is in accordance with the results reported by Smith et al. (2003).

As shown in Table 5, the distribution of oligomers is shifted to longer chain oligomers with the increasing ethylene pressure for catalyst *V* because the chain transfer plays a dominant role, which corresponds to the chain propagation when increasing the ethylene pressure. Therefore, the higher pressure, the higher catalytic activity and longer chain oligomers selectivity can be achieved.

Results of the oligomerization processes performed at various temperatures from 10°C to 55°C employing the complex at the reaction time of 0.5 h, 0.5 MPa and the Al/Ni ratio 500 are shown in Table 6. For catalyst *V*, the activity of the complex first increases and reaches the maximum value of 6.13×10^5 grams per mole of Ni catalyst per hour at about 35°C, then it decreases. This can be ascribed to the decomposition of the nickel complex at higher temperatures. Moreover, a decrease in the ethylene solubility at higher or lower temperatures results in a decrease of the catalytic activity, which is consistent with the findings of Mogorosi et al. (2011). Furthermore, temperature has no obvious influence on the length of the oligomers chain.

Preparation of an unsubstituted nickel complex is here reported and it was studied as a catalyst precursor for ethylene oligomerization with MAO as the co-catalyst (Wang et al., 2013). At the reaction temperature of 25°C, pressure of 0.5 MPa, and the Al/Ni ratio of 500 for 0.5 h, the unsubstituted nickel complex *VI* and the *tert*-butyl substituted nickel complex *V* both exhibit the best catalytic performance, but *VI* shows higher activity (4.8×10^6 grams per mole of Ni catalyst per hour) than catalyst *V* (6.13×10^5 grams per mole of Ni catalyst per hour). As shown in Fig. 7, the difference in the catalytic activities of *VI* and *V* can be ascribed to the reduced electrophilicity of the nickel metal center from the more electron-donating *tert*-butyl groups and the reduced rate of ethylene coordination during the catalysis (Ojwach et al., 2009). Hence, steric bulk can result in a decrease of the nickel complex activities.
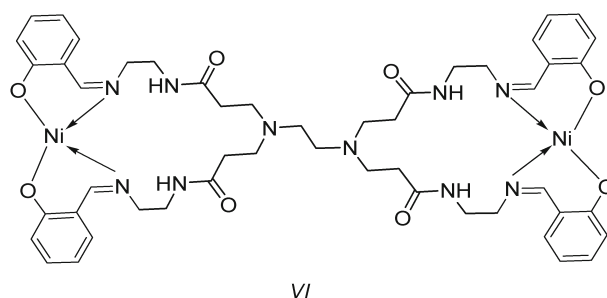
Fig. 7. Structure of unsubstituted nickel complex *VI*.

Conclusions

A novel dendritic ligand and its complex have been successfully synthesized and characterized by IR, UV, NMR, ESI-MS and elemental analyses. The complex was evaluated as a catalyst in ethylene oligomerizaton. It is clear that the catalytic activity of the nickel complex in ethylene oligomerizaton is dependent on the reaction conditions and on the structure of the complex. The optimal reaction conditions were determined to be: reaction temperature of 25°C, pressure of 0.5 MPa, and Al/Ni ratio of 500 for 0.5 h. There is a clear steric bulk effect for the catalyst in the ethylene oligomerization, they are the additional *tert*-butyl substitution of the benzene ring which decreases the activity of the catalyst.

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