

2-AMINOMETHYLPYRIDINE NICKEL(II) COMPLEXES — SYNTHESIS, MOLECULAR STRUCTURE AND CATALYSIS OF ETHYLENE POLYMERIZATION*

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Abstract A series of new nickel(II) complexes with 2-aminomethylpyridine ligands, (2-PyCH₂NHAr)₂NiBr₂ (Ar = 2,6-dimethylphenyl **2a**; 2,6-diisopropylphenyl **2b**, 2,6-difluorophenyl **2c**), have been synthesized and used as catalyst precursors for ethylene polymerization in the presence of methylaluminoxane (MAO). The catalysts containing *ortho*-alkyl-substituents afford high molecular weight branched polyethylenes as well as a certain amount of oligomers. Enhancing the steric bulk of the alkyl substituent of the catalyst resulted in higher ratio of solid polymer to oligomer and higher molecular weight of the polymer. Catalyst **2c** containing *ortho*-fluoro-substituents exhibited the highest catalytic activity, but only oligomers in which C₁₂H₂₄ had the maximum content were obtained by the catalyst. The molecular weight, molecular weight distribution, and microstructure of the resulted polymer were characterized by gel permeation chromatography and ¹³C-NMR spectrogram.

Keywords: 2-Aminomethylpyridine; Nickel(II) complex; Catalyst; Ethylene polymerization; Oligomer.

INTRODUCTION

In the past, nickel catalysts were best known to oligomerize ethylene and dimerize propylene and higher α -olefins because nickel metal was usually thought to generally prefer β -H elimination followed by reductive elimination^[1]. In 1995 cationic Ni(II) and Pd(II) catalysts derived from bulky aryl-substituted α -diimines were reported to convert ethylene and α -olefins to high molecular weight polyolefins^[2]. Otherwise, by comparison with early transition metal catalysis, late transition metal complexes are generally much more functional-group tolerant as the result of their less oxophilic nature^[3, 4]. Recently, olefin polymerization and oligomerization catalyzed by late transition metal complexes have attracted great attention in both academic and industrial research^[5].

Presently, for nickel catalysts, the salicylaldimine, α -diimine and β -diketoamine nickel complexes have been studied extensively. Yi *et al.* reported the ethylene polymerization by 2-iminopyridine nickel(II) dibromide **1** (Scheme 1) and found that the product produced by **1** was composed of oligomers (the primary ingredient C₄–C₁₀) with 45% α -olefin^[6]. Laine *et al.* found that these complexes could obtain solid polyethylene (M_w = 2700–40000) under the polymerization conditions of high ethylene pressure (P_E = 0.30–0.55 MPa) and high Al/Ni ratio (Al/Ni = 2000)^[7, 8]. Gibson *et al.* found that the aminopyridine iron(II) complexes were more efficient catalysts for styrene polymerization than their unsaturated 2-iminopyridine relatives^[9]. Being illuminated by this suggestion, we tried to reduce the 2-iminopyridine by LiAlH₄ to 2-aminopyridine and synthesize complexes **2** through the 2-aminomethylpyridine ligands reacting with 1,2-dimethoxyethane

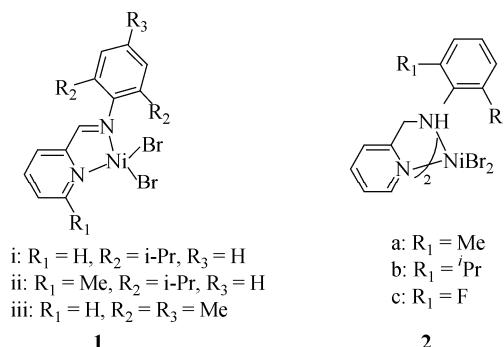
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nickel(II) bromide (DME)NiBr₂, and to research into the ethylene polymerization by using the Ni complexes as catalyst after activation with MAO.



Scheme 1 2-Iminopyridine nickel(II) dibromide (**1**) and 2-aminomethylpyridine nickel(II) dibromide (**2**)

EXPERIMENTAL

Solvents and Reagents

All manipulations involving air- and moisture-sensitive compounds were carried out under an atmosphere of dried and purified nitrogen with standard Schlenk techniques. Solvents were purified with standard procedures. 2-Pyridinecarboxaldehyde (99%), 2,6-dimethylaniline (98%), 2,6-diisopropylaniline (98%), 2,6-difluoroaniline (98%) and lithium aluminium hydride (LiAlH₄) were purchased from Aldrich Chemical Co. and used without further purification. (DME)NiBr₂ was synthesized by the reaction of 1,2-dimethoxyethane with anhydrous nickel(II) bromide. MAO was prepared by the hydrolysis of trimethylaluminum with Al₂(SO₄)₃·18H₂O in toluene with the H₂O/Al molar ratio of 1.3:1.

Measurements

Elemental analyses were performed on a Vario EL microanalyzer. ¹H-NMR spectra were carried out on an Inova instrument (300 MHz) at room temperature in CDCl₃ solution using tetramethylsilane as an standard for the ligands and ¹³C-NMR spectra were performed on an Inova instrument (500 MHz) at 120°C in *o*-dichlorobenzene-d₄ for the polymers (15 wt%) with the chemical shift (δ = 30.00) of the main backbone methylene as an internal standard. Gel permeation chromatography (GPC) analyses of the molecular weight and molecular weight distributions (MWD) of the polymers were performed on a Water-2000 at 135°C based on standard polystyrene as the reference with 1,2,4-trichlorobenzene as the solvent. Gas chromatography/mass spectrometry (GC-MS) of the oligomer was handled with a Voyager instrument from Finigan Co. Single-crystal X-ray diffraction data of complex **2c** was collected on a Bruker Smart CCD diffractometer at 173(2) K. The structures were solved by Patterson methods followed by difference Fourier syntheses and then refined by full-matrix least-squares techniques against F² with SHELXTL^[10].

Syntheses of Complexes (2a–2c)

The general procedure employed in preparation of the complexes is as follows. A quantity of the ligand synthesized as previously reported^[11] was added to 60 mL of dried dichloromethane, and the solution was stirred at room temperature until the ligands dissolved completely in the dichloromethane. (DME)NiBr₂ was added to the above solution and then stirred for 10 h at room temperature. The solution was filtered and washed by 5 mL dichloromethane for three times. The solution was evaporated to a little volume in vacuo, and 20 mL *n*-hexane was added. The mixture was stirred for 20 min and filtered, and then the residual solid was washed with *n*-hexane (3 × 5 mL). Drying in *vacuo* produced the desired nickel complex. The complex was purified further by crystallizing in the hexane/dichloromethane solution.

Bis-[N-2,6-dimethylphenylaminomethyl-2-pyridyl] Nickel(II) dibromide (**2a**) prepared with **1a** 0.44 g (2.07 mmol) and 0.32 g (DME)NiBr₂ was obtained as green crystal in 0.55 g (82.7%). ¹H-NMR (300 MHz, CDCl₃, δ): 1.32–1.36 (6H, d, 2CH₃), 5.33 (3H, s, CH₂, NH), 3.31–3.68 (2H, m, 2CH), 4.09 (2H, s, CH₂), 5.29

(1H, s, NH), 7.27 (overlapping, 7H, s, benzyl, Py). Anal. Calcd for $C_{28}H_{32}N_4NiBr_2$: C, 52.29%; H, 5.02%; N, 8.71%. Found: C, 52.15%; H, 5.17%; N, 8.59%.

Bis-[N-2,6-diisopropylphenylaminomethyl-2-pyridyl] Nickel(II) dibromide (**2b**) prepared with **1b** 0.26 g (0.97 mmol) and 0.18 g (DME)NiBr₂ was obtained as green crystal in 0.25 g (68.3%). ¹H-NMR (300 MHz, CDCl₃, δ): 1.29–1.32 (12H, d, 4CH₃), 3.26–3.40 (2H, m, 2CH), 4.28 (2H, s, CH₂), 5.13 (1H, s, NH), 7.18 (overlapping, 7H, s, benzyl, Py). Anal. Calcd for $C_{36}H_{48}N_4NiBr_2$: C, 57.25%; H, 6.41%; N, 7.42%. Found: C, 57.49%; H, 6.57%; N, 7.52%.

Bis-[N-2,6-difluorophenylaminomethyl-2-pyridyl] Nickel(II) dibromide (**2c**) prepared with **1c** 0.66 g (3.00 mmol) and 0.45 g (DME)NiBr₂ was obtained as green crystal in 0.52 g (52.6%). ¹H-NMR (300 MHz, CDCl₃, δ): 3.53–3.69 (2H, d, CH₂), 5.37 (1H, s, NH), 7.27 (overlapping, 7H, s, benzyl, Py). Anal. Calcd for $C_{24}H_{20}N_4F_2NiBr_2$: C, 43.75%; H, 3.06%; N, 8.50%. Found: C, 43.63%; H, 3.03%; N, 8.65%.

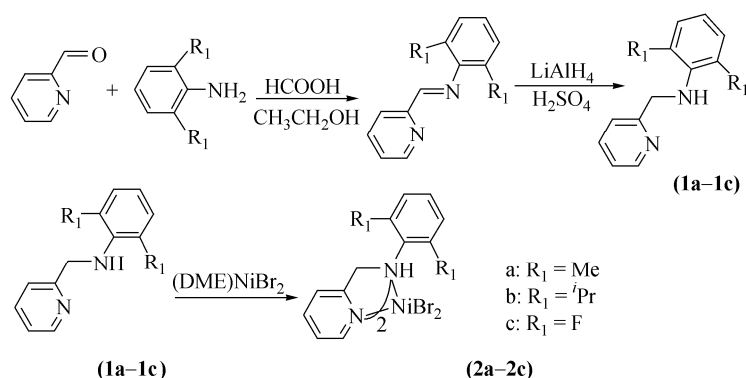
Ethylene Polymerization

Ethylene polymerizations were carried out in a 50 mL glass flask equipped with magnetic stirrer or 100 mL stainless steel autoclave. In the reactor filled with ethylene, desired amounts of MAO and toluene were added and the polymerization was initiated by injecting a CH₂Cl₂ solution of the nickel complex. Gaseous ethylene was continuously fed to replenish the consumed one and maintain a constant pressure. After 30 min, the reactor was cooled at –10°C and polymerization was terminated by addition of HCl acidified ethanol. The polymer was isolated, washed with ethanol and dried overnight at 60°C in vacuum oven. The solution was used for GC–MS analysis.

RESULTS AND DISCUSSION

Syntheses of Ligands and Catalysts

The synthesis routes of 2-aminomethylpyridine ligands and Ni(II) complexes bearing different substitution groups are shown in Scheme 2. 2-Iminomethylpyridines were synthesized based on condensation reaction of 2-pyridinecarboxaldehyde and the corresponding anilines. Deoxidization of the obtained 2-iminomethylpyridines by LiAlH₄ resulted in the desired ligands **1a–1c**^[12]. In the ¹H-NMR spectra of the obtained ligands **1a–1b**, hydrogen chemical shifts of –CH₂– and –NH– appear at δ = 4.30 and δ = 4.20, respectively, whereas the corresponding chemical shifts of **1c** move to the downfield region (δ = 4.61 and δ = 4.86).



Scheme 2 Synthesis route of ligands **1a–1c** and nickel complexes **2a–2c**

Complexes **2a–2c** were synthesized directly by the coordination reaction of ligands **1a–1c** and (DME)NiBr₂. Crystals of complexes **2c** suitable for single-crystal X-ray diffraction analysis were grown from their hexane/dichloromethane solution. The ORTEP diagram of complex **2c** is presented in the Fig. 1. The complex **2c** exists as bis-ligand single molecular (monomer) structure with octahedral geometries about nickel in solid state and a crystallographic C₂ axis of symmetry that make the two ligands equivalent. The bond distance of N₂–Ni

(0.2270(4) nm) is little longer than that of N₁—Ni (0.2063(4) nm), indicating that the binding ability of pyridine N with metal nickel is stronger than that of amino N with metal nickel. The atom C₆ connecting with the pyridine ring changes into the SP³ hybridization. The bond length of C₆—N₂ is 0.1423(6) nm and the bond angles (N₂—C₆—C₅) is 110.4(4)°, respectively. The five-member rings (N₁—C₁—C₆—N₂—Ni₁) is not the plane structure, the enough space around the active center nickel favoring the bis-ligand structure forming. The angle of plane Ni(1)—N(2)—C(6) and plane N-aryl is 70.9°. As reported in the literature^[13], the corresponding 2-position C atom connecting with the pyridine ring of the 2-imine pyridine nickel complex takes the SP² hybridization and the corresponding five-member ring (N₁—C₅—C₆—N₂—Ni₁) is the plane structure.

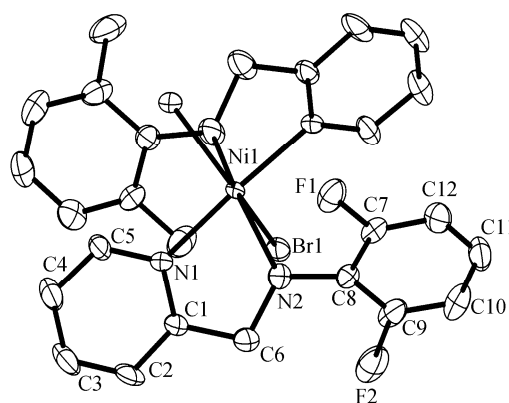


Fig. 1 ORTEP plot of complex **2c**

Hydrogen atoms are omitted for clarity;

Selected bond distance (nm) and angles (deg): Ni(1)—Br(1), 0.25206(9); Ni(1)—N(1), 0.2063(4), Ni(1)—N(2), 0.2270(4), N(1)—C(1), 0.1342(6); N(2)—C(6), 0.1424(6); C(1)—N(1)—Ni(1), 117.6(3); N(1)—C(1)—C(6), 116.1(4); N(2)—C(6)—C(1), 110.4(4), C(6)—N(2)—Ni(1), 106.4(3)

Ethylene Polymerization

The complexes **2a–2c** were efficient catalysts for ethylene polymerization in the presence of MAO and the polymerization results are presented in Table 1. Among these complexes, **2c** showed the highest catalytic activity. The products obtained by complexes **2a** and **2b** containing *ortho*-alkyl-substituent were composed of solid polymer with a certain amount of oligomer, but only oligomer was obtained by **2c** containing *ortho*-fluoro-substituent. For the *ortho*-alkyl-substitution complexes, enhancing the steric bulk of the substituent could increase the ratio of polymer to oligomer and molecular weight of the solid polymer under the same polymerization conditions. Otherwise, the GPC curves of the polymers obtained at various polymerization temperatures in normal atmospheric ethylene pressure exhibited single model with molecular weight distribution near 2, indicating that the polymers and oligomers are individually produced by different active centers. The phenomenon of ethylene polymer and oligomer coexisting could be attributed to different catalytic species yielded from isomerization equilibrium by the rotation of the amino-aryl bond. As reported by Zou *et al.*, the N-aryl rotation of the unsymmetrical α -diimine ligands could be observed by NMR analysis^[14]. Aydeniz *et al.* had investigated the pairs of rotational isomers for 3-(*o*-aryl)-5-methyl-rhodanines using NMR spectroscopy and density functional theory (DFT) calculations^[15].

Table 1 also lists the results of polymerizations at various polymerization conditions including ethylene pressure and polymerization temperature. For complex **2a**, with raising the ethylene pressure from 20.3 kPa to 2.0 MPa (entry 3 and 5 in Table 1), both the catalytic activity and molecular weight of the obtained polyethylene increased in large scope. This result indicated that the high ethylene pressure can enhance the rate of chain propagation. When the polymerization temperature increased gradually from −20°C to 30°C (entry 1–4 in Table 1), the catalytic activity increased and reached a maximum value at 15°C, and then decreased. The lower

catalytic activity at high polymerization temperature should be attributed to the catalytic center deactivate partly besides lower ethylene concentration in the toluene solution.

Table 1. Results of ethylene polymerizations catalyzed by **2a–2c**/MAO

Entry	Catalyst	T_p (°C)	Polymer yield (g)	Activity (kgE/(molNi.h)) Polymer	Oligomer	M_w	PDI	Branches /1000C
1	2a	–20	0.16	3.20	1.00	17500	2.46	6.4
2	2a	0	0.29	5.74	2.02	6980	2.38	
3	2a	15	0.51	10.2	3.40	2030	^b	98.2
4	2a	30	0.05	1.00	4.00			
5 ^a	2a	15	2.46	49.2	nd	13630	3.80	28.5
6	2b	–20	0.11	2.20	0.42	25800	2.26	
7	2b	0	0.20	4.21	0.70	8500	2.36	
8	2c	–20	0	–	7.00			
9	2c	0	0	–	22.6			

Conditions: catalyst 10 μ mol; time 30 min; toluene 20 mL; ethylene pressure 20.3 kPa; Al/Ni = 800;

^a Ethylene pressure 2.0 MPa; ^b The molecular weight are too low to get correct PDI values; nd = not detected

The polymers obtained by **2a** and **2b** were branched polyethylenes. The ^{13}C -NMR spectra of the polyethylenes obtained by **2a** at different polymerization temperatures and ethylene pressures are shown in Fig. 2. The spectra were analyzed according to the assignments of the resonance peaks based on the Linderman-Adams method^[16]. Branching density N described as branch number per 1000 carbons can be calculated with the following equation:

$$N = \frac{1000 (I_{\text{Me}}/0.90 + I_{\text{Et}}/0.84 + I_{\text{Pr}}/0.83 + I_{\text{Bu}}/0.90 + I_{\text{Pe}}/0.90 + I_{\text{Lg}}/0.80)}{I_{\text{main}} + 5.5(I_{\text{Et}}/0.84) + I_{\text{Pr}}/0.83 + 8.0(I_{\text{Bu}}/0.90 + I_{\text{Pe}}/0.90 + I_{\text{Lg}}/0.80)}$$

where I_{Me} , I_{Et} , I_{Pr} , I_{Bu} , I_{Pe} and I_{Lg} are assigned respectively to the integral areas of 1B₁, 1B₂, 1B₃, 2B₄, 2B₅ and 3B_n peaks.

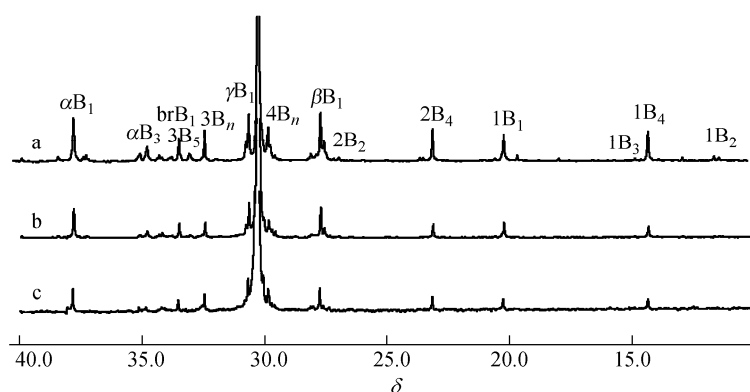


Fig. 2 ^{13}C -NMR spectra of polyethylenes obtained by **2a**/MAO at Al/Ni = 800 and different temperatures and ethylene pressures

a) 15°C and 20.3 kPa; b) 15°C and 2.0 MPa; c) –20°C and 20.3 kPa

The branching density was highly sensitive to polymerization temperature and ethylene pressure. The analysis results showed that the polyethylene prepared by **2a** at –20°C has low branching density of 6.4/1000C. When the polymerization temperature was raised up to 15°C, the branching density increased to 98.2/1000C. On the contrary, raising ethylene pressure in the polymerization process led to a decrease in the branching density of the polymer. When the ethylene pressure was raised from 20.3 kPa to 2.0 MPa at same temperature, the branching density reduced from 98.2/1000C to 28.5/1000C. Branching density of polyethylene depends on the

competition between ethylene insertion processes and “chain walking” of the active species along the growing polymer chain^[17]. The high branching density polyethylenes obtained at high polymerization temperature and low ethylene pressure can be attributed to the rapid chain walking process.

When the *ortho*-substituent of the aryl group was replaced with fluorine atom, the catalytic activity of **2c** increased obviously under the same conditions, but only oligomers were obtained by the catalyst. The electron-withdrawing ability of the *ortho*-fluoro-substituent makes the Ni atom more electrophilic, which is beneficial to the interaction of Ni and β -H of the propagation chains, thus speeding up β -H elimination reaction. Therefore, much faster chain transfer reaction could take place in the **2c** systems owing to the strong electron-withdrawing ability and small steric bulk of *ortho*-fluoro-substitution, resulting in no solid polymer in the product.

The obtained oligomer by **2c** in toluene was characterized by GC-Mass and the spectrum with the analysis results is presented in Fig. 3. The retention time of 1.75 and 4.97 min attached to the dichloromethane and toluene which was added as solvent for nickel complex and the reaction respectively. The oligomers of C₄H₈, C₆H₁₂, C₈H₁₆, C₁₀H₂₀, C₁₂H₂₄, C₁₄H₂₈, C₁₆H₃₂, C₁₈H₃₆, C₂₀H₄₀, C₂₂H₄₄, C₂₄H₄₈ and C₂₆H₅₂ can be distinguished in the spectrum and appear at the retention times of 1.55, 2.28, 5.81, 11.7, 17.4, 20.3, 22.3, 23.8, 25.2, 26.5, 27.6 and 28.6 min, respectively. In the oligomers obtained by **2c** at 0°C, C₁₂H₂₄ had the maximum content. The olefin distribution data were plotted based on the Anderson-Schulz-Flory (ASF) equation^[11]:

$$\lg\left(\frac{W_n}{n}\right) = n \lg \alpha + \text{const}$$

where W_n is the mass fraction of the species with carbon number n ^[18]. As shown in Fig. 3, two values of the chain growth probability α ($\alpha_1 = 0.95$, $\alpha_2 = 0.81$) are obtained from the slopes of the plot of $\lg(W_n/n)$ against n . The bimodal ASF distribution could be interpreted by differently structured active centers^[19].

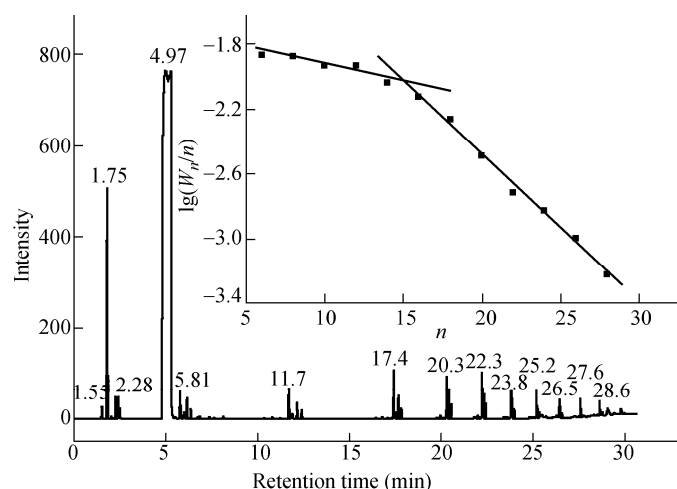


Fig. 3 GC-Mass spectrum of the oligomer obtained by **2c** at 0°C (entry 9 in Table 1)

CONCLUSIONS

2-Aminomethylpyridine nickel(II) complexes can be synthesized by the coordination reaction of 2-aminomethylpyridine ligands and (DME)NiBr₂. On the basis of single-crystal X-ray diffraction analysis, complex **2c** is C₂ axis of symmetry and exists as monomer structure with octahedral geometries about nickel in solid state. Complexes **2a–2c** are active catalysts for the ethylene polymerization. The *ortho*-alkyl-substitution complexes **2a** and **2b** afforded high molecular weight branched polyethylenes with a certain amount of oligomer in the presence of MAO, whereas only oligomers were obtained by *ortho*-fluoro-substitution complex **2c**. The olefin content of the oligomers obtained by **2c** suited approximately to bimodal ASF distribution in which C₁₂H₂₄ has the maximum content.

REFERENCES

- 1 Killian, C.M., Tempel, D.J., Johnson, L.K. and Brookhart, M., *J. Am. Chem. Soc.*, 1996, 118: 11664
- 2 Johnson, L.K., Killian, C.M. and Brookhart, M., *J. Am. Chem. Soc.*, 1995, 117: 6414
- 3 Zhang, D. and Jin, G.X., *Organometallics*, 2003, 22: 2851
- 4 Britovsek, G.J.P., Gibson, V.C. and Wass, D.F., *Angew. Chem.*, 1999, 111: 448
- 5 Held, A., Bauers, F.M. and Mecking, S., *Chem. Commun.*, 2000, 301
- 6 Yi, J.J., Xu, X.X. and Chen, W., *Chinese Journal of Catalysis*, 2002, 23: 69
- 7 Laine, T.V., Piironen, U. and Lappalainen, K., *J. Organomet. Chem.*, 2000, 606: 112
- 8 Laine, T.V. and Lappalainen, K., *J. Macromol. Rapid. Commun.*, 1999, 20: 487
- 9 Gibson, V.C., O'Reilly, R.K. and Wass, D.F., *Dalton Trans.*, 2003, 2824
- 10 Sheldrick, G.M., SHELXS-97: Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 1997
- 11 Huang, Z.F., Song, K.M., Liu, F.S. and Wu, Q., *J. Polym. Sci. Part A*, 2008, 46: 1618
- 12 Hu, W.Q., Sun, X.L. and Tang, Y., *Organometallics*, 2004, 23: 1684
- 13 Laine, T.V., Klinga, M. and Leskelä, M., *Eur. J. Inorg. Chem.*, 1999: 959
- 14 Zou, H., Hu, S., Huang, H.H., Zhu, F.M. and Wu, Q., *Eur. Polym. J.*, 2007, 43: 3882
- 15 Aydeniz, Y., Oğuz, F. and Aviyente, V., *Org. Biomol. Chem.*, 2004, 2: 2426
- 16 Linderman, L.P. and Adams, N.O., *Anal. Chem.*, 1971, 43: 1245
- 17 Camacho, D.H., Salo, E.V. and Guan, Z.B., *Angew. Chem. Int. Ed.*, 2004, 43: 1821
- 18 Tavakoli, A., Sohrabi, M. and Kargari, A., *Chem. Eng. J.*, 2008, 136(2-3): 358
- 19 Patzlaff, J., Liu, Y. and Graffmann, C., *Appl. Catal. A*, 1999, 186:109