

Synthesis, structure and norbornene polymerization behavior of nickel complexes bearing two β -ketoiminato chelate ligands

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Abstract

A series of nickel(II) complexes bearing two nonsymmetric bidentate β -ketoiminato chelate ligands have been prepared, and the structures of complexes $[(2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{NC}(\text{CH}_3)\text{C}(\text{H})\text{C}(\text{Ph})\text{O}]_2\text{Ni}$ (**4a**) and $[(2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{NC}(\text{CH}_3)\text{C}(\text{H})\text{C}(\text{CF}_3)\text{O}]_2\text{Ni}$ (**4c**) have been confirmed by X-ray crystallographic analysis. These nickel(II) complexes were investigated as catalysts for the vinylic polymerization of norbornene. Using modified methylaluminumoxane (MMAO) as a cocatalyst, these complexes display very high activities and produce high molecular weight polymers. Catalytic activity of up to 1.16×10^4 kg/mol_{Ni} · h and the viscosity-average molecular weight of polymer of up to 870 kg/mol were observed. Catalyst activity, polymer yield, and polymer molecular weight could be controlled over a wide range by the variation of the reaction parameters such as Al/Ni molar ratio, norbornene/catalyst molar ratio, monomer concentration, polymerization reaction temperature and time.

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1. Introduction

Norbornene is known to polymerize by ring-opening metathesis, cationic or radical polymerization, and vinylic polymerization (olefin addition polymerization) [1–4]. The vinylic polymerization of norbornene, yielding a 2,3-connected, rotationally strongly constrained vinyl-type polynorbornene, has been considerably attracted because of the polymer having unique physical properties, such as high glass transition temperature, optical transparency, and low birefringence [5,6]. The vinyl-type polynorbornene can be prepared using metal complexes based on nickel [7–16], chromium [17], titanium [18–24], zirconium [25–28], iron [29], cobalt [30–32], and palladium [16,33–42] as catalyst. Zirconocenes and cationic palladium complexes are two types of important catalysts for the vinylic polymerization of norbornene. Zirconocenes exhibit only low catalytic activity and afford high molecular weight polymers that de-

compose in air at high temperatures before they melt and are insoluble in organic solvents [25–28]. Cationic palladium complexes, such as $[\text{Pd}(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$, display extremely high catalytic activity and produce high molecular weight polymers that are soluble in organic solvents such as chlorobenzene and *o*-dichlorobenzene, and exhibit high glass transition temperature ($T_g > 350$ °C). Recently, the research works in our group and others indicated that well-defined neutral nickel(II) complexes are efficient catalysts for vinylic polymerization of norbornene in the presence of methylaluminumoxane (MAO) or MMAO, producing high molecular weight and amorphous polynorbornenes displaying good thermal stability [43–47]. However, in comparison with neutral nickel(II) complexes bearing single chelate ligand, corresponding bis(chelate)nickel(II) complexes are more stable and more easily synthesized, which promote us to investigate if they are also able to catalyze efficiently vinyl-polymerization of norbornene. In this paper, we report the synthesis, structure characterization, and norbornene polymerization behavior of a series of new nickel complexes bearing two β -ketoiminato

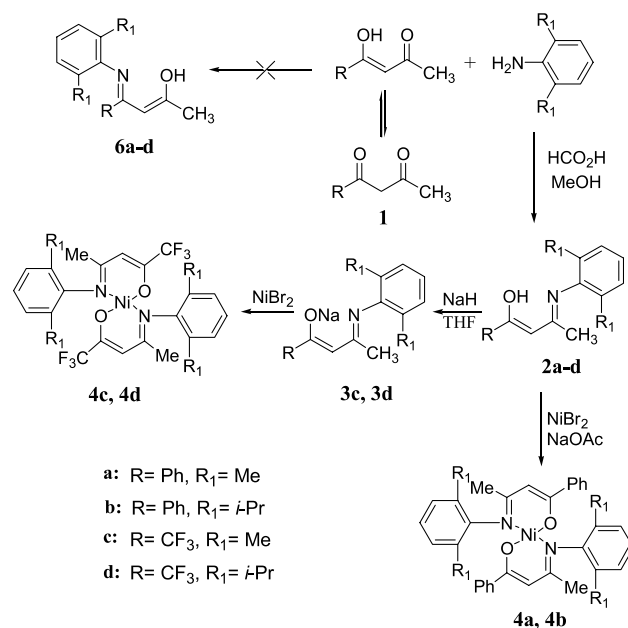
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chelate ligands. ^{13}C NMR suggested that the polynorbornenes obtained are vinyl addition products, in which no ring opened product was observed.

2. Results and discussion

2.1. Synthesis and characterization of complexes

In this study, we utilized nickel complexes that possess asymmetric bidentate β -ketoiminato chelate ligands. A general synthetic route for these nickel(II) complexes is shown in Scheme 1. The β -ketoimines **2a–d** were prepared in good yields (**2a**, 93.0%; **2b**, 94.5%; **2c**, 68.3%; **2d**, 72.1%) by the condensation of the corresponding β -diketones **1** with 2,6-dimethyl or 2,6-diisopropyl aniline in methanol containing a little of formic acid as the catalyst. The reason why the compounds **6a–d** cannot be formed is that the β -diketones exhibit keto-enol tautomerism and R_1 representing an aryl or a trifluoromethyl group with great electron-drawing effect increases the enol percentage, and/or there is the steric effect between bulky R_1 and N -aryl group in the β -ketoimines. The bis(β -ketoiminato)–nickel complexes **4a** and **4b** were synthesized as blackish green crystals in good yields (**4a**, 67.5%; **4b**, 66.3%) by the reaction of anhydrous nickel dibromide with the corresponding β -ketoimines **2a** and **2b**, respectively, in absolute alcohol



Scheme 1.

containing excessive anhydrous sodium acetate. However, no expected products were obtained when β -ketoimines, **2c** and **2d**, containing trifluoromethyl with great electron-drawing effect, were utilized. Therefore, an alternative synthetic route was used for the prepa-

Table 1
Crystal data and structure refinements of **4a** and **4c**

| | 4a | 4c |
|---|--|--|
| Empirical formula | $\text{C}_{36}\text{H}_{36}\text{N}_2\text{NiO}_2$ | $\text{C}_{26}\text{H}_{26}\text{F}_6\text{N}_2\text{NiO}_2$ |
| Formula mass | 587.38 | 571.20 |
| Crystal size (mm) | $0.602 \times 0.440 \times 0.297$ | $0.50 \times 0.36 \times 0.32$ |
| Crystal system | Monoclinic | Triclinic |
| Space group | $C2$ | $P\bar{1}$ |
| a (Å) | 23.3527(2) | 7.7001(17) |
| b (Å) | 13.4909(2) | 7.9997(9) |
| c (Å) | 14.7194(3) | 11.1129(13) |
| α (°) | 90 | 76.793(10) |
| β (°) | 99.905(3) | 79.098(14) |
| γ (°) | 90 | 79.704(14) |
| V (Å ³) | 4568.21(12) | 647.80(18) |
| Z | 6 | 1 |
| ρ_{calc} (Mg cm^{-3}) | 1.281 | 1.464 |
| Absorption coefficient (mm^{-1}) | 0.671 | 0.818 |
| $F(000)$ | 1860 | 294 |
| μ ($\text{Mo K}\alpha$) (cm^{-1}) | 0.71073 | 0.71073 |
| θ range for data collected (°) | 1.77–27.48 | 1.91–25.99 |
| Reflection collected | 5406 | 3185 |
| Data/restraints/parameters | 5406/1/564 | 2537/0/172 |
| Independent reflections (R_{int}) | 5406 (0.0000) | 2537 (0.0206) |
| Final R indices [$I > 2\sigma(I)$] | $R_1 = 0.0412$, $wR_2 = 0.0809$ | $R_1 = 0.0320$, $wR_2 = 0.0900$ |
| R indices (all data) | $R_1 = 0.0578$, $wR_2 = 0.0845$ | $R_1 = 0.0345$, $wR_2 = 0.0908$ |
| Absorption correction | Empirical | Psi-scan |
| Goodness-of-fit on F^2 | 0.937 | 1.051 |
| Maximum and minimum transmission | 1.4273 and 0.5205 | 0.5988 and 0.5097 |
| Largest peak/hole in final difference map ($\text{e}\text{Å}^{-3}$) | +0.358/−0.516 | +254/−0.250 |

Table 2
Selected bond lengths (Å) and bond angles (°) for complex **4a**

| | | | |
|-----------------|------------|---------------------|-----------|
| Ni(1)–O(1) | 1.844(3) | Ni(2)–O(3)#1 | 1.851(2) |
| Ni(1)–O(2) | 1.841(2) | Ni(2)–O(3) | 1.851(2) |
| Ni(1)–N(1) | 1.945(3) | Ni(2)–N(3)#1 | 1.906(3) |
| Ni(1)–N(2) | 1.901(3) | Ni(2)–N(3) | 1.906(3) |
| O(1)–C(11) | 1.295(5) | O(3)–C(47) | 1.290(5) |
| O(2)–C(29) | 1.279(5) | | |
| N(1)–C(1) | 1.438(5) | N(3)–C(37) | 1.458(5) |
| N(2)–C(19) | 1.450(5) | | |
| O(1)–Ni(1)–O(2) | 177.28(16) | O(3)#1–Ni(2)–O(3) | 168.2(2) |
| O(1)–Ni(1)–N(2) | 86.36(13) | O(3)#1–Ni(2)–N(3)#1 | 93.74(2) |
| O(1)–Ni(1)–N(1) | 91.97(13) | O(3)#1–Ni(2)–N(3) | 87.30(12) |
| O(2)–Ni(1)–N(1) | 88.01(13) | O(3)–Ni(2)–N(3)#1 | 87.30(12) |
| O(2)–Ni(1)–N(2) | 93.89(13) | O(3)–Ni(2)–N(3) | 93.74(12) |
| N(1)–Ni(1)–N(2) | 174.92(15) | N(3)#1–Ni(2)–N(3) | 169.9(2) |

ration of the bis(β -ketoiminato)–nickel complexes **4c** and **4d**. The sodium salts **3c** and **3d** were obtained by treatment of **2c** and **2d**, respectively, with excessive NaH in tetrahydrofuran, followed by the reaction with anhydrous nickel dibromide to give the bis(β -ketoiminato)–nickel complexes **4c** and **4d** as black crystals (yields: **4c**, 48.2%; **4d**, 46.7%).

Crystals of **4a** and **4c** suitable for X-ray structure determination were grown from a hexane–THF (5:1) solution. The data collection and refinement data of the analysis are summarized in Table 1, the selected bond lengths (Å) and bond angles (°) for complexes **4a** and **4c** are summarized in Tables 2 and 3, respectively, and the molecule structures are shown in Figs. 1 and 2. The unit cell of **4a** (**4a(1)** and **4a(2)**) in the solid state contains two crystallographically independent, but chemically similar molecules that are related by a non-crystallographic pseudo-inversion center, and the molecule adopts distorted square-planar coordination geometry, as shown in Fig. 1. The torsion angle of the plane (O1, Ni1, N1)

Table 3
Selected bond lengths (Å) and bond angles (°) for complex **4c**

| | | | |
|---------|------------|------------|------------|
| Ni–O#1 | 1.8336(13) | O#1–Ni–O | 180.00(13) |
| Ni–O | 1.8336(13) | O#1–Ni–N#1 | 92.71(6) |
| Ni–N#1 | 1.9201(15) | O#1–Ni–N | 87.29(6) |
| Ni–N | 1.9201(15) | O–Ni–N#1 | 87.29(6) |
| O–C(11) | 1.280(2) | O–Ni–N | 92.71(6) |
| N–C(9) | 1.351(3) | N#1–Ni–N | 180.00(10) |

and the plane (O2, Ni1, N2) is 10.7°, and that of the plane (O3, Ni2, N3) and the plane (O3#1, Ni2, N3#1) is 17.0°. The torsion angle of the plane (O1, Ni1, N2) and the plane (O2, Ni1, N1) is 5.6°, and that of the plane (O3, Ni2, N3#1) and the plane (O3#1, Ni2, N3) is 15.9°.

Contrarily, the unit cell of **4c** in the solid state contains only a single molecule, and the molecule adopts nearly ideal square-planar coordination geometry, as shown in Fig. 2. The torsion angle of the plane (O, Ni, N) and the plane (O#1, Ni, N#1) is 0°, and that of the plane (O, Ni, N#1) and the plane (O#1, Ni, N) is 0° too.

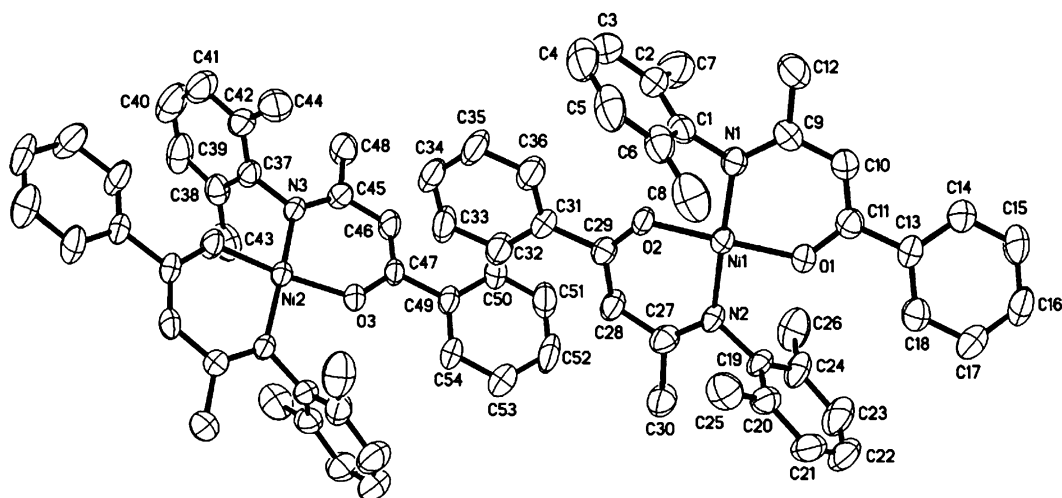


Fig. 1. Molecular structure of the nickel complex **4a**. Thermal ellipsoids at the 30% level are shown. Hydrogen atoms are omitted for clarity.

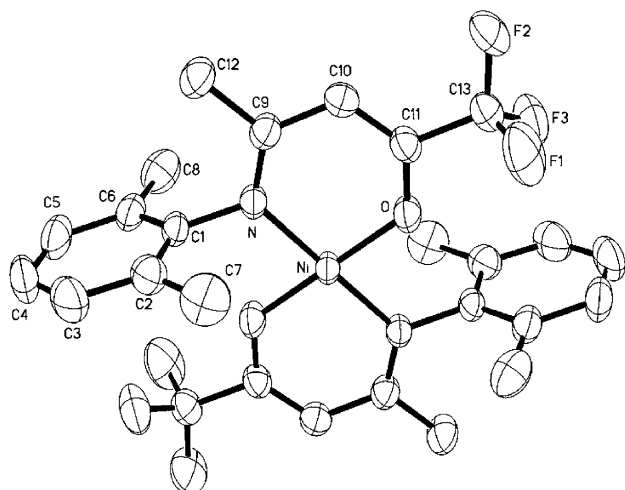


Fig. 2. Molecular structure of the nickel complex **4c**. Thermal ellipsoids at the 30% level are shown. Hydrogen atoms are omitted for clarity.

O, O#1, Ni, N, and N#1 atom are located in same plane. The lengths of Ni–O bonds are same, and the lengths of Ni–N bonds are same too.

2.2. Catalysis

Preliminary blank experiments were carried out with each of the nickel complexes **4a–d**. No polymer was obtained in the absence of MMAO. Therefore, all the other experiments were carried out in the presence of MMAO. All the nickel complexes **4a–d** activated with MMAO exhibit high catalytic activity for the vinylic polymerization of norbornene.

Polymer yields and molecular weights as well as catalyst activities depended significantly on the reaction

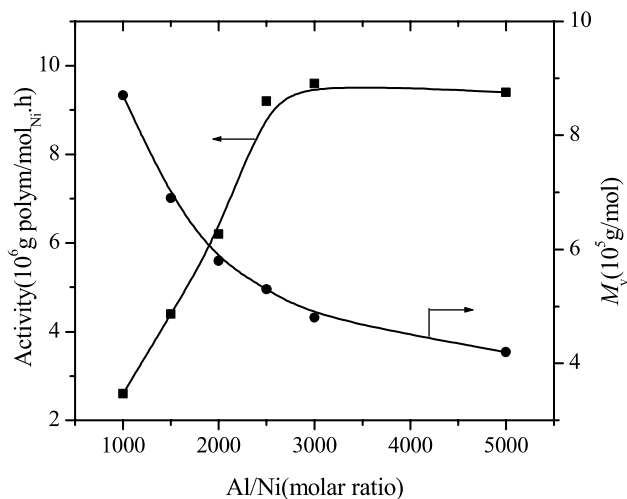


Fig. 3. Plot of activity (■) and \bar{M}_n (●) versus Al/Ni (molar ratio). 0.5 μ mol the nickel complex **4c**, [Norbornene]/[Ni] = 32 000, $V_{\text{total}} = 20$ ml, polymerization reaction at 30 °C for 15 min.

conditions. Variation of the ratio of MMAO/**4c**, which is expressed here as Al/Ni molar ratio, showed considerable effects on polymer yields, polymer molecular weights and catalyst activities. As shown in Fig. 3, the catalytic activity of the complex **4c** rapidly increases first with increase of Al/Ni ratio, and then keep steady when the Al/Ni molar ratio reached 2500/1. Contrarily, the molecular weight of polymer decreases gradually with increase of Al/Ni molar ratio.

Reaction temperature also affects considerably the activities of catalysts and the molecular weights of polymers. As shown in Fig. 4, with increase of reaction temperature, the catalytic activity of the complex **4c** gradually increases first and then decreases. Contrarily, in low reaction temperature region, the molecular weight of polymer increases slowly with increase of reaction temperature, and in high reaction temperature region, the molecular weight of polymer increases rapidly. As for the catalytic activity, the optimum reaction temperature is ca. 25 °C.

Considerable effects of the molar ratio of monomer to catalyst on the activities of catalysts and the molecular weights of polymers were also observed. An increase of the norbornene/Ni molar ratio, which also means an increase of the monomer concentration (the reaction volume was kept constant), caused a dramatic increase of the catalytic activity of the complex **4c** combined with a linear increase of the molecular weights of polymers, as shown in Fig. 5.

The polymerization results using the bis(β -ketoiminato)–nickel complexes **4a–d** and the bis(β -diketonato)–nickel complexes **5a–d**, bis(salicylaldiminato)–nickel complex **6a**, and neutral nickel complexes **6b** and **6c** activated with MMAO are summarized in Table 4. The structures of the bis(β -ketoiminato)–nickel complexes

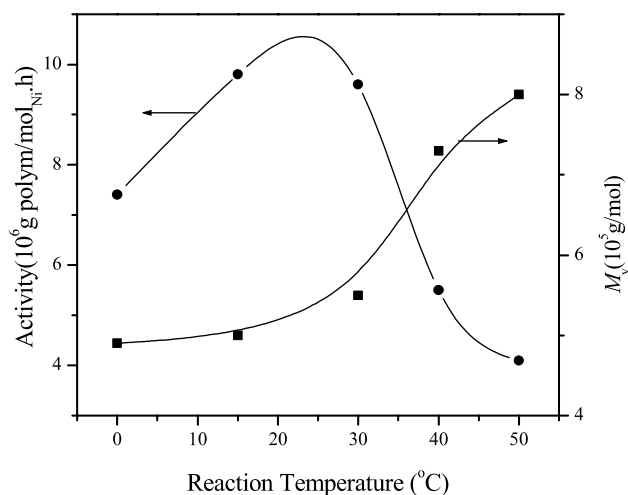


Fig. 4. Plot of activity (■) and \bar{M}_n (●) versus reaction temperature. 0.2 μ mol the nickel complex **4c**, Al/Ni = 2500, [Norbornene]/[Ni] = 3200, $V_{\text{total}} = 20$ ml, polymerization reaction for 15 min.

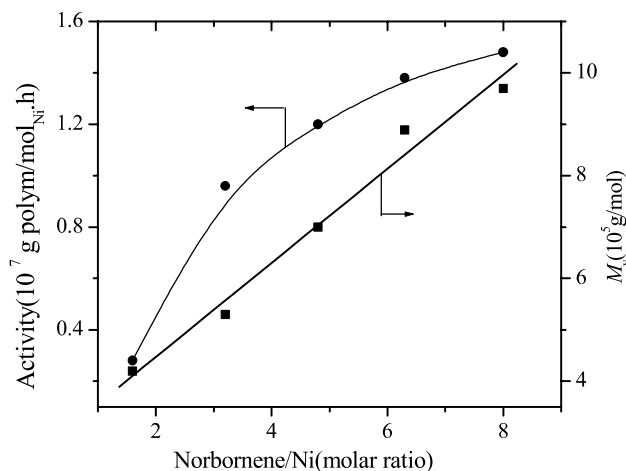


Fig. 5. Plot of activity (■) and \bar{M}_v (●) versus norbornene concentration. 0.2 μ mol the nickel complex **4c**, Al/Ni = 2500, $V_{\text{total}} = 20$ mL, polymerization reaction at 30 °C for 15 min.

also affect considerably the catalytic activities, polymer yields, and polymer molecular weights under the same experiment conditions. The complex **4d**/MMAO system exhibited higher catalytic activity (1.16×10^4 kg of polynorbornene (PNB)/mol_{Ni}·h, $\bar{M}_v = 590$ kg/mol) than the complex **4b**/MMAO system (7.0×10^3 kg of PNB/mol_{Ni}·h, $\bar{M}_v = 640$ kg/mol), and the complex **4c**/MMAO system displayed higher catalytic activity (1.04×10^4 kg of PNB/mol_{Ni}·h, $\bar{M}_v = 550$ kg/mol) than the complex **4a**/MMAO system (6.2×10^3 kg of PNB/mol_{Ni}·h, $\bar{M}_v = 610$ kg/mol), indicating that the CF₃ group with a strong electron-withdrawing effect increases the catalytic activity towards norbornene polymerization. A comparison of **4a** with **4b**, and **4c** with **4d**, indicates that the catalytic activity can be slightly increased by introducing bulky substituents into the *ortho* position of the N-aryl system.

The bis(β -diketonato)-nickel complex (**5b**) bearing two phenyl groups displays higher catalytic activity towards norbornene polymerization (8.4×10^3 kg of PNB/mol_{Ni}·h) than the bis(β -diketonato)-nickel complex (**5a**) (7.0×10^3 kg of PNB/mol_{Ni}·h), indicating that the introduction an electron-withdrawing group into β -diketonato ligands could increase the catalytic activity of bis(β -diketonato)-nickel complex. CF₃ is a stronger electron-withdrawing group than phenyl group, so the catalytic activities of the bis(β -diketonato)-nickel complexes towards norbornene polymerization gradually increase (from 7.0 through 8.4 and 9.0 to 11.4×10^3 kg of PNB/mol_{Ni}·h) from **5a** through **5b** and **5c** to **5d**. High catalytic activity means fast rate of chain propagation, while fast chain propagation is often gone with faster chain transfer reaction. This cause that the molecular weights of the polymers obtained with bis(β -diketonato)-nickel complexes, except **5b**, gradually decrease (from 390 through 380 to 284 kg/mol) with the

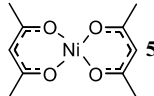
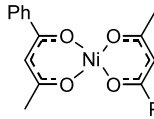
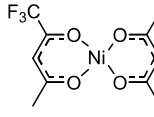
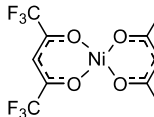
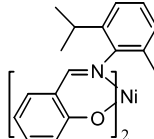
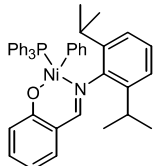
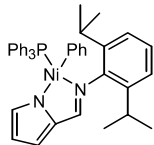
increase of catalytic activities. Phenyl group is not only an electron-withdrawing group, but also a bulky substituent. It is well known that bulky substituent is capable of controlling chain transfer reaction. As a result, **5b** produces higher molecular weight polymers ($\bar{M}_v = 430$ kg/mol) than **5a** and **5c**.

As a rule, steric hindrance will be propitious to control chain transfer reaction and increase the molecular weight of polymer if a late transition metal catalyst is used to promote the polymerization of olefin. To compare with β -diketonato ligands, β -ketoiminato ligands possess steric effect, so the bis(β -ketoiminato)-nickel complexes **4a** and **4b** produce higher molecular weight polymers ($\bar{M}_v = 610$ and 640 kg/mol, respectively) than the corresponding bis(β -diketonato)-nickel complex **5b** ($\bar{M}_v = 430$ kg/mol) under the same conditions. On the other hand, steric hindrance will go against inserting olefin into metal-carbon bonding. In other words, steric effect will decrease the rate of olefin polymerization. As a consequence, the bis(β -ketoiminato)-nickel complexes **4a** and **4b** exhibit slight lower catalytic activities of norbornene polymerization (6.2 and 7.0×10^3 kg of PNB/mol_{Ni}·h, respectively) than the corresponding bis(β -diketonato)-nickel complex **5b** (8.4×10^3 kg of PNB/mol_{Ni}·h).

When phenyl group in β -ketoiminato ligands are replaced by smaller CF₃ group bearing stronger electron-withdrawing, the catalytic activity of bis(β -ketoiminato)-nickel complex considerably increase (**4c** to **4a**, **4d** to **4a**), while the molecular weights of polynorbornenes obtained slight decrease. Furthermore, it is very interesting that the bis(β -ketoiminato)-nickel complexes **4c** and **4d** not only exhibit higher catalytic activity (1.04 and 1.16×10^4 kg of PNB/mol_{Ni}·h, respectively) than the bis(β -diketonato)-nickel(II) complex (**5c**) (9.0×10^3 kg of PNB/mol_{Ni}·h), but also yield higher molecular weight polymers ($\bar{M}_v = 550$ and 590 kg/mol, respectively) than the bis(β -diketonato)-nickel complex (**5c**) ($\bar{M}_v = 380$ kg/mol). This indicates that the bis(β -ketoiminato)-nickel complexes are more favorable catalysts for norbornene polymerization than the bis(β -diketonato)-nickel complexes.

To understand well differences between bis(chelate)-nickel catalysts and neutral nickel catalysts reported previously [43,44], we synthesized and evaluated bis(salicylaldiminato)-nickel **6a**, and the catalytic behavior of the neutral nickel catalysts **6b** and **6c** were also evaluated again under the same conditions. The typical results as well as those reported previously are listed in Table 4. The catalytic activity of **6a** towards norbornene polymerization (9.6×10^3 kg of PNB/mol_{Ni}·h) is comparable with that of neutral-nickel complex **6b** (10.4×10^3 kg of PNB/mol_{Ni}·h) under the same conditions, although **6b** yields much higher molecular weight polymers ($\bar{M}_v = 1230$ kg/mol) over **6a** ($\bar{M}_v = 746$ kg/mol). Moreover, that data of entries 3, 4, 10, and 11 also

Table 4
The results of the vinylic polymerization of norbornene^a

| Entry | Catalyst | Norbornene (g) | Al/Ni (mol ratio) | Polymer (g) | Yield (%) | Activity (10 ³ kg/mol _{Ni} · h) | \bar{M}_v (kg/mol) |
|----------------|---|----------------|-------------------|-------------|-----------|---|----------------------|
| 1 | 4a | 0.6 | 2500 | 0.31 | 52 | 6.2 | 610 |
| 2 | 4b | 0.6 | 2500 | 0.35 | 58 | 7.0 | 640 |
| 3 | 4c | 0.6 | 2500 | 0.52 | 87 | 10.4 | 550 |
| 4 | 4d | 0.6 | 2500 | 0.58 | 97 | 11.6 | 590 |
| 5 |  5a | 0.6 | 2500 | 0.35 | 58 | 7.0 | 390 |
| 6 |  5b | 0.6 | 2500 | 0.42 | 70 | 8.4 | 430 |
| 7 |  5c | 0.6 | 2500 | 0.45 | 75 | 9.0 | 380 |
| 8 |  5d | 0.6 | 2500 | 0.57 | 95 | 11.4 | 284 |
| 9 |  6a | 0.6 | 2500 | 0.48 | 80 | 9.6 | 746 |
| 10 |  6b | 0.6 | 2500 | 0.52 | 87 | 10.4 | 1230 |
| 11 |  6c | 0.6 | 2500 | 0.49 | 82 | 9.8 | 720 |
| Reference [43] | 6b^b | 1.83 | 2000 | 1.61 | 87.9 | 33.0 | 1310 |
| Reference [44] | 6c^c | 2.40 | 2000 | 1.61 | 67.0 | 39.0 | 650 |

^a 0.2 μmol catalyst, $V_{\text{total}} = 15$ ml, polymerization reaction for 15 min at 30 °C.

^b 0.2 μmol catalyst, $V_{\text{total}} = 15$ ml, polymerization reaction for 15 min at 30 °C, see [43].

^c 0.5 μmol catalyst, $V_{\text{total}} = 30$ ml, polymerization reaction for 5 min at 30 °C, see [44].

indicate that bis(β-diketonato)–nickel catalysts, **4c** and **4d**, bearing CF₃ display similar catalytic activities towards norbornene polymerization to the neutral nickel catalysts **6b** and **6c**, despite they produce lower molecular weight polymers than **6b** and **6c**.

Figs. 6 and 7 show ¹H NMR spectra and ¹³C NMR spectra of the typical polynorbornene obtained by the complex **4c**/MMAO catalytic system. No trace of double bonds, which are typical for metathesis-type polynorbornene, was observed in ¹H NMR spectra of polymer,

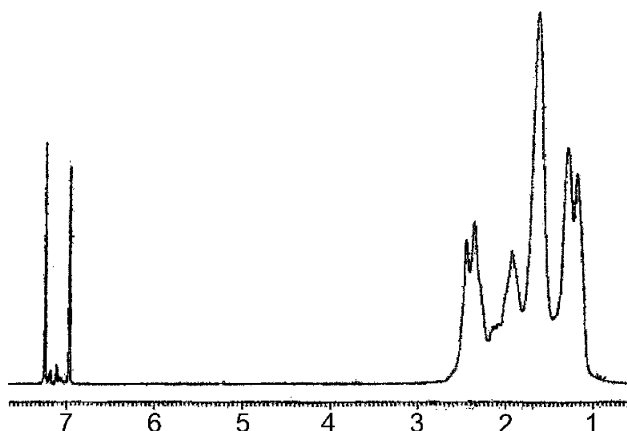


Fig. 6. ^1H NMR spectra of polynorbornene recorded in $o\text{-C}_6\text{D}_4\text{Cl}_2$ at 135°C .

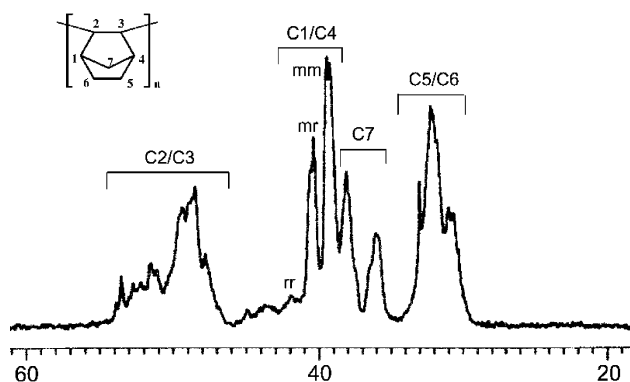


Fig. 7. ^{13}C NMR spectra of polynorbornene recorded in $o\text{-C}_6\text{D}_4\text{Cl}_2$ at 135°C .

indicating that the polynorbornene obtained was a vinyl-type (2,3-linked) addition product. As shown in Fig. 7, the resonances of methenes and methines appear at 29.5–33.5 ppm for carbon-5 and carbon-6, 35.5–38.5 ppm for carbon-7, 38.5–42.5 ppm for carbon-1 and carbon-4, and 46.6–54 ppm for carbon-2 and carbon-3. The ^{13}C NMR spectrum is similar to that reported by Greiner's and Wu's groups [10,18]. These data further confirm that the polynorbornenes obtained were the products of vinylic polymerization.

3. Conclusions

The nickel(II) complexes bearing two asymmetric bidentate β -ketoiminato chelate ligands **4a–d** were easily synthesized and activated with MMAO are highly active in the vinylic polymerization of norbornene. Catalytic activities of up to $1.16 \times 10^4 \text{ kg/mol}_{\text{Ni}} \cdot \text{h}$ and viscosity-average molecular weights of up to $8.7 \times 10^5 \text{ g/mol}$ were observed. Polymer yields and catalyst activities are considerably affected by the steric effects and electron-

withdrawing effects of substituents on the catalyst backbone under the same polymerization conditions. Activity, polymer yield, and polymer molecular weight can also be controlled by variation of the reaction parameters. The polynorbornenes obtained here exhibit high thermal stability, and are amorphous and soluble at room temperature in halogenated aromatic hydrocarbons.

4. Experimental

4.1. General procedures and materials

All work involving air and moisture sensitive compounds was carried out using standard Schlenk techniques. NMR analyses of polymers were performed on a Varian Unity 400 MHz spectrometer at 135°C , using $o\text{-C}_6\text{D}_4\text{Cl}_2$ as solvent. NMR data of ligands and complexes were obtained on a Varian Unity 300 MHz spectrometer at ambient temperature, CDCl_3 as solvent. Viscosity-average molecular weights were calculated from the intrinsic viscosity by using the Mark–Houwink coefficients: $a = 0.56$, $K = 5.97 \times 10^{-4} \text{ dl/g}$ [48].

2,6-Dimethylaniline and 2,6-diisopropylaniline were obtained from Acros and purified by distillation before use. 1,1,1-Trifluoro-2,4-pentanedione and 1-benzoyl-acetone were obtained from Aldrich and used without purification. Nickel(II) hexafluoroacetylacetonate (**5d**) was purchased from STREM and purified by recrystallization hot toluene before use. Bis(diketonato)–nickel complexes **5a–c** were prepared according to the published procedure. The bis(salicylaldiminato)–nickel complex **6a** was prepared in good yields according to a published procedure by Yamanouchi [49]. Norbornene was dried over Na, vacuum-transferred, and degassed by repeated freeze-pump-thaw cycles. Anhydrous tetrahydrofuran was refluxed and distilled from Na-K/benzophenone under dry nitrogen. o -Dichlorobenzene- d_4 was obtained from Aldrich and used without further purification. Modified methylaluminoxane (MMAO, 7% aluminum in heptane solution) was purchased from Akzo Nobel Chemical Inc.

4.2. Synthesis of ligands (2a–d)

(2,6- $\text{Me}_2\text{C}_6\text{H}_3$) $\text{NC}(\text{CH}_3)\text{C}(\text{H})\text{C}(\text{Ph})\text{OH}$ (**2a**): To a stirred solution of 1-benzoyl-acetone (3.24 g, 20 mmol) in dried methanol (10 ml) was added 2,6-dimethylaniline (3.65 ml, 30 mmol) and formic acid (0.5 ml) as catalyst. The reaction mixture was stirred and refluxed for 48 h under N_2 , and then cooled. The colorless precipitate was separated by filtration, washed with cold methanol and then dried to afford **2a** as colorless crystals in 93.0% (4.93 g). The other ligands **2b–d** were prepared via the same procedure.

2a: ^1H NMR (CDCl_3): δ 12.53 (s, 1H, OH), 7.43 (m, 8H, Ph-H), 5.94 (s, 1H, =C-H), 2.25 (s, 6H, Ph-CH₃), 1.79 (s, 3H, CO-CH₃). ^{13}C NMR (CDCl_3): δ 188.95, 165.10, 136.38, 131.13, 128.62, 127.89, 127.47, 92.73, 19.82, 18.66. Anal. Calc. for C₁₈H₁₉NO: C, 81.47; H, 7.22; N, 5.28. Found: C, 81.65; H, 7.27; N, 5.25%.

$[(2,6\text{-iPr}_2\text{C}_6\text{H}_3)\text{NC}(\text{CH}_3)\text{C}(\text{H})\text{C}(\text{Ph})\text{OH}]_2\text{Ni}$ (**2b**): Yield: 94.5%. ^1H NMR (CDCl_3): δ 12.63 (s, 1H, OH), 7.96 (d, 2H, Ph-H), 7.46–7.42 (m, 3H, Ph-H), 7.32 (t, 1H, Ph-H), 7.20 (d, 2H, Ph-H), 5.93 (s, 1H, =C-H), 3.12–3.06 (m, 2H, iPr-C-H), 1.79 (s, 3H, CO-CH₃), 1.24–1.16 (dd, 12H, iPr-CH₃). ^{13}C NMR (CDCl_3): δ 188.28, 164.98, 146.02, 139.93, 133.40, 130.61, 128.27, 128.09, 126.97, 123.48, 92.05, 28.41, 24.49, 22.57, 19.58. Anal. Calc. for C₂₂H₂₇NO: C, 82.20; H, 8.47; N, 4.36. Found: C, 82.09; H, 8.43; N, 4.40%.

$[(2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{NC}(\text{CH}_3)\text{C}(\text{H})\text{C}(\text{CF}_3)\text{OH}]_2\text{Ni}$ (**2c**): Yield: 68.3%. ^1H NMR (CDCl_3): δ 12.13 (s, 1H, O-H), 7.18 (m, 3H, Ph-H), 5.60 (s, 1H, =C-H), 2.25 (s, 6H, Ph-CH₃), 1.87 (s, 3H, -CH₃). ^{13}C NMR (CDCl_3): δ 177.36, 170.36, 135.69, 135.46, 128.99, 128.81, 119.91, 90.00, 19.70, 18.46. Anal. Calc. for C₁₃H₁₄F₃NO: C, 60.70; H, 5.49; N, 5.44. Found: C, 60.83; H, 5.46; N, 5.41%.

$[(2,6\text{-iPr}_2\text{C}_6\text{H}_3)\text{NC}(\text{CH}_3)\text{C}(\text{H})\text{C}(\text{CF}_3)\text{OH}]_2\text{Ni}$ (**2d**): Yield, 72.1%. ^1H NMR (CDCl_3): δ 12.22 (s, 1H, O-H), 7.46 (t, 1H, Ph-H), 7.22 (d, 2H, Ph-H), 5.59 (s, 1H, =CH), 2.96 (m, 2H, iPr-CH), 1.84 (s, 3H, -CH₃), 1.27–1.18 (dd, 12H, iPr-CH₃). ^{13}C NMR (CDCl_3): δ 170.41, 145.44, 132.02, 129.23, 123.53, 89.49, 28.58, 24.40, 22.53, 19.57. Anal. Calc. for C₁₇H₂₂F₃NO: C, 65.16; H, 7.08; N, 4.47. Found: C, 65.28; H, 7.12; N, 4.51%.

4.3. Synthesis of bis(β -ketoiminato)-nickel(II) complexes (**4a–d**)

$[(2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{NC}(\text{CH}_3)\text{C}(\text{H})\text{C}(\text{Ph})\text{O}]_2\text{Ni}$ (**4a**): To a solution of ligand **2a** (0.617 g, 2.4 mmol) in absolute alcohol (15 ml) were added anhydrous sodium acetate (0.2 g, 2.45 mmol) and NiBr₂ (0.262 g, 1.2 mmol). The reaction mixture was stirred at 40 °C for 36 h under nitrogen atmosphere, and then a blackish green solid was isolated by filtration and washed several times by cold absolute alcohol to yield 0.47 g (67.5%) **4a** as a blackish green crystal. The nickel complex **4b** was prepared by the same procedure with similar yields.

4a: ^1H NMR (CDCl_3): δ 7.03 (m, 12H, Ph-H), 6.48 (m, 4H, Ph-H), 5.45 (s, 2H, =C-H), 2.60 (s, 12H, Ph-CH₃), 1.39 (s, 6H, CH₃). ^{13}C NMR (CDCl_3): 170.13, 165.65, 148.11, 138.64, 133.43, 129.11, 128.58, 127.65, 126.65, 124.78, 98.26, 24.85, 19.28. Anal. Calc. for C₃₆H₃₆N₂NiO₂: C, 73.61; H, 6.18; N, 4.77. Found: C, 73.56; H, 6.15; N, 4.33%.

$[(2,6\text{-iPr}_2\text{C}_6\text{H}_3)\text{NC}(\text{CH}_3)\text{C}(\text{H})\text{C}(\text{Ph})\text{O}]_2\text{Ni}$ (**4b**): Yield, 66.3%. ^1H NMR (CDCl_3): δ 7.09 (m, 12H, Ph-H), 6.30 (d, 4H, Ph-H), 5.53 (s, 2H, =C-H), 4.26 (m,

4H, iPr-CH), 1.47 (s, 6H, -CH₃), 1.26 (dd, 12H, iPr-CH₃). ^{13}C NMR (CDCl_3): 170.34, 166.94, 145.27, 142.86, 137.18, 129.07, 127.51, 126.91, 125.51, 124.24, 97.69, 28.94, 25.55, 24.41, 24.10. Anal. Calc. for C₄₄H₅₂N₂NiO₂: C, 75.54; H, 7.49; N, 4.00. Found: C, 75.63; H, 7.44; N, 3.97%.

$[(2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{NC}(\text{CH}_3)\text{C}(\text{H})\text{C}(\text{CF}_3)\text{O}]_2\text{Ni}$ (**4c**): A solution of ligand **2c** (0.513 g, 2.0 mmol) in THF (20 ml) was added to sodium hydride (96 mg, 4 mmol). The reaction mixture was stirred at room temperature for 5 h, filtered, and evaporated. The solid residue was washed with pentane (20 ml), and a yellow-orange solution of sodium salts **3c** was obtained. NiBr₂ (0.219 g, 1.0 mmol) and ethylene glycol dimethyl ether (0.09 g, 1.0 mmol) were added into the solution of sodium salts, and then stirred for 24 h at 30 °C under a nitrogen atmosphere, the solution became celadon and a solid precipitate formed. The reaction mixture was filtered by cannula filtration, and then the filtrate was concentrated in vacuo to ca. 5 ml, to which pentane (30 ml) was added. Subsequently, a black crystal precipitated from the solution and was isolated by filtration, washed several times by cold pentane to yield 0.275 g (48.2%) **4c**. The nickel complex **4d** was prepared by the same procedure with similar yield.

4c: ^1H NMR (CDCl_3): δ 6.99 (m, 6H, Ph-H), 5.14 (s, 2H, =C-H), 2.59 (s, 12H, Ph-CH₃), 1.42 (s, 6H, -CH₃). ^{13}C NMR (CDCl_3): δ 167.89, 156.59, 145.64, 132.10, 128.05, 125.97, 97.89, 24.49, 18.87. Anal. Calc. for C₂₆H₂₆F₆N₂NiO₂: C, 54.67; H, 4.59; N, 4.90. Found: C, 54.59; H, 4.57; N, 4.88%.

$[(2,6\text{-iPr}_2\text{C}_6\text{H}_3)\text{NC}(\text{CH}_3)\text{C}(\text{H})\text{C}(\text{CF}_3)\text{O}]_2\text{Ni}$ (**4d**): Yield, 46.7%. ^1H NMR (CDCl_3): δ 7.14 (m, 6H, Ph-H), 5.35 (s, 2H, =C-H), 3.78 (m, 4H, iPr-CH), 1.55 (d, 12H, iPr-CH₃), 1.23 (s, 6H, -CH₃). ^{13}C NMR (CDCl_3): δ 167.89, 157.03, 140.75, 126.35, 124.00, 97.16, 29.03, 25.58, 24.16, 24.06. Anal. Calc. for C₃₄H₄₂N₂F₆NiO₂: C, 59.76; H, 6.19; N, 4.10. Found: C, 59.84; H, 6.16; N, 4.12%.

4.4. Typical polymerization procedure

0.2 ml of a fresh catalyst solution (chlorobenzene, 0.2 μmol catalyst), 0.75 ml of a solution of norbornene (6.4 mmol, 0.60 g) in chlorobenzene, and 18.0 ml of chlorobenzene were added under inert gas atmosphere into a Schlenk flask with a mechanical stirrer. The reaction was started by the addition of 0.5 ml of a MMAO solution (0.5 mmol in chlorobenzene) at 30 °C. Total reaction volume was 20 ml, unless otherwise stated. This was achieved by variation of the amount of chlorobenzene if necessary. After 15 min, the reaction mixture was poured into 200 ml of acidic ethanol (ethanol/HCl_{conc.} = 50/1). The polymer was isolated by filtration, washed with methanol, and dried under vacuum at 80 °C for 24 h.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 216265 and 216266 for the complexes **4a** and **4c**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or [www: http://ccdc.cam.ac.uk](http://ccdc.cam.ac.uk)).

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References

- [1] M.R. Buchmeiser, *Chem. Rev.* 100 (2000) 1565.
- [2] C. Janiak, P.G. Lassahn, *J. Mol. Catal. A* 166 (2001) 193.
- [3] N.C. Gaylord, B.M. Mandal, M. Martan, *J. Polym. Sci. Polym. Lett. Ed.* 14 (1976) 555.
- [4] M.C. Sacchi, M. Sonzogni, S. Losio, F. Forlini, P. Locatelli, I. Tritto, M. Licchelli, *Macromol. Chem. Phys.* 202 (2001) 2052.
- [5] N.R. Grove, P.A. Kohl, S.A.B. Allen, S. Jayaraman, R. Shick, *J. Polym. Sci. B* 37 (1999) 3003.
- [6] C. Janiak, P.G. Lassahn, *J. Mol. Catal. A* 166 (2001) 193.
- [7] W. Massa, N. Faza, H.-C. Kang, C. Focke, W. Heitz, *Acta Polym.* 48 (1997) 432.
- [8] M. Arndt, M. Gosmann, *Polym. Bull.* 41 (1998) 433.
- [9] F. Peruch, H. Cramail, A. Deffieux, *Macromol. Chem. Phys.* 199 (1998) 2221.
- [10] C. Mast, M. Krieger, K. Dehnicke, A. Greiner, *Macromol. Rapid Commun.* 20 (1999) 232.
- [11] S. Brorkar, P.K. Saxena, *Polym. Bull.* 44 (2000) 167.
- [12] A.O. Patil, S. Zushma, R.T. Stibrany, S.P. Pucker, L.M. Wheeler, *J. Polym. Sci. A* 41 (2003) 2095.
- [13] X. Mi, Z. Ma, L.Y. Wang, Y.C. Ke, Y.L. Hu, *Macromol. Chem. Phys.* 204 (2003) 868.
- [14] X. Mi, Z. Ma, N. Cui, L.Y. Wang, Y.C. Ke, Y.L. Hu, *J. Appl. Polym. Sci.* 88 (2003) 3273.
- [15] H.J. Yang, Z.L. Li, W.H. Sun, *J. Mol. Catal. A* 206 (2003) 23.
- [16] B. Berchtold, V. Lozan, P.G. Lassahn, C. Janiak, *J. Polym. Sci. A* 40 (2002) 3604.
- [17] U. Peucker, W. Heitz, *Macromol. Rapid Commun.* 19 (1998) 159.
- [18] Q. Wu, Y.Y. Lu, *J. Polym. Sci. A* 40 (2002) 1421.
- [19] T. Hasan, K. Nishii, T. Shiono, T. Ikeda, *Macromolecules* 35 (2002) 8933.
- [20] R. Manivannan, G. Sundararajan, W. Kaminsky, *Macromol. Rapid Commun.* 21 (2000) 968.
- [21] X. Mi, W.D. Yan, H. Hong, Y.C. Ke, Y.L. Hu, *Acta Polym. Sin.* (2001) 604.
- [22] Y.Y. Lu, Q. Wu, Z.J. Lu, *Chem. J. Chin. Univ.* 22 (2001) 160.
- [23] T. Hasan, K. Nishii, T. Shiono, T. Ikeda, *Macromolecules* 35 (2002) 8933.
- [24] X. Mi, D.M. Xu, W.D. Yan, C.Y. Guo, Y.C. Ke, Y.L. Hu, *Polym. Bull.* 47 (2002) 521.
- [25] W. Kaminsky, A. Bark, M. Arndt, *Makromol. Chem. Macromol. Symp.* 47 (1991) 83.
- [26] W. Kaminsky, A. Noll, *Polym. Bull.* 31 (1993) 175.
- [27] W. Kaminsky, A. Bark, *Polym. Int.* 28 (1992) 251.
- [28] W. Kaminsky, A. Bark, R. Steiger, *J. Mol. Catal.* 74 (1992) 109.
- [29] X. Mi, Z. Ma, W.D. Yan, Y.X. Liu, H. Wang, Y.C. Ke, Y.L. Hu, *Chem. Res. Chin. Univ.* 18 (2002) 462.
- [30] F.P. Alt, W. Heitz, *Macromol. Chem. Phys.* 199 (1998) 1951.
- [31] F.P. Alt, W. Heitz, *Acta Polym.* 49 (1998) 477.
- [32] F. Pelascini, F. Peruch, P.J. Lutz, M. Wesolek, J. Kress, *Macromol. Rapid Commun.* 24 (2003) 768.
- [33] C. Tanielian, A. Kiennemann, T. Osparpucu, *Can. J. Chem.* 57 (1979) 2022.
- [34] A. Sen, T.-W. Lai, R.R. Thomas, *J. Organomet. Chem.* 368 (1988).
- [35] N. Seehof, C. Mehler, S. Breunig, W. Risse, *J. Mol. Catal.* 76 (1992) 219.
- [36] C. Mehler, W. Risse, *Macromolecules* 25 (1992) 4226.
- [37] T.F.A. Haselwander, W. Heitz, S.A. Krügel, J.H. Wendorff, *Macromol. Chem. Phys.* 197 (1996) 3435.
- [38] A.S. Abu-Surrah, K. Lappalainen, T. Repo, M. Klinga, M. Leskelä, H.A. Hodali, *Polyhedron* 19 (2000) 1601.
- [39] B.S. Heinz, F.P. Alt, W. Heitz, *Macromol. Rapid Commun.* 19 (1998) 251.
- [40] A.S. Abu-Surrah, K. Lappalainen, M. Kettunen, T. Repo, M. Leskelä, H.A. Hodali, B. Rieger, *Macromol. Chem. Phys.* 202 (2001) 599.
- [41] J. Lipian, R.A. Mimna, J.C. Fondran, D. Yandulov, R.A. Shick, B.L. Goodall, L.F. Rhodes, *Macromolecules* 35 (2002) 8969.
- [42] P.G. Lassahn, V. Lozan, C. Janiak, *J. Chem. Soc., Dalton Trans.* (2003) 927.
- [43] X.F. Li, Y.S. Li, *J. Polym. Sci. A* 40 (2002) 2680.
- [44] Y.S. Li, Y.R. Li, X.F. Li, *J. Organomet. Chem.* 667 (2003) 185.
- [45] H.J. Yang, W.H. Sun, F. Chang, Y. Li, *Appl. Catal. A* 252 (2003) 261.
- [46] D.A. Barnes, G.M. Benedikt, B.L. Goodall, S.S. Huang, H.A. Kalamarides, S. Lenhard, H.L. McIntosh III, K.T. Selvy, R.A. Shick, L.F. Rhodes, *Macromolecules* 36 (2003) 2623.
- [47] W.H. Sun, H.J. Yang, Z.L. Li, Y. Li, *Organometallics* 22 (2003) 3678.
- [48] T.F.A. Haselwander, W. Heitz, *Macromol. Rapid Commun.* 18 (1997) 689.
- [49] K. Yamanouchi, *Bull. Chem. Soc. Jpn.* 55 (1982) 1083.