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Vinyl polymerizations of norbornene catalyzed by nickel complexes with acetoacetamide ligands

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On the basis of a remote effect, a series of acetoacetamide ligands and corresponding nickel complexes *N*-(R-phenyl) acetoacetamide Ni(CH_2Ph) (PMe_3) (R = H, 1; R = 2-methyl, 2; R = 2,6-dimethyl, 3; R = 2,6-diisopropyl, 4; R = 4-NO_2, 5) were synthesized and characterized. The solid structure of complex 3 was confirmed by X-ray single-crystal analysis to be of *cis* form. ^{1}H and ^{31}P NMR spectroscopy confirmed that *cis* and *trans* isomers of nickel complexes were present in solution. Norbornene polymerizations with acetoacetamide nickel complexes activated with modified methylaluminoxane (MMAO) were investigated in detail. Remote steric and electronic effects of acetoacetamide ligand on catalytic activity and molecular weight of polynorbornenes (PNBs) were observed. Characterizations of the obtained PNBs show that the obtained polymer products are non-crystalline vinylic-addition polynorbornenes. Copyright © 2013 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this article.

Keywords: norbornene; acetoacetamide; nickel catalyst; vinyl polymerization

Introduction

Olefin polymerization based on late-transition-metal catalysts has been one of the most exciting developments in the area of catalysis, organometallic chemistry and polymer science in recent years.[1–3] Interest in polymers of cyclic olefins such as norbornene (NB) (bicyclo[2.2.1]hept-2-ene) has increased dramatically because of the attractive properties of this addition type of polymer such as high chemical resistance, good UV resistance, low dielectric constant, high glass transition temperature, excellent transparency, large refractive index and low birefringence.[4–10] Up to now, vinyl-addition polymerization of norbornene has been reported using many transition metal catalysts, including Ti,[11,12] Zr,[13,14] Fe,[15] Ni,[15–21] Pd,[22–24] Co,[25,26] Cu[27–30] and Cr.[31,32] Janiak and Bao have given a full literature and patent account on the work describing the addition polymerization of norbornene.[33,34] Among these catalysts, late transition metal catalysts (Ni and Pd) exhibited especially high activity.[33] It is known that the polynorbornenes (PNBs) catalyzed by palladium-based catalysts are usually insoluble in common solvents,[22,24,33] whereas those obtained by-nickel based catalysts are soluble in chlorohydrocarbons.[15–21] Therefore, nickel-based catalysts show great potential for application in norbornene homopolymerization.

Currently, nickel complexes bearing chelate [N,O] and [N,N] ligands are mostly synthesized and applied for norbornene polymerization.[18–21,26–29] Compared to these two types of ligand, [O,O] ligand has rarely been used to coordinate nickel for norbornene polymerization because of the difficultly in modifying features for steric and electronic effects.[35–39] Indeed, the reported literature has addressed that nickel catalyst bearing [O,O] ligands can also show very high activity toward norbornene polymerization.[36,38] In this paper, we synthesized novel [O,O] acetoacetamide ligands and corresponding nickel complexes, and studied their catalytic properties toward norbornene polymerization. The influence of polymerization parameters such as polymerization temperature and Al/Ni molar ratio on norbornene polymerization with acetoacetamide nickel catalysts was examined in detail. More importantly, remote steric and electronic effects on catalytic activity and molecular weight of the produced polymer were observed, which provides visible access to facilely tuning steric and electronic effects of [O,O] acetylacetone type ligand.

Experimental

All manipulations involving air- and moisture-sensitive compounds were carried out under an atmosphere of dried and purified nitrogen with standard vacuum line, Schlenk or glovebox techniques.

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Materials

Toluene, THF and hexane were dried over sodium metal and distilled under nitrogen. Dichloromethane and chlorobenzene were dried and distilled from calcium hydride. Ethyl acetoacetate was purchased from Alfa Aesar. 2,6-Diisopropylaniline (90%; Aldrich) and 2,6-dimethylaniline (97%; Aldrich) were distilled prior to use. Norbornene (bicyclo-[2.2.1]hept-2-ene; Acros) was purified by distillation over potassium and used as a solution in chlorobenzene. Modified methylaluminoxane (MMAO; 7 wt% Al in heptane) was purchased from Akzo-Nobel and used as received. (η^1-CH_2Ph)$NiCl(PMe_3)_2$ was synthesized according to a previous method.[40] Other commercially available reagents were purchased and used without purification.

Norbornene Polymerization

In a typical procedure, the appropriate MMAO solution was introduced into a chlorobenzene solution of norbornene in a 50 ml round-bottom glass flask. Chlorobenzene and nickel complex solution were syringed into the well-stirred solution in order, and the total reaction volume was kept at 25 ml. The reaction was continuously stirred for 20 min at polymerization temperature. Polymerization was terminated by addition of acidic methanol (methanol–HCl, 90:10). The resulting precipitated polymer was collected and treated by filtering, washing with methanol several times and drying under vacuum at 60 °C to constant weight.

Characterization

Elemental analyses were performed on a Vario EL microanalyzer. Electron impact (EI) mass spectra were obtained with a Shimazu LCMS-2010A instrument. ^1H, ^{13}C and ^{31}P NMR spectra of ligands and complexes were obtained using a Bruker 400 MHz instrument at room temperature in $CDCl_3$ or benzene-d_6. ^1H NMR and ^{13}C NMR spectra of PNBs in *o*-dichlorobenzene-d_4 were recorded on a Bruker 500 MHz spectrometer. Analysis by gel permeation chromatography (GPC) of the molecular weight and molecular weight distribution (MWD) of the PNBs was performed using a PL-GPC 220 instrument with standard polystyrene as the reference and with 1,2,4-trichlorobenzene (TCB) as the eluent at 150 °C. FT-IR spectra were recorded on a Nicolet Nexus 670 FT-IR spectrometer. Differential scanning calorimetry (DSC) analysis was conducted with a PerkinElmer DCS-7 system. The DSC curve was recorded at a heating rate of 10 °C min^{-1}. The cooling rate was 10 °C min^{-1}. TGA data was measured with a TG-290C thermal analysis system instrument under a nitrogen atmosphere up to 600 °C with heating rate of 10 °C min^{-1}. A wide-angle X-ray diffraction (WAXD) curve of the polymer powder was obtained using a D/Max-IIIA powder X-ray diffractometer.

Crystal Structure Determination

Crystal data obtained with the ω-2θ scan mode were collected on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 293 K. The structure was solved using direct methods, while further refinements with full-matrix least squares on F^2 were obtained with the SHELXTL program package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in calculated positions with the displacement factors of the host carbon atoms.

Synthesis of Ligand

Acetoacetanilide ligands were prepared by condensation reaction of substituted anilines with ethyl acetoacetate by the microwave irradiation method. Ethyl acetoacetate (5.20 g), the desired amount of substituted amines (1.2 equiv.) and a catalytic amount of potassium *tert*-butoxide were added to the tube and the reaction was irradiated in a domestic microwave oven. After 1 h, the reaction mixture was cooled and triturated with ice-cold ether. The product separated was filtered, washed with small portions of ice-cold ether and dried. Purification by recrystallization from ethanol afforded a colorless or yellow crystalline solid. **L1**, **L2** and **L5** are known compounds and characterization data can be seen in the supporting information.

N-Phenyl acetoacetamide (**L1**)

4.46 g aniline was used in the reaction. Yield 5.88 g, 83%.

N-(2-Methylphenyl) acetoacetamide (**L2**)

5.14 g 2-methylaniline was used in the reaction. Yield 6.19 g, 81%.

N-(2,6-Dimethylphenyl) acetoacetamide (**L3**)

5.81 g 2,6-dimethylaniline was used in the reaction. Yield 6.48 g, 79%. IR (KBr): 3290 (N—H), 3062 (C—H, Ph), 1775 (C O amide), 1587 (C O) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz), δ (ppm): 9.12 (s, 1H, CO—NH), 7.16 (m, 1H, 4-H on Ph), 7.09 (m, 2H, 3,5-H on Ph), 3.65 (s, 2H, CH_2), 2.35 (s, 3H, CO—CH_3), 2.21 (s, 3H, Ph—CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz), δ (ppm): 205.3 (CH_3C O), 166.2 (HN—C O), 133.6 (1-C on Ph), 131.2 (2,6-C on Ph), 127.9 (3,5-C on Ph), 126.1 (4-C on Ph), 50.0 (CH_2), 31.3 (CH_3—CO), 18.6 (CH_3—Ph). EI-MS (*m/z*): 206 [M^+]. Anal. Calcd for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37; N, 6.82%. Found: C, 70.08; H, 7.25; N, 6.70%.

N-(2,6-Diisopropylphenyl) acetoacetamide (**L4**)

8.50 g 2,6-diisopropylaniline was used in the reaction. Yield 7.41 g, 71%. IR (KBr): 3298 (N—H), 3071 (C—H, Ph), 1780 (C O amide), 1562 (C O) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz), δ (ppm): 10.60 (s, 1H, CO—NH), 7.21–7.14 (m, 3H, Ph), 3.35 (s, 2H, CH_2), 3.16 (sp, *J* = 7.6 Hz, 2H, CH), 2.36 (s, 3H, CO—CH_3), 1.24–1.19 (d, *J* = 7.6 Hz 24H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz), δ (ppm): 205.4 (CH_3C O), 166.5 (HN—C O), 144.9 (2,6-C on Ph), 131.8 (1-C on Ph), 125.1 (4-C on Ph), 123. 6 (3,5-C on Ph), 50.4 (CH_2), 31.4 (CH_3—CO), 28.3 (CH), 23.5 (CH_3—Ph). EI-MS (*m/z*): 217 [M^+]. Anal. Calcd for $C_{16}H_{23}NO_2$: C, 73.53; H, 8.87; N, 5.36%. Found: C, 73.46; H, 8.76; N, 5.50%.

N-(4-Nitrophenyl) acetoacetamide (**L5**)

6.62 g 2-nitroaniline was used in the reaction. Yield 4.80 g, 54%.

Synthesis of nickel complex

Ligand was dissolved in 20 ml THF in a flame-dried Schlenk flask, and a desired amount of KH (1.1 equiv.) was added. After 4 h, the solution was obtained by filtration and (η^1-CH_2Ph)$NiCl(PMe_3)_2$ was added. The mixture was stirred at room temperature overnight, and the crude reaction mixture was followed by filtration to remove inorganic salt under nitrogen. The solution was evaporated to low volume under vacuum and then *n*-hexane (20:1) was added. Solvent was removed from the precipitate via cannula filtration, and the residual solid was washed with *n*-hexane (3 × 5 ml). Drying under vacuum afforded the desired nickel complex. The nickel complex was dissolved in hot hexane/toluene solvents and cooled in a freezer for several days to afford the product as brown crystals.

*Nickel complex **1***

The general procedure was employed with 0.885 g ligand **L1**, 0.22 g KH and 1.68 g $(\eta^1\text{-}CH_2Ph)NiCl(PMe_3)_2$ to afford 1.64 g (82%) of the desired complex **1**. ^{1}H NMR (C_6D_6, 400 MHz, 20 °C): 7.76 (d, $J = 8.0$ Hz, 2H, 2,6-H on Ph, major), 7.29–6.78 (m, 8H, Ph, major + minor), 5.30 (s, 1H, NH, minor), 5.01 (s, 1H, NH, minor), 4.64, (s, 1H, CH, major), 4.31(s, 1H, CH, major), 2.32 (s, 3H, CO—Me, major), 2.14 (s, 3H, CO—Me, minor), 1.70 (s, 2H, CH_2Ph, major), 1.58 (s, 2H, CH_2Ph, minor), 0.74 (d, $J = 8.0$ Hz, 9H, $P(Me)_3$, major), 0.43 (d, $J = 8.0$ Hz, 9H, $P(Me)_3$, minor). ^{31}P NMR (C_6D_6, 162 MHz, 20 °C): −72.1, −75.0. The ratio of *cis* to *trans* complex was ~1/1. EI-MS (*m/z*): 403, 402, 401, 325, 177. Anal. Calcd For $C_{20}H_{26}NNiO_2P$: C, 59.74; H, 6.52; N, 3.48%. Found: C, 59.60; H, 6.68; N, 3.50%.

*Nickel complex **2***

The general procedure was employed with 0.955 g ligand **L2**, 0.22 g KH and 1.68 g $(\eta^1\text{-}CH_2Ph)NiCl(PMe_3)_2$ to afford 1.66 g (80%) of the desired complex **2**. ^{1}H NMR (C_6D_6, 400 MHz, 20 °C): 7.75 (d, $J = 8.0$ Hz, 2H, 2,4-H on Ph, major), 7.30–6.80 (m, 6H, Ph, major + minor), 5.31 (s, 1H, NH, minor), 5.04 (s, 1H, NH, minor), 4.72, (s, 1H, CH, major), 4.40 (s, 1H, CH, major), 2.26 (s, 3H, CO—Me, major), 2.18 (s, 3H, CH_3Ph, minor), 2.10 (s, 3H, CO—Me, minor), 1.96 (s, 3H, CH_3Ph, major), 1.73 (s, 2H, CH_2Ph, major), 1.60 (s, 2H, CH_2Ph, minor), 0.75 (d, $J = 8.0$ Hz, 9H, $P(Me)_3$, major), 0.42 (d, $J = 8.0$ Hz, 9H, $P(Me)_3$, minor). ^{31}P NMR (C_6D_6, 162 MHz, 20 °C): −72.0, −74.9. The ratio of *cis* to *trans* complex was ~5/4. EI-MS (*m/z*): 418, 417, 416, 340, 191. Anal. Calcd for $C_{21}H_{29}NNiO_2P$: C, 60.47; H, 7.01; N, 3.36%. Found: C, 60.72; H, 7.25; N, 3.28%.

*Nickel complex **3***

The general procedure was employed with 1.03 g ligand **L3**, 0.22 g KH and 1.68 g $(\eta^1\text{-}CH_2Ph)NiCl(PMe_3)_2$ to afford 1.69 g (79%) of the desired complex **3**. ^{1}H NMR (C_6D_6, 400 MHz, 20 °C): 7.74 (d, $J = 8.0$ Hz, 2H, 3,5-H on Ph, major), 7.31–6.82 (m, 4H, Ph, major + minor), 5.33 (s, 1H, NH, minor), 5.06 (s, 1H, NH, minor), 4.83, (s, 1H, CH, major), 4.52 (s, 1H, CH, major), 2.18 (s, 3H, CO—Me, major), 2.10 (s, 6H, CH_3Ph, minor), 2.04 (s, 3H, CO—Me, minor), 1.94 (s, 6H, CH_3Ph, major), 1.75 (s, 2H, CH_2Ph, major), 1.62 (s, 2H, CH_2Ph, minor), 0.75 (d, $J = 8.0$ Hz, 9H, $P(Me)_3$, major), 0.41 (d, $J = 8.0$ Hz, 9H, $P(Me)_3$, minor). ^{31}P NMR (C_6D_6, 162 MHz, 20 °C): −72.0, −74.8. The ratio of *cis* to *trans* complex was ~3/2. EI-MS (*m/z*): 431, 430, 429, 354, 205. Anal. Calcd for $C_{22}H_{30}NNiO_2P$: C, 61.43; H, 7.03; N, 3.26%. Found: C, 61.64; H, 7.14; N, 3.19%.

*Nickel complex **4***

The general procedure was employed with 1.08 g ligand **L4**, 0.22 g KH and 1.68 g $(\eta^1\text{-}CH_2Ph)NiCl(PMe_3)_2$ to afford 1.65 g (68%) of the desired complex **4**. ^{1}H NMR (C_6D_6, 400 MHz, 20 °C): 7.72 (d, $J = 8.0$ Hz, 2H, 3,5-H on Ph, major), 7.35–6.86 (m, 6H, Ph, major + minor), 5.65 (s, 1H, NH, major), 5.37 (s, 1H, NH, minor), 5.03, (s, 1H, CH, major), 4.61 (s, 1H, CH, minor), 3.25 (sp, $J = 7.6$ Hz, 2H, $CH(Me_3)_2$, major), 2.93 (sp, $J = 7.6$ Hz, 2H, $CH(Me_3)_2$, minor), 2.04 (s, 3H, CO—Me, major), 1.77 (s, 2H, CH_2Ph, major), 1.64 (s, 2H, CH_2Ph, minor), 1.45 (s, 3H, CO—Me, minor), 1.16–1.02 (m, 12H, $CH(CH_3)_2$ major + minor), 0.75 (d, $J = 8.0$ Hz, 9H, $P(Me)_3$, major), 0.41 (d, $J = 8.0$ Hz, 9H, $P(Me)_3$, minor). ^{31}P NMR (C_6D_6, 162 MHz, 20 °C): −71.8, −74.6. The ratio of *cis* to *trans* complex was ~2/1. EI-MS (*m/z*): 487, 486, 485, 409, 261. Anal. Calcd for $C_{26}H_{38}NNiO_2P$: C, 64.22; H, 7.88; N, 2.88%. Found: C, 64.54; H, 7.94; N, 3.03%.

*Nickel complex **5***

The general procedure was employed with 1.11 g ligand **L5**, 0.22 g KH and 1.68 g $(\eta^1\text{-}CH_2Ph)NiCl(PMe_3)_2$ to afford 0.96 g (52%) of the desired complex **5**. ^{1}H NMR (C_6D_6, 400 MHz, 20 °C): 7.80 (d, $J = 8.0$ Hz, 2H, 2,6-H on Ph, major), 7.26–6.74 (m, 8H, Ph, major + minor), 5.38 (s, 1H, NH, minor), 5.12 (s, 1H, NH, minor), 5.09, (s, 1H, CH, major), 4.72(s, 1H, CH, major), 4.36 (s, 1H, CH, major), 2.40 (s, 3H, CO—Me, major), 2.32 (s, 3H, CO—Me, minor), 1.86 (s, 2H, CH_2Ph, major), 1.72 (s, 2H, CH_2Ph, minor), 0.80 (d, $J = 8.0$ Hz, 9H, $P(Me)_3$, major), 0.51 (d, $J = 8.0$ Hz, 9H, $P(Me)_3$, minor).^{31}P NMR (C_6D_6, 162 MHz, 20 °C): −72.5, −75.7. The ratio of *cis* to *trans* complex is ~1/1. EI-MS (*m/z*): 449, 448, 447, 371, 222. Anal. Calcd for $C_{20}H_{26}N_2NiO_4P$: C, 53.61; H, 5.85; N, 6.25%. Found: C, 53.17; H, 5.93; N, 6.48%.

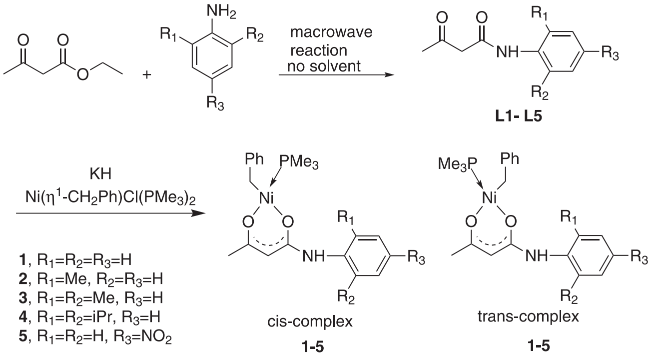
Results and Discussion

Synthesis of Nickel Complex and Molecular Structure

Previously, acetoacetanilide ligands have been synthesized by conventional methods under the condition of reflux of solvent.[41–43] Herein, the microwave irradiation method without any solvents was used to prepare the target product. The reaction was performed in a microwave oven for 1 h. In comparison with the conventional method, there are many virtues of microwave irradiation reaction, including no solvent, high isolated yield, short time and easy work-up. Two new acetoacetanilide ligands **L2** and **L3** were synthesized by the microwave irradiation method, but **L1**, **L4** and **L5** compounds were reported previously. The structures of ligand **L1**, **L4** and **L5** were confirmed by comparing their ^{1}H and ^{13}C NMR with those found in the literature.[41–43] Ligands **L2** and **L3** were fully characterized by FT-IR, ^{1}H and ^{13}C NMR, EI-MS and elemental analysis (EA).

After the obtained ligands were treated with KH in THF, $(\eta^1\text{-}CH_2Ph)NiCl(PMe_3)_2$ was added to the solution and corresponding nickel complexes were obtained in good yields (Scheme 1). New nickel complexes bearing acetoacetamide ligands were characterized by EA and NMR. Note that two isomers of nickel complexes are present in solution on the basis of two sets of resonances in ^{1}H NMR spectroscopy (see Experimental section), which is a result of the orientation of the η^1-benzyl and phosphine ligands. The ^{31}P NMR spectrum also revealed two PMe_3 signals, which further supports the presence of *cis* and *trans* isomers in solution (Scheme 1).[40] A clear tendency is that the ratio of *cis* isomer to *trans* isomer increases (1/1, 5/4, 3/2, 2/1) with an increase in the steric hindrance of the aniline moiety from H atoms to 2,6-diisopropyl groups (**1** to **4**), which may be attributed to a steric effect. However, introduction of an electron-withdrawing nitro group on the aryl ring has no influence on the ratio of *cis* isomer to *trans* isomer in solution.

A crystal of complex **3** suitable for X-ray diffraction analysis was obtained by slow diffusion of *n*-hexane into nickel complex solution in CH_2Cl_2. The molecular structure of the nickel complex supports the *O,O*-bound connectivity pattern deduced from NMR analysis in solution. Data collection and refinement data are summarized in Table 1. The ORTEP diagram of complex **3** is shown in Fig. 1, along with selected bond lengths and bond angles. The nickel complex **3** adopts a slightly distorted



Scheme 1. Synthesis of acetoacetamide nickel complex.

Table 1. Crystal data and structure refinement for nickel complex **3**

Empirical formula	$C_{22}H_{30}NNiO_2P$
Formula weight	430.15
Crystal system	Tetragonal
Space group	*P*4(3)
a (Å)	12.4576(16)
b (Å)	12.4576(16)
c (Å)	14.424(4)
α (°)	90
β (°)	90
γ (°)	90
Volume (Å^3)	2238.5(7)
Z	4
D (calc.) (g cm^{-3})	1.276
F (000)	912
Crystal size (mm)	0.36 × 0.25 × 0.22
θ range (°)	2.16–26.75
Index ranges	$-15 \le h \le 15$ $-15 \le k \le 15$ $-17 \le l \le 18$
Reflections collected/unique	15 000/4539 [*R*(int) = 0.0223]
Data completeness	98.2 %
Data/restraints/parameters	4539/ 1/251
Goodness-of-fit on F^2	1.039
Final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.0263, *wR*2 = 0.0664
R indices (all data)	*R*1 = 0.0279, *wR*2 = 0.0677
Largest diff. peak and hole (e Å^{-3})	0.200, −0.184

square-planar coordination geometry around the nickel center with a *cis* relationship between PMe_3 group and the carboxamide oxygen. Because of the conjugate effect of the acetoacetate ring, the two bond lengths of O—Ni are similar (Ni—O1, 1.9090 Å; Ni-O2, 1.9042 Å). The PMe_3 ligand is tilted 11.3° out of the six-membered chelate plane, while the benzyl group is tilted 9.3° out of the chelate ring.

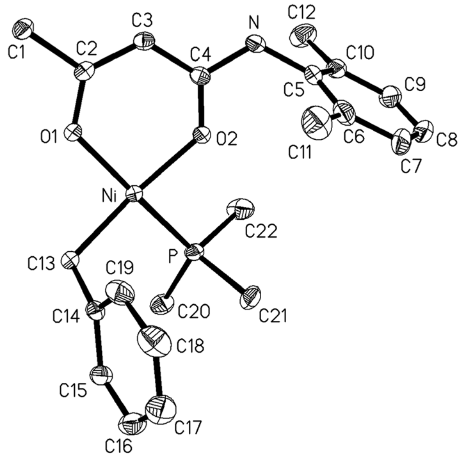


Figure 1. ORTEP plots of complex **3**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Ni—O(1), 1.9090(14); Ni—O(2), 1.9042(15); Ni—C(13), 1.957(2); Ni—P, 2.1467(7); O(1)—Ni—O(2), 92.97(6); O(1)—Ni—C(13), 88.72(8); O(2)—Ni—C(13), 169.87(9); O(1)—Ni—P, 169.94(5); O(2)—Ni—P, 87.02(5); C(13)—Ni—P, 93.05(7).

Table 2. Norbornene polymerizations with nickel complexes **1–5**/MMAO under various conditions[a]

Entry	Catalyst	T_p (°C)	Al/Ni (mol/mol)	Activity[b]	M_n[c]	M_w/M_n
1	**1**	0	2500	8.9	384	2.62
2	**1**	25	2500	14.3	432	2.36
3	**1**	50	2500	26.2	315	2.14
4	**1**	75	2500	23.1	257	2.53
5	**2**	50	2500	32.8	362	2.12
6	**3**	0	2500	9.6	438	2.54
7	**3**	25	2500	25.3	526	2.28
8	**3**	50	2500	45.6	401	2.09
9	**3**	75	2500	38.5	287	2.46
10	**4**	0	2500	12.2	471	2.43
11	**4**	25	2500	34.7	683	2.26
12	**4**	50	2500	68.1	506	2.06
13	**4**	75	2500	52.4	348	2.39
14	**4**	50	500	21.0	495	1.94
15	**4**	50	1500	54.1	585	2.04
16	**4**	50	3500	48.9	257	3.78
17	**5**	50	2500	43.9	388	2.44

[a] Polymerization conditions: reaction time, $t = 20$ min; Ni catalyst addition, 1 μmol; co-catalyst, MMAO; norbornene addition, 4 g; solvent, 25 ml chlorobenzene.

[b] In units of 10^6 g PNB (mol Ni h)$^{-1}$.

[c] In units of kg mol^{-1}, determined by high-temperature GPC.

Norbornene Polymerization

A series of norbornene polymerizations were carried out using acetoacetamide nickel catalyst precursors **1**, **2**, **3**, **4** and **5** under various conditions (Table 2). In the presence of MMAO, five nickel complexes **1–5** exhibited very high activities for norbornene polymerization. Figure 2 demonstrates that a remote steric characteristic of the acetoacetamide ligand plays an important role in the catalytic performances. Under the same polymerization conditions, complex **4** with *N*-2,6-diisopropylphenyl groups shows the highest activity, up to 68.1×10^6 g PNB (mol Ni h)$^{-1}$, while complex **1** with *N*-phenyl groups exhibits the lowest activity. This result clearly supports a positive steric effect on catalytic activity for norbornene polymerization, although the bulky substituent on the *N*-aryl moiety is remote from the nickel center. Compared with **1**, electron-deficient complex **5** with NO_2 can exhibit a higher catalytic activity for norbornene polymerization. This result shows that a remote electronic effect can also work on the nickel active center for norbornene polymerization. Currently, [O,O] ligands are rarely used to coordinate nickel for olefin polymerization because this type of ligand is hardly modified from steric and electronic effects. Our study herein provides a visible access to tuning steric and electronic effects of [O,O] acetylacetone type ligand by a remote effect. Besides, the steric characteristic of the chelate ligand has the same tendency to influence the molecular weight of the obtained PNB (Fig. 2). The highest molecular weight of the produced polymer is achieved using complex **4**/MMAO catalytic system under the same conditions, suggesting that a remote effect can suppress the occurrence of chain transfer/termination.

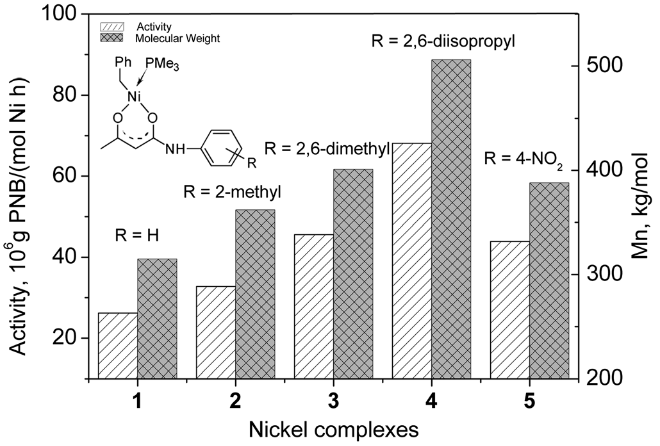


Figure 2. Influence of catalyst structure on norbornene polymerization with nickel complexes **1–5**/MMAO. Polymerization conditions: catalyst addition, 1 μmol; Al/Ni = 2500; polymerization temperature, 50 °C; reaction time, *t* = 20 min; norbornene addition, 4 g; solvent, 25 ml chlorobenzene.

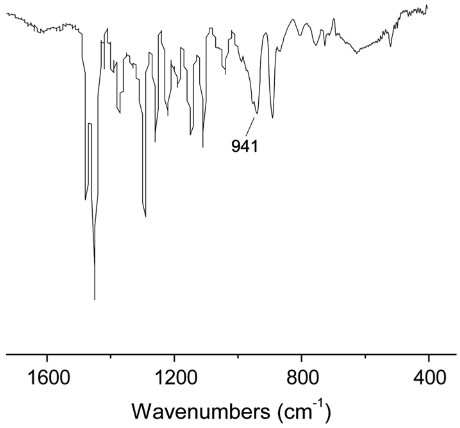


Figure 3. FT-IR spectrum of PNB (entry 12).

The reaction temperature also strongly affects catalytic activity, and the results of norbornene polymerizations using **1**, **3**, **4**/MMAO at various temperatures are summarized in Table 2. For **1**, **3** and **4**/MMAO catalytic systems, the lowest catalytic activities are observed when the reaction temperature is 0 °C. With an increase in reaction temperature, the catalytic activity obviously increases. Three nickel complexes show the highest activity for norbornene polymerization at 50 °C. A higher temperature (75 °C) causes a decrease in the catalytic activity for norbornene polymerization because of the instability or decomposition of the active species. Therefore, the optimum polymerization temperature is 50 °C. The polymerization temperature also affects the molecular weights of the obtained polymers. A basic tendency is observed for the M_n value of the obtained polymer to increase, and then decrease with an increase in the reaction temperature. When polymerizations are carried out at 25 °C, the highest molecular weights of the obtained PNB are observed. Further increasing the temperature to 75 °C leads to decreasing molecular weight, suggesting that chain transfer or termination begins to accelerate above 25 °C.

Influence of Al/Ni molar ratio is typically investigated using the **4**/MMAO catalytic system at a fixed temperature of 50 °C, and the results are summarized in Table 2 (entries 12 and 14–16). When the Al/Ni molar ratio is 500, a low activity for norbornene polymerization is observed. With an increase in Al/Ni molar ratio from 500 to 3500, the catalytic activity for norbornene polymerization increases and then decreases. An optimum Al/Ni molar ratio is 2500 for **4**/MMAO catalytic systems. Moreover, Al/Ni molar ratio also influences the molecular weight of the obtained PNB. With an increase in Al/Ni molar ratio, the molecular weight of PNB increases and then decreases. When the Al/Ni molar ratio is 1500, the highest molecular weight is observed. This result suggests that excess MMAO (Al/Ni > 1500) gives rise to easy chain transfer.

Polynorbornene Characterizations

All of the obtained PNBs catalyzed by acetoacetamide nickel catalytic systems are soluble in organic solvents such as chlorobenzene, 1,2-dichlorobenzene and 1,2,4-trichlorobenzene, which is consistent with previous observations.[18,19,21] The FT-IR spectrum of PNB (Fig. 3) clearly shows no traces of double bond, which is present at 1680–1620, 966 and 735 cm^{-1}. A vibration band of bicyclics of the norbornene unit is clearly observed at 941 cm^{-1}, proving that the obtained PNB is a vinyl-addition polymer.

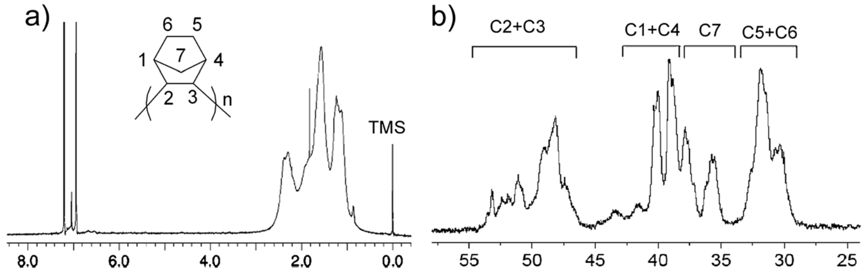


Figure 4. ^{1}H and ^{13}C NMR spectra of PNB (entry 12).

As showed in Fig. 4(a), the ^{1}H NMR spectrum of PNB is in a range of chemical shift from 0.5 to 3.0 ppm, and no traces of any double bond at 5.0–7.0 ppm are observed. The absence of double bond further supports the occurrence of vinyl-type polymerization rather than ring-opening metathesis polymerization. The ^{13}C NMR spectrum (Fig. 4b) also further confirms that the obtained polymers are vinyl-type PNB. Several signals are observed from 25 to 55 ppm. According to previous assignment of the PNB,[18,19,21,27] the resonances of methenes and methines appear at 28.5–33.0 ppm for C5 and C6, 35.0–38.0 ppm for C7, 38.5–42.5 ppm for C1 and C4, and 45.5–55.0 ppm for C2 and C3.

The DSC spectrum of the PNB cannot show well-defined endothermic signals upon heating to the decomposition temperature, and no glass transition temperature (T_g) of PNB from DSC curve is observed. The TGA curve shows that the PNB sample is stable up to 450 °C (see supporting information). The WAXD analysis of the obtained PNB shows two major broad peaks ($2\theta = 9–11°$ and 17–19°), which implies that the obtained PNB is non-crystalline (see supporting information).

Conclusions

In summary, a series of acetoacetamide nickel complexes has been successfully synthesized and characterized. The solid structure of complex **3** is confirmed by X-ray single-crystal analysis to be a *cis* form, while there are two isomers in solution. Acetoacetamide nickel complexes activated by MMAO are highly active toward norbornene polymerization. Obvious steric and electronic effects of acetoacetamide ligand on catalytic activity and molecular weight for norbornene polymerization can be observed, although substituents on the *N*-aryl moiety are remote from the nickel center. Our study provides a visible access to tuning steric and electronic effects of [O,O] acetylacetone type ligand by a remote effect.

Acknowledgments

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Supporting Information

Additional supporting information may be found in the online version of this article at the publisher's web site.

Appendix

CCDC 948848 contains the supplementary crystallographic data for complex **3**. The data can be obtained free of charge via http://www.ccdc.cam.ac.uk, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.