Polymerization of methyl methacrylate catalyzed by nickel complexes with hydroxyindanone-imine ligands†

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A series of new hydroxyindanone-imine ligands [PhN=$CC_2H_3(CH_3)C_6H_2(CH_3)OH$] (**HL$_1$**) and [ArN=$CC_2H_3(CH_3)C_6H_2(R)OH$] (Ar = 2,6-*i*-$Pr_2C_6H_3$, R = Me (**HL$_2$**), R = H (**HL$_3$**), and R = Cl (**HL$_4$**)) were synthesized and characterized. Reactions of hydroxyindanone-imines with $Ni(OAc)_2 \cdot 4H_2O$ result in the formation of the trinuclear hexa(indanone-iminato)tri(nickel(II)) complex Ni_3[PhN=$CC_2H_3(CH_3)C_6H_2(CH_3)O]_6$ (**1**) and the mononuclear bis(indanone-iminato)nickel(II) complexes Ni[ArN=$CC_2H_3(CH_3)C_6H_2(R)O]_2$ (Ar = 2,6-*i*-$Pr_2C_6H_3$, R = Me (**2**), R = H (**3**), and R = Cl (**4**)). All nickel complexes were characterized by their IR, NMR spectra and elemental analyses. In addition, X-ray structure analyses were performed for complexes **1** and **2**. After being activated with methylaluminoxane (MAO), these nickel(II) complexes can be used as catalysts for the polymerization of methyl methacrylate (MMA) to produce syndiotactic-rich PMMA. Catalytic activities and the degree of syndiotacticity of PMMA have been investigated for various reaction conditions.

Introduction

Stereospecific polymerization of methyl methacrylate (MMA) has attracted increasing attention from both academia and industry. Noteworthy successes in this regard included the discoveries by Yasuda *et al.*[1] and Collins and Ward[2] that lanthanocenes[3] and zirconocenes[4] were efficient initiators for the controlled polymerization of MMA, providing isotactic or syndiotactic PMMA based on the ligand structures.

Late transition metal complexes are generally considered to be more tolerant toward polar functional monomers due to their less oxophilic nature relative to early transition metal complexes, and make them likely targets for the development of catalysts for the polymerization of the polar monomers including MMA.[5] Nevertheless, there are few reports on stereospecific polymerization of MMA catalyzed by late transition metal complexes with methylaluminoxane (MAO) systems. The $Ni(acac)_2$/MAO catalyst system was first found to be an effective catalyst for the polymerization of MMA.[6] A series of nickelocene complexes evidenced good activity in the polymerization of MMA with syndiotactic-rich PMMA.[7] Carlini *et al.*[8] reported the polymerization of MMA catalyzed by nickel complexes based on salicylaldimine ligands, which provided syndiotactic-rich PMMA with high molecular weight and broad polydispersity index. Kim *et al.*[9] reported that late transition metal complexes such as (α-diimine)nickel, (pyridyl bisimine)iron(II) and (pyridyl bisimine)cobalt(II), which were widely used for the olefin polymerization,[10] polymerized MMA in combination with MAO to give syndiotactic-rich PMMA. Wu and co-workers[11] reported bis(β-ketiminato)nickel complexes could polymerize MMA to give syndiotactic-rich PMMA with relatively wide molecular weight distribution activated with MAO. Recently several reports had also appeared claiming coordination polymerization of MMA based on copper(II) complexes.[12]

Our group have designed and synthesized a number of the early transition metal and late transition metal complexes based on [O, N], [N, N], [C, N] and [N, P] ligands for polymerization of ethylene and norbornene.[13] Herein, we reported the synthesis of a series of nickel(II) complexes bearing hydroxyindanone-imine ligands. After activation with MAO, those nickel(II) complexes can be used as catalysts for the polymerization of MMA, providing the syndiotactic-rich PMMA.

Results and discussion

Synthesis of ligands HL$_1$–HL$_4$ and complexes 1–4

The hydroxyindanone-imine ligands **HL$_1$–HL$_4$** can be obtained by the condensation reaction of the corresponding hydroxyindanone with aniline or 2,6-diisopropylaniline. According to a modified method,[14] ligand **HL$_1$** without substituted groups on aniline can be obtained in 80% yield by the condensation of corresponding hydroxyindanone with aniline in ethanol using formic acid as a catalyst, and ligands **HL$_2$–HL$_4$** were synthesized in about 40% yield by the Schiff base condensation of the corresponding hydroxyindanone with 2,6-diisopropylaniline in toluene using $TiCl_4$ as a Lewis acid catalyst (Scheme 1).

Like the procedure of preparing bis(salicylaldiminato) nickel(II) complexes,[15] nickel complexes **1–4** were prepared by the reaction of $Ni(OAc)_2 \cdot 4H_2O$ with two equivalents of the corresponding hydroxyindanone-imine. Green trinuclear nickel complex **1** was synthesized from ligand **HL$_1$**, while brown mononuclear nickel complexes **2–4** were synthesized from ligands **HL$_2$–HL$_4$** (Scheme 1). This is due to the steric hindrance of substituted groups at the 2- and the 6-position of aniline. All complexes are stable in dry air. They are readily soluble in dichloromethane, toluene and THF, but sparingly soluble in ethanol and methanol.

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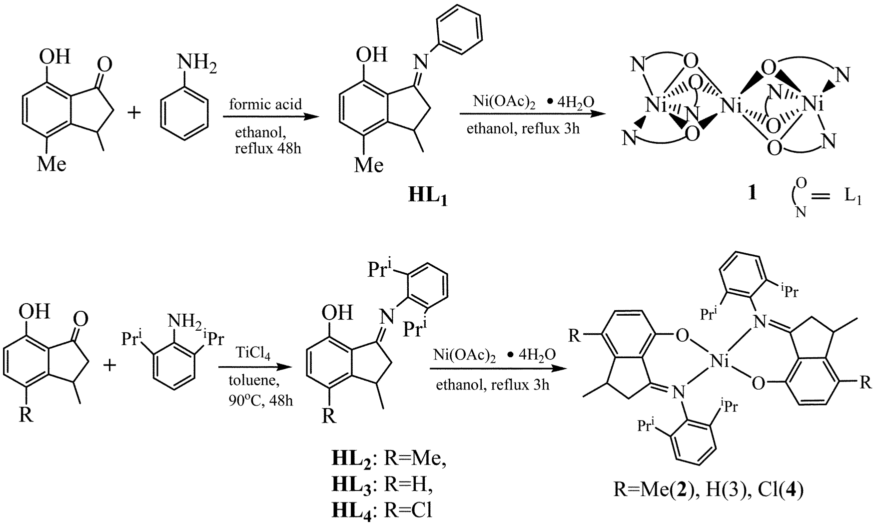

Scheme 1 The synthesis of ligands HL_1–HL_4 and complexes **1–4**.

The trinuclear complex **1** is paramagnetic, while mononuclear complexes **2–4** are diamagnetic. The ^1H NMR spectra of complexes **2–4** show signals at δ 5.3–5.4 ppm (δ 5.35 (**2**), 5.41 (**3**), 5.34 ppm(**4**)) assigned to the phenoxy C_2–H signals, while the C_2–H signals of the ligands $\mathbf{HL_2}$–$\mathbf{HL_4}$ were found at about δ 6.8 ppm (δ 6.77 ($\mathbf{HL_2}$), 6.84 ($\mathbf{HL_3}$), 6.82 ppm($\mathbf{HL_4}$)). The shift to high field results from the ring current, formed by the delocalized π electrons of the phenyl of *N*-aryl system to other hydroxyindanone-imine moiety. Compared to bis(indaniminato)-nickel(II) complexes, the signals of aromatic protons of bis[(*N*-2,6-diisopropylphenyl)salicylaldiminate] nickel(II) complex ranged between δ 6.9 and 7.3 ppm,[16] which indicates no presence of any ring current.

X-Ray single crystal structures of complexes 1 and 2

Crystals suitable for X-ray crystallography of **1** was obtained by slow diffusion of ethanol into a dichloromethane solution of complex **1**. The crystallographic data and processing parameters are given in Table 1. The ORTEP diagram of **1** is presented in Fig. 1. The X-ray structure analysis clearly indicates that complex **1** is octahedral and trimeric, the two terminal nickel atoms (Ni(2) and Ni(2A)) are symmetrical. The molecular structure shows the six-coordinate geometry about every nickel atom, in which each terminal nickel atom is tri-chelated and the central one is not part of any chelate ring, with six oxygen donor atoms only. The Ni–O distances vary from 2.053(4) to 2.075(4) Å, the mean distance of Ni(1)–O is similar to that of Ni(2)–O (2.0607(4) and 2.0597(4) Å, respectively). The Ni(2)–N distances vary from 2.108 to 2.127 Å. The Ni(1)–Ni(2) and Ni(1)–Ni(2A) distances are 2.8258(9) and 2.8257(9) Å, respectively. The Ni–Ni distance is shorter than the sum of the nickel(II) atomic van der Waals radii, 3.3 Å, at which point the chemical interaction may be considered to be insignificant.[17] It indicates that there is direct chemical Ni-Ni interactions in the structure of complex **1**. The Ni(2)–Ni(1)–Ni(2A) angle is 175.57 (6)°. The trimeric nickel complex **1** is an approximately linear Ni_3 cluster.

Crystals of **2** suitable for X-ray crystallography were obtained by slow diffusion of ethanol into a toluene solution of complex **2**. The crystallographic data and processing parameters are given in Table 1. For complex **2**, there are two independent molecules in the crystal cell, and the nickel atoms Ni(1) and Ni(2) lie on independent inversion centers. The ORTEP diagram of one of two molecules of complex **2** is shown in Fig. 2. Each nickel coordinates the two ligands in a planar fashion with a *trans*-N_2O_2 arrangement of the donor atoms. The *N*-2,6-diisopropylphenyl groups are also roughly perpendicular to the remainder of the ligand L, making an angle of 93.6° With the hydroxyindanone-imine residues. The Ni(1)–O (1.837(3) Å) and Ni(1)–N (1.926(3)Å) distances are slightly longer than those

Table 1 Crystallographic data and structure refinement details for **1** and **2**

Complex	1	2
Formula	$C_{102}H_{96}N_6Ni_3O_6$	$C_{46}H_{56}N_2NiO_2$
F_w	1677.98	727.64
T/K	293(2)	293(2)
Crystal system	Trigonal	Triclinic
Space group	*P*3(1)21	*P*-1
Crystal size/mm^3	0.40 × 0.40 × 0.30	0.20 × 0.15 × 0.10
a/Å	22.826(4)	9.878(4)
b/Å	22.826(4)	11.226(5)
c/Å	17.511(4)	19.901(9)
α/°	90	79.860(7)
β/°	90	78.497(7)
γ/°	120	72.554(6)
V/Å^3	7901(2)	2047.0(15)
Z	3	2
ρ_{calcd}/g cm^{-3}	1.058	1.181
μ/mm^{-1}	0.579	0.512
θ range/°	1.03–25.01	1.05–25.01
Reflections collected	33593	8640
Independent reflections	9289	7129
R_{int}	0.1222	0.0991
GOF on F^2	0.818	0.861
R_1	0.0522	0.0692
wR_2	0.1370	0.1783
Absolute structure parameter	−0.01(2)	—

$R_1 = \Sigma(||F_o|-|F_c||)/\Sigma|F_o|$, $wR_2 = [\Sigma(|F_o|^2 - |F_c|^2)^2/\Sigma(F_o^2)]^{1/2}$.

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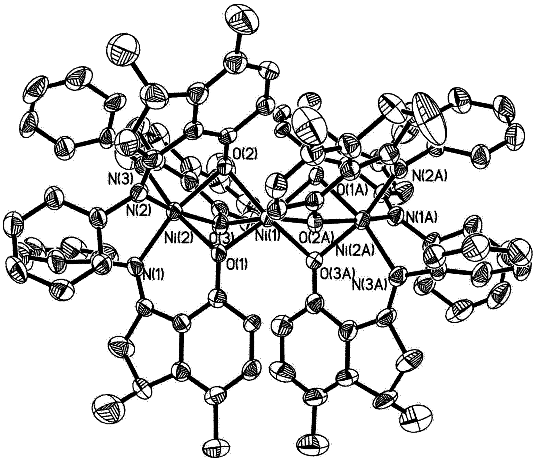

Fig. 1 Molecular structure of complex **1** with 30% probability (the hydrogen atoms are omitted for clarity). The additional "A" letter indicates the symmetry operation ($-x + 2$, $-x + y + 1$, $-z + 7/3$). Selected bond lengths (Å) and angles (°): Ni(1)–O(1) 2.054(4), Ni(1)–O(2) 2.053(4), Ni(1)–O(3) 2.075(4), Ni(2)–O(1) 2.056(4), Ni(2)–O(2) 2.055(4), Ni(2)–O(3) 2.068(4), Ni(2)–N(1) 2.119(5), Ni(2)–N(2) 2.127(5), Ni(2)–N(3) 2.108(5), Ni(1)–Ni(2) 2.8258(9), Ni(1)–Ni(2A) 2.8257(9); O(1)–Ni(1)–O(2) 79.07(15), O(1)–Ni(1)–O(3) 77.45(16), O(1)–Ni(1)–O(1A) 168.4(3), O(1)–Ni(1)–O(2A) 93.96(15), (1)–Ni(1)–O(3A) 110.36(17), O(2)–Ni(1)–O(3) 77.76(16), O(2)–Ni(1)–O(2A) 106.9(2), (2)–Ni(1)–O(3A) 169.48(16), O(3)–Ni(1)–O(3A) 99.3(2), O(1)–Ni(2)–N(1) 90.34(19), O(2)–Ni(2)–O(2) 89.2(2), O(3)–Ni(2)–N(3) 91.3(2) and Ni(2)–Ni(1)–Ni(2A) 175.57(6).

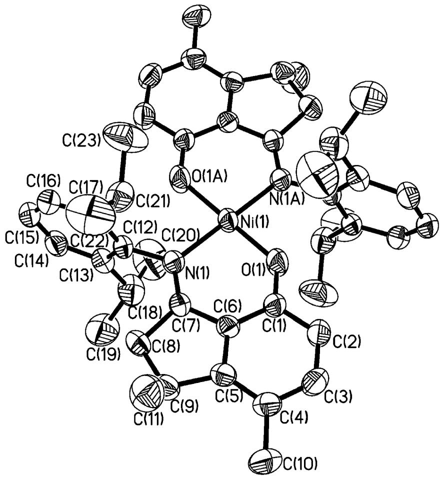

Fig. 2 Molecular structure of complex **2** with 30% probability (the hydrogen atoms are omitted for clarity). The additional "A" letter indicates the symmetry operation ($-x+1$, $-y+1$, $-z+1$). Selected bond lengths (Å) and angles (°): Ni(1)–O(1) 1.837(3), Ni(1)–N(1) 1.926(3); O(1)–Ni(1)–N(1) 94.74(13), O(1)–Ni(1)–N(1A) 85.26(13), N(1)–C(7)–C(6) 125.1(4).

(1.8285(9) Å and 1.9087(11) Å, respectively) found in the bis[(*N*-2,6-diisopropylphenyl)salicylaldiminate]nickel(II) complex.[16] The O(1)–Ni(1)–N(1) angle (94.74(13)°) is bigger than the angle of 93.03(4)° for the bis[(*N*-2,6-diisopropylphenyl) salicylaldiminate]nickel(II) complex.[16] The N(1)–C(7)–C(6) angle (125.1(4)°) is smaller than the angle (126.27(12)°) found in the bis[(*N*-2,6-diisopropylphenyl) salicylaldiminate]nickel(II) complex, which indicates the orientation of nitrogen atom in the space is limited due to the presence of five-membered ring. It indicates that the structures of nickel complexes with hydroxyindanone-imine ligands are very different from those of nickel complexes with salicylaldimine ligands with the introduction of the five-membered ring.

Polymerization of methyl methacrylate (MMA)

Prior to this study, an attempt to polymerize MMA by using the nickel complexes **1–4** or MAO alone was made. Due to the reaction conditions, no polymer was obtained in any of these cases. This result showed that MAO is indispensable for the activation of the nickel complexes **1–4** for MMA polymerization.

Table 2 shows polymerization results using Ni(II) complexes **1–4** activated with MAO. After activation with MAO, all Ni (II) complexes can catalyze the polymerization of MMA to produce syndiotactic-rich PMMA with high activities. The results suggest that the structure of the complex has a significant affect on the activity, stereotacticity, molecular weight and molecular weight distribution. At the same polymerization conditions, the trinuclear complex **1** showed the lowest activity, while the mononuclear complex **2** showed the highest activity of 4.25 × 10^4 g PMMA mol^{-1} Ni h^{-1} (Table 2, run 2). All complexes produced a polymer with a rather high degree of syndiotacticity, and the highest degree of syndiotacticity (*rr* triads up to 79.0%) was observed in PMMA produced by complex **3** (Table 2, run 3). All polymers obtained showed high number-average molecular weight ($M_n = 5.7$–10.6×10^4 g mol^{-1}) and relatively wide molecular weight distribution (M_w/M_n = 4.0–6.0). Taking into account that the viscosity of the medium gradually increased during polymerization, diffusion phenomena could be responsible for the wide molecular weight distribution.

The polymerization temperature also affects considerably the catalytic activities and molecular weight as well as molecular weight distribution (Table 3). For both complexes **1** and **2**, the catalytic activities first increased and then sharply decreased with increasing polymerization temperature, and the highest activity

Table 2 Polymerization of MMA with different nickel complexes[a]

Run	Catalyst	Yield/g	Activity[b]	%*mm*	%*mr*	%*rr*	M_n[c,d]	M_w/M_n[c]
1	**1**	0.54	2.70	9.1	22.1	68.8	5.7	4.8
2	**2**	0.85	4.25	3.1	27.7	69.2	10.6	4.0
3	**3**	0.78	3.90	1.9	19.1	79.0	6.5	5.1
4	**4**	0.61	3.05	4.6	20.5	74.9	7.2	6.0

[a] Polymerization conditions: Ni = 20 μmol, Al/Ni = 150, MMA = 18.6 mmol, toluene = 10 ml, T = 60 °C, time = 1 h. [b] 10^4 g PMMA mol^{-1} Ni h^{-1}. [c] Determined by GPC analysis. [d] 10^4 g mol^{-1}.

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Table 3 Influence of the polymerization temperature on the polymerization of MMA[a]

Run	Catalyst	T/°C	Yield/g	Activity[b]	%*mm*	%*mr*	%*rr*	M_n[c][d]	$M_\mathrm{w}/M_\mathrm{n}$[c]
1	**1**	20	0.094	0.47	9.4	31.4	59.2	1.5	4.1
2	**1**	60	0.54	2.70	9.1	22.1	68.8	5.7	4.8
3	**1**	90	0.21	1.05	5.2	25.7	69.1	2.9	5.0
4	**2**	20	0.24	1.20	5.0	27.7	67.3	2.8	10.0
5	**2**	60	0.85	4.25	3.1	27.7	69.2	10.6	4.0
6	**2**	90	0.34	1.70	6.9	26.5	66.6	4.3	6.0

[a] Polymerization conditions: Ni = 20 μmol, Al/Ni = 150, MMA = 18.6 mmol, toluene = 10 ml, time = 1 h. [b] 10^4 g PMMA mol^{-1} Ni h^{-1}. [c] Determined by GPC analysis. [d] 10^4 g mol^{-1}.

Table 4 Influence of Al/Ni on the polymerization of MMA[a]

Run	Catalyst	Al/Ni	Yield/g	Activity[b]	% *mm*	% *mr*	% *rr*	M_n[c][d]	$M_\mathrm{w}/M_\mathrm{n}$[c]
1	**2**	50	0.45	2.25	2.8	17.1	80.1	7.6	6.7
2	**2**	100	0.64	3.20	6.1	16.0	77.9	8.1	6.4
3	**2**	150	0.85	4.25	3.1	27.7	69.2	10.6	4.0
4	**3**	50	0.62	3.10	3.2	19.5	77.3	4.2	5.4
5	**3**	150	0.78	3.90	1.9	19.1	79.0	6.5	5.1

[a] Polymerization conditions: Ni = 20 μmol, MMA = 18.6 mmol, toluene = 10 ml, T = 60 °C, time = 1 h. [b] 10^4 g PMMA mol^{-1} Ni h^{-1}. [c] Determined by GPC analysis. [d] 10^4 g mol^{-1}.

values were achieved at 60 °C (Table 3, run 2 and 5). The number-average molecular weight obviously depended on the polymerization temperature. However, the degree of syndiotacticity showed slightly variation under different polymerization temperature.

For a binary catalyst system, the ratios of Al/Ni will influence the catalytic activities, stereotacticity, molecular weight and molecular weight distribution (Table 4). For both complexes **2** and **3**, when the Al/Ni ratio increased from 50 to 150, an improvement of both the activity and number-average molecular weight was observed, but a decrease in molecular weight distribution was observed. For complex **2**, the degree of syndiotacticity decreased with increasing the ratio of Al/Ni, the highest degree of syndiotacticity (*rr* = 80.1%) was obtained at the Al : Ni ratio of 50 : 1 (Table 4, run 1). For complex **3**, the varied trend of the degree of syndiotacticity was contrary to that of complex **2**.

To investigate the catalytic lifetime of complex **2**, the polymerizations of MMA were conducted for 1, 2, 4, and 12 h. The relationship between the polymerization time and the polymer yield indicates that the **2**/MAO has a catalytic lifetime of about 2 h, as shown in Table 5. With increasing polymerization time, the degree of syndiotacticity first increases and then decreased.

In the above polymerization reactions (Tables 2–5), the nickel precursor was dissolved at room temperature in toluene, then MMA and MAO were added in that order (see Experimental). When MAO was allowed to react with complex **2** before the introduction of MMA, an improvement in the activity and degree of syndiotacticity was observed (Table 6, run 2). When the activation was performed under an ethylene atmosphere, the activity sharply increased up to 6.35 × 10^4 g PMMA mol^{-1} Ni h^{-1} (Table 2, run 2), agreed with the results reported by Carlini *et al.*[8] The activation effect caused by the presence of ethylene might be attributed to the fact that the olefin helps MAO to remove one chelate ligand from the metal nickel and at the same time stabilizes the resulting active species by coordination to the center metal nickel, increasing the concentration of active sites capable of polymerizing MMA.[8c] Finally, some polymerization reactions were performed by the amount of the nickel complex and/or MMA monomer being reduced to decrease the polymerization rates (Table 6, run 4–6). When both nickel complex and MMA monomer were reduced to 1/4, the polymerization reaction did not occur (Table 6, run 4). The decrease in activity was observed when reducing the nickel complex or MMA monomer by 75% (Table 6, run 5 and 6). However, the degree of syndiotacticity varied slightly.

Table 5 Influence of polymerization time on the polymerization of MMA catalyzed by complex **2**/MAO[a]

Run	Time/h	Yield/g	Activity[b]	% *mm*	% *mr*	% *rr*
1	1	0.85	4.25	3.1	27.7	69.2
2	2	0.96	2.40	3.4	23.2	73.4
3	4	0.98	1.22	5.2	17.3	77.5
4	12	1.02	0.42	5.8	22.8	71.4

[a] Polymerization conditions: Ni = 20 μmol, MMA = 18.6 mmol, toluene = 10 ml, T = 60 °C. [b] 0^4 g PMMA mol^{-1} Ni h^{-1}.

Table 6 Influence of other polymerization conditions on the polymerization of MMA catalyzed by complex **2**/MAO[a]

Run	Yield/g	Activity[b]	% *mm*	% *mr*	% *rr*
1	0.85	4.25	3.1	27.7	69.2
2[c]	0.91	4.55	11.9	15.0	73.1
3[d]	1.27	6.35	8.3	17.7	74.0
4[e]	0.0	—	—	—	—
5[f]	0.65	3.26	8.6	24.2	67.2
6[g]	0.25	1.25	4.3	23.1	72.6

[a] Polymerization conditions: Ni = 20 μmol, Al/Ni = 150, MMA = 18.6 mmol, toluene = 10 ml, T = 60 °C, time = 1 h. [b] 10^4 g PMMA mol^{-1} Ni h^{-1}. [c] The order is Ni, MAO, MMA. [d] The catalyst was prepared in the presence of an ethylene atmosphere. [e] Ni = 5.0 μmol, MMA = 4.65 mmol. [f] Ni = 5.0 μmol. [g] MMA = 4.65 mmol.

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Conclusion

In this report, a series of nickel(II) complexes containing hydroxyindanone-imine ligands were synthesized and characterized, which were air-stable. A combination of spectroscopic and X-ray crystallographic studies confirmed the structure of these nickel complexes. After activation with MAO, the resulting nickel(II) complexes can be used as catalysts for the polymerization of MMA to produce syndiotactic-rich PMMA. The degree of syndiotacticity and molecular weight of polymer can be controlled by the structure of nickel complexes and polymerization parameters including polymerization temperature and the ratio of Al/Ni.

Experimental

General procedures

All air-sensitive experiments were carried out under nitrogen using standard Schenk techniques. Toluene was dried over sodium/benzophenone and distilled under nitrogen prior to use. MMA was purified by drying from CaH_2 and distilling under vacuum. Methylaluminoxane (MAO) was purchased from Aldrich as 10% weight of a toluene solution and used without further purification. 2,6-Diisopropylaniline (90%) was purchased from Lancaster. Other chemicals were of analytical grade and were used as received. FTIR spectra were recorded on a Nicolet FT-IR spectrometer. Element analyses were performed on an Elementar vario EL III Analyzer. ^{1}H and ^{13}C NMR spectra were carried out on a Bruker AC 500 spectrometer instrument at room temperature in $CDCl_3$ solution for ligands and polymers using TMS as internal standard. Gel permeation chromatography (GPC) analyses of the molecular weight and molecular weight distribution of the polymers were performed on an Agilent 1100 instrument using standard polystyrene as calibration and with THF as the eluent at 35 °C. The tacticity of PMMA was determined by the methyl resonance of ^{1}H NMR. 7-Hydroxy-3-methylindan-1-one, 7-hydroxy-3,4-dimethylindan-1-one and 4-chloro-7-hydroxy-3- methylindan-1-one were prepared according to literature procedures.[18]

Synthesis of 7-hydroxy-3,4-dimethylindan-1-(*N*-phenylimine) (HL$_1$). To a stirred mixture of 7-hydroxy-3,4-dimethylindan-1-one (2 g, 11.4 mmol) and molecular sieves 4Å (0.7 g) in ethanol (30 mL) was added aniline (1.4 mL, 15.0 mmol) and formic acid (0.10 mL) at room temperature. The mixture was refluxed for 48 h and filtered. The molecular sieves 4Å were washed with ethyl acetate (15 mL). The combined organic filtrates were concentrated under reduced pressure and allowed to crystallize at −20 °C. Purification by recrystallization from diethyl ether gave compound **HL$_1$** (2.3 g, 80%) as yellow crystals. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 1.27 (d, 3H, CH_3), 2.35 (s, 3H, CH_3), 2.40 (dd, 1H, CH_2), 3.06 (dd, 1H, CH_2), 3.45 (m, 1H, CH), 6.74 (d, 1H, aromatic-H), 7.03 (m, 2H, aromatic-H), 7.14 (m, 2H, aromatic-H), 7.37 (m, 2H, aromatic-H), 11.14 (br, 1H, OH); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 17.5, 21.2, 35.4, 38.9, 113.8, 121.3, 122.7, 124.5, 124.7, 129.2, 135.6, 149.5, 153.1, 156.0 (C–O), 177.9 (C=N); IR (KBr): ν 3048 (w), 2956 (w), 1642 (s), 1593 (m), 1484 (m), 1444 (m), 1374 (w), 1344 (w), 1284 (w), 1257 (m), 1209 (m), 1162 (w), 1069 (w), 1018 (w), 915 (w), 861 (w), 818 (m), 774 (m), 735 (w), 705 (m) cm^{-1}; Anal. Calc. for $C_{17}H_{17}NO$: C 81.24, H 6.82, N 5.57; Found: C 80.98, H 6.74, N 5.59%.

Synthesis of 7-hydroxy-3,4-dimethylindan-1-(*N*-2,6-diisopropylphenylimine) (HL$_2$). To a stirred solution of 2,6-diisopropylaniline (8.6 mL, 45.4 mmol) in toluene (40 mL) was added $TiCl_4$ (1.3 mL, 11.4 mmol) in toluene (30 mL) at room temperature during 30 min. The resulting mixture was stirred at 90 °C for 30 min followed by the addition of 7-hydroxy-3,4-dimethylindan-1-one (2.0 g, 11.4 mmol). The mixture was stirred for 48 h at 90 °C, poured into saturated Na_2CO_3 solution, and extracted with ethyl ether. The organic phase was dried over anhydrous Mg_2SO_4. Evaporating the solvent, purification by column chromatography on silica gel using hexane : ethyl acetate (200 : 1) as eluent gave compound **HL$_2$** (1.54 g, 40%) as an orange-red oil. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 1.11–1.28 (m, 15H, CH_3), 2.08 (dd, 1H, CH_2), 2.30 (s, 3H, Me), 2.67 (dd, 1H, CH_2), 2.84(m, 1H, CH), 2.96 (m, 1H, CH), 3.43 (m, 1H, CH), 6.77 (d, 1H, aromatic-H), 7.14–7.18 (m, 4H, aromatic-H), 11.78 (br, 1H, OH); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 17.4, 21.4, 22.6, 22.9, 23.1, 23.7, 23.9, 28.0, 28.4, 35.1, 39.7, 113.8, 118.6, 122.9, 123.3, 124.7, 132.5, 137.4, 145.4, 153.5, 156.1 (C-O), 178.9 (C=N); IR (KBr): ν 3060 (w), 2961 (s), 2868 (m), 1634 (s), 1594 (m), 1461 (m), 1381 (w), 1361 (w), 1319 (w), 1287 (m), 1253 (m), 1221 (m), 1184 (w), 1107 (w), 1050 (w), 933 (w), 900 (w), 823 (m), 764 (w), 733 (m), 691 (w) cm^{-1}; Anal. Calc. for $C_{23}H_{29}NO$: C 82.34, H 8.71, N 4.18; Found: C 82.22, H 8.78, N 4.22%.

Synthesis of 7-hydroxy-3-methylindan-1-(*N*-2,6-diisopropylphenylimine) (HL$_3$). Analogous synthesis to **HL$_2$**, except that 7-hydroxy-3-methylindan-1-one instead of 7-hydroxy-3,4-dimethylindan-1-one was used. Purification by column chromatography on silica gel using hexane : ethyl acetate (200 : 1) as eluent gave compound **HL$_3$** (1.57 g, 43%) as a red-yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 1.13–1.30 (m, 15H, CH_3), 2.05 (dd, 1H, CH_2), 2.67 (dd, 1H, CH_2), 2.89 (m, 2H, CH), 3.41 (m, 1H, CH), 6.84–7.40 (m, 6H, aromatic-H), 11.78 (br, 1H, OH); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 22.8, 23.2, 24.2, 28.7, 35.9, 39.7, 113.9, 115.4, 118.8, 122.8, 123.1, 123.6, 125.1, 132.5, 134.6, 137.6, 145.7, 156.2 (C–O), 158.3, 178.8 (C=N); IR (KBr): ν 3062 (w), 2962 (s), 2927 (m), 2869 (m), 1640 (s), 1596 (m), 1471 (m), 1437 (w), 1382 (w), 1362 (m), 1318 (w), 1290 (m), 1263 (m), 1216 (m), 1184 (m), 1158 (w), 1106 (w), 1051 (w), 955 (w), 879 (w), 835 (w), 796 (m), 741 (m), 690 (w) cm^{-1}; Anal. Calc. for $C_{22}H_{27}NO$: C 82.20, H 8.46, N 4.36; Found: C 81.92, H 8.41, N 4.40%.

Synthesis of 4-chloro-7-hydroxy-3-methylindan-1-(*N*-2,6-diisopropylphenylimine) (HL$_4$). Analogous synthesis to **HL$_1$**, except that 4-chloro-7-hydroxy-3-methylindan-1-one instead of 7-hydroxy-3,4-dimethylindan-1-one was used. Purification by column chromatography on silica gel using hexane : ethyl acetate (200 : 1) as eluent gave compound **HL$_4$** (1.62 g, 40%) as a red-yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 1.12–1.35 (m, 15H, CH_3), 2.14 (dd, 1H, CH_2), 2.69 (dd, 1H, CH_2), 2.80 (m, 1H, CH), 2.91 (m, 1H, CH), 3.50 (m, 1H, CH), 6.82 (d, 1H, aromatic-H), 7.14–7.31 (m, 4H, aromatic-H), 11.76 (br, 1H, OH); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 20.7, 22.9, 23.1, 23.8, 23.9, 28.5, 35.7, 39.4, 115.8, 120.9, 123.5, 125.0, 134.3, 137.4, 144.9, 151.9, 156.8 (C–O), 178.3 (C=N); IR (KBr): ν 3062 (w), 2962 (s), 2927 (m), 2869 (m), 1640 (s), 1596 (m), 1471 (m), 1437 (w),

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1382 (w), 1362 (m), 1318 (w), 1290 (m), 1263 (m), 1216 (m), 1184 (m), 1158 (w), 1106 (w), 1051 (w), 955 (w), 879 (w), 835 (w), 796 (m), 741 (m), 690 (w) cm^{-1}; Anal. Calc. for $C_{22}H_{26}ClNO$: C 74.24, H 7.36, N 3.94; Found: C 74.11, H 7.29, N 3.90%.

Synthesis of nickel(II) complexes (1–4). 7-hydroxy-3,4-dimethylindan-1-(*N*-phenylimine) (0.245 g, 0.98 mmol) was allowed to react with $Ni(OAc)_2 \cdot 4H_2O$ (0.122 g, 0.49 mmol) in anhydrous ethanol (20 mL) at the refluxing temperature for 3 h. After cooling, the solid was filtered and recrystallized from a dichloromethane–ethanol solution at room temperature to give complex **1** (0.33 g, 20%) as light green crystals. The other nickel complexes **2–4** were prepared by the same procedure.

Complex **1**: IR (KBr): ν 3058 (w), 2960 (w), 2922 (w), 2868 (w), 1609 (s), 1555 (m), 1474 (m), 1395 (w), 1336 (m), 1259 (w), 1207 (m), 1165 (w), 1098 (m), 1022 (m), 917 (w), 868 (w), 803 (m), 747 (w), 708 (m) cm^{-1}; Anal. Calc. for $C_{102}H_{96}N_6Ni_3O_6$: C 73.01, H 5.77, N 5.01; Found: C 73.01, H 5.69, N 5.04%.

Complex **2**: Complex **2** was obtained from a toluene–ethanol solution at room temperature as brown crystals (0.50 g, 70%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 1.09–1.56 (m, 30H, CH_3), 1.93 (dd, 2H, CH_2), 2.06 (s, 6H, CH_3), 2.51 (dd, 2H, CH_2), 3.20 (m, 2H, CH), 3.81–4.15 (m, 4H, CH), 5.35 (d, 2H, aromatic-H), 6.68 (d, 2H, aromatic-H), 7.10–7.26 (m, 6H, aromatic-H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 15.7, 19.8, 23.2, 23.4, 27.6, 34.4, 43.2, 116.0, 116.7, 121.9, 122.2, 124.3, 136.2, 139.8, 140.4, 141.9, 151.8, 158.7 (C–O), 176.6 (C=N); IR (KBr): ν 3052 (w), 2959 (m), 2866 (w), 2924 (w), 1607 (s), 1561 (m), 1482 (m), 1403 (w), 1352 (m), 1252 (m), 1184 (w), 1161 (w), 1101 (w), 909 (w), 869 (w), 818 (w), 777 (w) cm^{-1}; Anal. Calc. for $C_{46}H_{56}N_2NiO_2$: C 75.93, H 7.76, N 3.85; Found: C 75.85, H 7.69, N 3.87%.

Complex **3**: Complex **3** was obtained from a THF–ethanol solution at room temperature as brown crystals (0.52 g, 75%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 1.12–1.53 (m, 30H, CH_3), 1.84 (dd, 2H, CH_2), 2.50 (dd, 2H, CH_2), 3.12 (m, 2H, CH), 3.92–4.06 (m, 4H, CH), 5.41 (d, 2H, aromatic-H), 6.21 (d, 2H, aromatic-H), 7.11–7.25 (m, 8H, aromatic-H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 21.1, 23.9, 24.4, 28.8, 36.0, 43.0, 108.6, 116.8, 123.0, 123.9, 125.6, 135.0, 141.1, 141.3, 142.8, 156.4 (C–O), 161.4, 177.7 (C=N). IR (KBr): ν 3058 (w), 2959 (m), 2924 (w), 2866 (w), 1605 (s), 1598 (s), 1567 (m), 1470 (m), 1413 (w), 1381 (w), 1359 (m), 1265 (w), 1245 (m), 1182 (w), 1091 (w), 1050 (w), 968 (w), 793 (m), 746 (w) cm^{-1}; Anal. Calc. for $C_{44}H_{52}N_2NiO_2$: C 75.54, H 7.49, N 4.00; Found: C 75.47, H 7.45, N 4.03%.

Complex **4**: Complex **4** was obtained from a THF–ethanol solution at room temperature as brown crystals (0.64 g, 87%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 1.18–1.54 (m, 30H, CH_3), 1.94 (dd, 2H, CH_2), 2.49 (dd, 2H, CH_2), 3.21 (m, 2H, CH), 3.88–3.93 (m, 4H, CH), 5.34 (d, 2H, aromatic-H), 6.78 (d, 2H, aromatic-H), 7.09–7.27 (m, 6H, aromatic-H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 19.0, 22.6, 23.2, 27.7, 34.8, 41.9, 113.0, 117.7, 122.0, 123.4, 124.8, 134.4, 139.6, 140.1, 141.2, 150.3, 159.1 (C–O), 176.6 (C=N). IR (KBr): ν 3059 (w), 2959 (m), 2923 (w), 2865 (w), 1611 (s), 1591 (m), 1560 (m), 1467 (s), 1406 (w), 1370 (w), 1360 (m), 1324 (w), 1247 (m), 1171 (m), 1113 (w), 1060 (w), 935 (w), 882 (w), 819 (m), 799 (w), 742 (w), 686 (w) cm^{-1}; Anal. Calc. for $C_{44}H_{50}Cl_2N_2NiO_2$: C 68.77, H 6.56, N 3.64; Found: C 68.69, H 6.49, N 3.69%.

Polymerization of MMA

In a typical procedure (Table 1, run 2), 20.0 μmol of nickel(II) complex **2** in 2.0 mL of toluene, 18.6 mmol (2.0 mL) of MMA and 10 mL toluene were added into a polymerization bottle with a strong stirred under a nitrogen atmosphere. After the mixture was kept at 60 °C for 5 min, 2.0 mL of MAO was charged into the polymerization system by means of a syringe and the reaction was initiated. After 1 h, acidic methanol ($V_{\text{ethanol}} : V_{\text{concd.HCl}} = 10 : 1$) was added to terminate the reaction. The polymer was isolated by filtration, washed with methanol and dried at 80 °C for 48 h under vacuum.

X-Ray crystallography

Diffraction data of complexes **1** and **2** were collected on a Bruker Smart APEX CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). All data were collected at room temperature and the structures were solved by direct methods and subsequently refined on F^2 by using full-matrix least-squares techniques (SHELXL),[19] absorption corrections were applied to the data. The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located at calculated positions.

CCDC reference numbers 633235 (**1**) and 633236 (**2**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b708048d.

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