# Nickel(II) Complexes with Mono(imino)pyrrole Ligands: Preparation, Structure, and MMA Polymerization Behavior

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Abstract—A simplified synthetic method was initiated to prepare the corresponding nickel complexes NiL<sub>2</sub> (I–III) with direct condensation of mono(imino)pyrroles (L<sup>1</sup>–L<sup>3</sup>) and nickel dichloride, the structures and methyl methacrylate (MMA) catalytic polymerization behavior of this series of mono(imino)pyrrole nickel complexes were presented. The mono(imine)pyrrole ligands and the corresponding nickel complexes were determined by <sup>1</sup>H NMR, <sup>13</sup>C NMR, IR and MS, etc. Complexes I and III were further characterized by X-ray crystal diffraction (CIF files CCDC nos. 1890965 (I), 1890964 (III)). Both of the structures showed that the ligand chelated to nickel with 2 : 1 molar ratio. The systematic studies were focused on the relationship between the catalytic behavior of these complexes for MMA polymerization and catalyst structure, reaction time, reaction temperature, and ratio of monomer with catalyst. The optimum reaction conditions of the nickel complex with two bulky substituents on the *o*-position of phenyl ring linked with imine showed excellent catalytic activities for MMA polymerization (4.791 × 10<sup>4</sup> g mol<sup>-1</sup> h<sup>-1</sup>), high molecular weight ( $M_n = 65.873 \times 10^3 \text{ g mol}^{-1}$ ), and narrow molecular mass distribution (polymer dispersity index = 3.9877), and azo-diisobutyronitrile acted as co-catalyst during MMA polymerization.

*Keywords:* mono(imino)pyrrole, nickel complex, MMA polymerization, catalytic activity **DOI:** 10.1134/S1070328420050073

## **INTRODUCTION**

Poly(methyl methacrylate) (PMMA) is a kind of excellent and cost-effective variety in synthetic transparent materials [1]. It is the most widely used class of acrylic resin, commonly known as plexiglass, and has excellent transparency, surface visibility and arc resistance. PMMA is mainly used in the automotive industry, pharmaceutical industry, consumer goods and electronic products [2]. In 2015, China has become the world's largest consumer of PMMA with a of  $80 \times$  $10^4$  t [3–5]. As a polar monomer, the catalyst used for the polymerization of methyl methacrylate is mainly metallocene catalyst [6, 7], recently much work has been devoted to late transition metal catalysts due to their low affinity for oxygen and strong tolerance to polar groups, which make them to be used for homopolymerization of polar monomers and copolymerization of olefins and polar monomers [8]. In those catalysts, Ni and Pd-based olefin polymerization catalysts [9] are the most important class of late transition metal catalyst systems [10]. In 1995, authors of [11, 12] developed Ni and Pd catalysts containing  $\alpha$ -diimine ligands and applied them to the polymerization of ethylene. These catalysts showed very high catalytic activities, especially the activity of

Ni catalyst was as high as  $1.1 \times 10^7$  g mol<sup>-1</sup> h<sup>-1</sup>. In 2003,  $\alpha$ -diimine Ni catalyst was firstly applied into the polymerization of methyl methacrylate (MMA) under the activation of co-catalyst methylaluminoxane (MAO) [13]. Authors of [14, 15] first developed a class Ni or Pd catalysts bearing [N,O] chelating ligands, called Schiff base catalysts, and showed that ethylene polymerization can be carried out without the aid of MAO activation. A chelated salicylaldimine Schiff base nickel catalyst was synthesized with high activity of  $1.5 \times 10^5$  g mol<sup>-1</sup> h<sup>-1</sup> when  $n_{Al}/n_{Ni}$  is 100 in [16, 17]. An asymmetric [N,O] neutral Ni complex, used as catalytic system with the aid of MAO for polymerization of MMA, has been reported in [18]. Authors of [19] designed a series of bis[N,O] ligand Ni complexes as the main catalyst and used MAO as a promoter to catalyze the polymerization of MMA in toluene. Hu Yangjian et al. [20] designed the [N,O] chelated nickel complex as catalyst [10], using aluminum alkyl as promoter and *n*-hexane as solvent, the solution polymerization of MMA indicated that the catalytic activity could reach  $1.107 \times 10^5$  g mol<sup>-1</sup> h<sup>-1</sup>.

Herein we reported a series of nickel complexes with asymmetric [N,N] mono(imino)pyrrole ligands and studied their catalytic performance for PMMA. In order to increase coordination ability of heteroatom N, CH<sub>3</sub> group was introduced into the side arm of pyrrole imine, to get novel five-membered heterocyclic imine compounds mono(imino)pyrroles [21]. During the synthesis of mono(imino)pyrroles, an efficient microwave irradiation method was used to accelerate Schiff base condensation, which offered several advantages, such as shorter reaction time, improved yield, and a simplified reaction process as compared with traditional liquid phase reflux reaction. In addition, this solvent-free reaction was in keeping with the green chemistry principle. The novel direct coordination of mono(imino)pyrrole ligand with nickel dichloride, without traditional deprotonation process, was applied successfully in the preparation of nickel complexes [22]. As the mono(imino)pyrrole nickel complex was used in polymerization of MMA with the aid of co-catalyst azodiisobutyronitrile (AIBN), the excellent activity was afforded, this was in sharp contrast with the polymerization result of ethylene using the similar nickel catalyst system [23].

#### **EXPERIMENTAL**

Methods and materials. All experiments concerning air and moisture sensitive compounds were carried out under nitrogen protection using standard Schlenk techniques. Solvents were refluxed over an appropriate drying agent and distilled prior to use. CHN analyses were performed with a HP-MOD 1106 micro analyzer. Melting points were determined in a X-5 Micro-melting point apparatus. Fourier transform infrared (FT-IR) spectra were obtained with a Perkin-Elmer FT-IR 2000 spectrometer. <sup>1</sup>H NMR spectra were recorded with a Bruker DMX-300 spectrometer. Mass spectral (MS) analyses were performed with a Kratos AEI MS-50 instrument using the electron impact (EI) method. Single-crystal XRD was performed using a Bruker Smart 1000 CCD at a temperature of 296 K. Powder X-ray diffractions (PXRD) were tested using Shimadzu XRD-6000. Microwaveassisted reactions were carried out in a Midea PJ 21B-A 800w (21L) domestic oven. 2-Acetylpyrrole, 2-methvlaniline, 3-methylaniline, and 4-methylaniline were purchased from Acros Co. and used as received. AIBN in toluene was from Cologne Chemicals Co. LTD. Polymerization MMA monomer, produced by Chengdu Cologne Chemicals Co. LTD, was used without further purification.

Synthesis of ligand 2-{1-[(2-methylphenyl)imino]ethyl}pyrrole  $(L^1).$ 2-Acetylpyrrole (152.8 mg, and 2-methylaniline (300.0 mg, 1.400 mmol) 2.802 mmol) were added to a 50 mL beaker with a 1:2 M ratio, then 0.5 mL of glacial acetic acid was added and blended well. The mixture was put in a microwave oven and irradiated at 600 W for 5 min. The obtained black brown product was purified by chromatographic column to afford a mass of white solid with a yield of 40.9%; mp 123.3-125.7°C; elutes: petroleum ether-EtOAc (5:1, V/V).

FT-IR (v, cm<sup>-1</sup>): 1609.0 v(C=N). <sup>1</sup>H NMR ( $\delta$ , ppm): 9.76 (s., pyrrole N–H), 7.20 (t., benzene ring aromatic H), 7.15 (t., benzene ring aromatic H), 6.89 (t., benzene ring aromatic H), 6.66 (d., benzene ring aromatic H), 6.65 (d., pyrrole ring aromatic H), 6.23 (t., pyrrole ring aromatic H), 2.08 (s.,  $-N=C(CH_3)-$ ), 2.04 (s., phenyl–CH<sub>3</sub>). <sup>13</sup>C NMR ( $\delta$ , ppm): 159.66, 157.38, 149.03, 139.77, 133.56, 130.25, 125.36, 124.01, 120.85, 118.39, 116.33, 115.12, 111.76, 79.43, 76.78, 31.98, 19.50.

For C<sub>13</sub>H<sub>14</sub>N<sub>2</sub>

Anal. calcd., %	C. 78.75	H. 7.12	N. 14.13
Found, %	C, 78.22	Н, 6.95	N, 14.68

Synthesis of ligand 2-{1-[(3-methylphenyl)imino]ethyl}pyrrole (L<sup>2</sup>) was carried out by the same procedure used for L<sup>1</sup>. White solid of L<sup>2</sup> was obtained with a yield of 25.7%; mp 128.9–130.0°C; elutes: petroleum ether–EtOAc (3 : 1, V/V).

FT-IR (v, cm<sup>-1</sup>): 1594.5 v(C=N). <sup>1</sup>H NMR ( $\delta$ , ppm): 9.67 (s., pyrrole N–H), 7.23 (t., benzene ring aromatic H), 7.19 (t., benzene ring aromatic H), 6.90 (t., benzene ring aromatic H), 6.60 (d., benzene ring aromatic H), 6.59 (t., pyrrole ring aromatic H), 6.24 (t., pyrrole ring aromatic H), 2.34 (s., phenyl–CH<sub>3</sub>), 2.12 (s., –N=C(CH<sub>3</sub>)–). <sup>13</sup>C NMR ( $\delta$ , ppm): 157.45, 157.39, 150.75, 138.77, 132.59, 128.79, 124.12, 121.05–121.87, 117.39, 112.29, 109.76–109.80, 76.73–77.37, 29.74, 21.51.

For C<sub>13</sub>H<sub>14</sub>N<sub>2</sub>

Anal. calcd., %	C, 78.75	H, 7.12	N, 14.13
Found, %	C, 78.84	Н, 6.79	N, 13.99

Synthesis of ligand 2-{1-[(4-methylphenyl)imino]ethyl}pyrrole (L<sup>3</sup>) was carried out by the same procedure used for L<sup>1</sup>. White solid of L<sup>3</sup> was obtained with a yield 26.7%; mp 134.3–135.0°C; elutes: petroleum ether–EtOAc (3 : 1, V/V).

FT-IR (v, cm<sup>-1</sup>): 1631.8 v(C=N). <sup>1</sup>H NMR ( $\delta$ , ppm): 9.72 (s., pyrrole N–H), 7.14 (t., benzene ring aromatic H), 6.81 (t., benzene ring aromatic H), 6.71 (t., pyrrole ring aromatic H), 6.63 (t., pyrrole ring aromatic H), 2.35 (s., phenyl–CH<sub>3</sub>), 2.12 (s., –N=C(CH<sub>3</sub>)–). <sup>13</sup>C NMR ( $\delta$ , ppm): 157.57, 148.24, 132.76, 132.68, 129.53, 121.72, 120.36, 112.08, 109.70, 76.74–77.37, 20.90, 16.41.

For C<sub>13</sub>H<sub>14</sub>N<sub>2</sub>

Anal. calcd., %	C, 78.75	H, 7.12	N, 14.13
Found, %	C, 78.26	Н, 6.77	N, 13.89

Synthesis of bis{2-[(2-methylphenyl)iminoethyl]-**1***H***-pyrrol-1-ido-k^2N,** *N***}nickel(II) (I). NiCl<sub>2</sub> · 6H<sub>2</sub>O** (0.45 mmol) was dissolved in 10 mL of MeOH and added dropwise into 10 mL of MeOH solution of L<sup>1</sup> (0.45 mmol) with stirring. The mixture was stirred for 8 h at room temperature and then concentrated to 5-6 mL. After placing for 2 h without disturbance, the red brown solid was precipitated from the solution. The powder was collected and washed with small amount of distilled water for three times, the red brown powder was obtained after vacuum drying suitable for PXRD analysis. Red brown crystals of complex I suitable for XRD analysis was grown from trichloromethane-acetone-methanol (1:1:1, V/V/V)solution at room temperature. The yield was 65.9%. FT-IR (v, cm<sup>-1</sup>): 1598.3 v(C=N), 1588.6 v(C=N).

For C<sub>26</sub>H<sub>26</sub>N<sub>4</sub>Ni

Anal. calcd., %	C, 68.90	H, 5.78	N, 12.36	Ni, 12.96
Found, %	C, 68.44	H, 5.29	N, 12.33	Ni, 13.94

Synthesis of bis{2-[(3-methylphenyl)iminoethyl]-1*H*pyrrol-1-ido- $k^2N$ ,*N*}nickel(II) (II) was carried out by the same procedure used for I. Yellow brown powder of II was prepared suitable for PXRD analysis. Regarding the crystal of complex II, different methods, such as the direct evaporation of the original solution, the liquid-liquid diffusion, and the gas-liquid diffusion method were used to grow crystals of complex II but crystals did not come out. Similar method applied to complexes I and III was also applied but it didn't work for complex II. The solvents used were chloroform, acetone, methanol, ethanol and the different combination ratios, but the results were not satisfactory. The yield was 65.7%. FT-IR (v, cm<sup>-1</sup>): 1611.4 v(C=N), 1610.2 v(C=N).

For C<sub>26</sub>H<sub>26</sub>N<sub>4</sub>Ni

Anal. calcd., %	C, 68.90	H, 5.78	N, 12.36	Ni, 12.96
Found, %	C, 68.78	H, 5.65	N, 12.23	Ni, 13.34

Synthesis of bis{2-[(4-methylphenyl)iminoethyl]-1*H*-pyrrol-1-ido- $k^2N$ ,*N*}nickel(II) (III) was carried out by the same procedure used for I. Yellow brown powder of III was prepared suitable for PXRD analysis. Yellow brown crystals of complex III suitable for XRD analysis was grown from trichloromethane–acetone–methanol (1 : 1 : 1, *V*/*V*/*V*) solution at room temperature. The yield was 65.2%. FT-IR (v, cm<sup>-1</sup>): 1611.6 v(C–N), 1609.8 v(C=N).

For C<sub>26</sub>H<sub>26</sub>N<sub>4</sub>Ni

Anal. calcd., % C, 68.90 H, 5.78 N, 12.36 Ni, 12.96 Found, % C, 68.91 H, 5.70 N, 12.35 Ni, 13.04

General procedure for MMA polymerization. A certain amount of nickel complex was placed into a

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Schlenk tube containing a magneton, air was expelled by three vacuum/nitrogen cycles before appropriate amounts of monomer MMA, initiator AIBN (12.1 µmol), and toluene (5 mL) were added. All liquids were transferred into the Schlenk tube with dried syringes under nitrogen. The tube was capped under N<sub>2</sub> atmosphere, and then immediately immersed in an oil bath previously heated to the desired temperature. After the reaction mixture was stirring for a certain period of time, the polymerization was stopped and the reaction quenched with acidic ethanol solution. The precipitated polymer was filtered and washed several times with ethanol and then dried under vacuum at room temperature for 24 h. Molecular weight and molecular weight distribution of the obtained polymer were tested with the PL-GPC50 polystyrene column of Agilent, UK, at temperature of 40°C, using THF as mobile phase. A small amount of the treated polymer was dissolved in a chromatographic grade of THF to form a uniform solution, and then injected into the tester with a syringe with a filter needle, the obtained gel chromatographic data was compared with the styrene standard sample to get final  $M_{\rm n}$  and  $M_{\rm w}/M_{\rm n}$ . The catalytic activity was calculated by the total mass of PMMA product (g) dividing the molar amount of metal catalyst (mol) and polymerization time (h).

X-ray structure determination. Diffraction intensity data of the single crystals of I and III were collected on a Bruker SMART 1000 diffractometer with graphitemonochromated Mo $K_{\alpha}$  radiation ( $\lambda = 0.71073$  Å). The Smart program package was used to determine the unit cell parameters. A SADABS absorption correction was applied [24]. The structures were solved by direct methods and refined by full-matrix leastsquares techniques with anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were placed at calculation positions and were included in the structure calculation without further refinement of the parameters. All calculations were performed using the SHELXS-97 program [25, 26]. Crystal data and structure refinement for complexes I and III are summarized in Table 1.

Supplementary material for structures has been deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 1890965 (I), 1890964 (III); deposit@ccdc. cam.ac.uk or http://www.ccdc.cam.ac.uk).

## **RESULTS AND DISCUSSION**

The syntheses of ligands  $L^1-L^3$  and corresponding Ni(II) complexes I–III are shown in Scheme 1.

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 $L^{1}/I: R^{1} = CH_{3}, R^{2} = H, R^{3} = H$  $L^{2}/II: R^{1} = H, R^{2} = CH_{3}, R^{3} = H$  $L^{3}/III: R^{1} = H, R^{2} = H, R^{3} = CH_{3}$ 

Scheme 1.

Initially, 2-acetylpyrrole reacts with a series of aniline derivatives by Schiff base condensation to get three novel mono(imino)pyrrole ligands  $(L^1-L^3)$ , herein, a new microwave irradiation method are employed to accelerate the reactions instead of conventional liquid-phase reaction [27–29] and all the reactions proceeded under mild microwave conditions (600 W, 5–8 min), then the combination of column chromatography and recrystallization methods was used to obtain pure products.

Complexes  $L^1 - L^3$  were synthesized by reacting Ni(II) dichloride with a 1:1 stoichiometric amount of ligands  $L^1 - L^3$ , respectively, in methanol at room temperature. All complexes were isolated as air-stable solids in high purity. In the synthesis of imino pyrrole transition metal complexes, the weak acidities in pyrrole N–H were always thought to interfere with coordination, so the most commonly used method was to deprotonate the ligand using butyl lithium to produce a lithium complex [30], then reacted with a transition metal to get an imino pyrrole transition metal complex. Accidently, it was found that mono(imino)pyrrole nickel complex can be synthesized with the direct chelation of mono(imino)pyrrole ligand and Ni(II) dichloride under very mild conditions (e.g. methanol solvent, room temperature) [22]. The process is of significance in terms of the procedure simplification and cost reduction.

Complexes I and III were further characterized using single-crystal XRD analysis. The crystal structures of I and III are shown in Fig. 1, and selected bond lengths and angles are listed in Table 2.

As shown by Fig. 1, complexes I and III have the similar molecular structure, in both of which Ni atom is coordinated by two inverted N,N'-bidentate mono(imino)pyrrole ligands using two imino and two pyrrolide nitrogen atoms to form a four-coordinate geometry. Ni atom is located in a crystallographic inversion center with the pyrrolide rings and the imine groups trans to each other. In complex I, the five-

membered chelate rings formed bv atoms Ni(1)/N(1)/C(1)/C(5)N(2) and Ni(2)/N(3)/C(18)/C(14)/N(4) are essentially coplanar, and the maximum deviations from their planes are -0.023(2) and -0.021(7) Å, respectively, for atoms N(1) and N(4). While in complex III, the five-membered chelate rings formed by Ni(1)/N(1)/C(3)/C(4)N(2) and Ni(2)/N(6)/C(30)/C(29)/N(5) are also essentially coplanar, the maximum deviations of atoms N(1) and N(5) from their planes are -0.025(7) and -0.023(9) Å, respectively. In addition, we notice that in complexes I and III, the two equatorial Ni-N<sub>imine</sub> distances (mean 1.942(2) Å in I, mean 1.941(2) Å in III) are substantially longer than the equatorial Ni-N<sub>pyrrole</sub> bonds (mean 1.906(2) Å in I, 1.918(2) Å in III), this has been considered as combination result of the anionic nature of pyrrolyl nitrogen and the steric bulk of methyl substituents on phenyl ring. All Ni-N bond lengths in complexes I and III are obviously shorter than the normal values for typical Ni–N bonds (2.07 Å) [31], particularly Ni-N<sub>imine</sub> distances. This may indicate a stronger  $\sigma$ -donor character of imino N atom induced by the methyl (C(6)) substituent in iminio carbon (C(5)), which may also cause a higher degree of steric congestion around Ni cation, as exhibited by I.

From the bond angles data, it could be found that both in I and III sum of all the angles around nickel center are ca. 360°, indicating that the central Ni atoms are in essentially square-planar conformation. In complex I, the phenyl substituents at imine nitrogen atoms are nearly perpendicular to NiN<sub>4</sub> square plane (86.38°, 87.03°) and parallel to each other (0°). In complex III, the phenyl substituents at imine nitrogen atoms are also nearly perpendicular to NiN<sub>4</sub> square plane (75.93°, 72.50°) and form a acute angle to each other (19.62°). The difference about relative space position of phenyl substituents to NiN<sub>4</sub> square and each other between I and III, maybe because different hindrance effect brought by different methyl substituent position on the phenyl ring. It is noticeable

Table 1.	Crystallog	raphic data	and and str	ucture refin	ement for ]	and III
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Daramatar	Value			
Parameter	Ι	III		
Empirical formula	C <sub>26</sub> H <sub>26</sub> N <sub>4</sub> Ni	C <sub>26</sub> H <sub>26</sub> N <sub>4</sub> Ni		
Formula weight	453.22	453.22		
Crystal system	Triclinic	Monoclinic		
Space group	$P\overline{1}$	C2/c		
<i>a</i> , Å	10.0928(11)	22.730(6)		
b, Å	10.4996(11)	9.728(2)		
<i>c</i> , Å	11.6897(12)	31.025(7)		
α, deg	78.160(2)	90		
β, deg	66.297(2)	98.210(6)		
γ, deg	89.174(2)	90		
Volume, Å <sup>3</sup>	1106.9(2)	6790(3)		
$Z$ ; $\rho_{calcd}$ , mg m <sup>-3</sup>	2; 1.360	4; 1.330		
$\mu$ , mm <sup>-1</sup>	0.90	0.88		
Crystal size, mm	$0.31 \times 0.24 \times 0.16$	$0.35 \times 0.25 \times 0.14$		
Diffractometer	Bruker APEX-II CCD	Bruker APEX-II CCD		
Absorption correction	Multi-scan (SADABS; Bruker, 2008)	Multi-scan (SADABS; Bruker, 2008)		
<i>F</i> (000)	476	2856		
Crystal color; habit	Brown-yellow; needle	Yellow; needle		
$\theta$ Range for data collection, deg	2.2-26.3	2.4-17.5		
Index ranges	$-11 \le h \le 11,$	$-27 \le h \le 28,$		
	$-8 \le k \le 12,$	$-11 \le k \le 12,$		
	$-11 \le l \le 13$	$-3 \le l \le 38$		
$T_{\min}, T_{\max}$	0.770, 0.873	0.625, 0.745		
Number of measured/independent/ observed ( $I > 2\sigma(I)$ ) reflections	5613/3901/3102	17921/6764/4328		
<i>R</i> <sub>int</sub>	0.018	0.146		
$(\sin\theta/\lambda)_{max}, Å^{-1}$	0.597	0.597		
$R(F^2 > 2\sigma(F^2)), wR(F^2); S$	0.044, 0.12; 1.19	0.176, 0.35; 1.25		
Number of parameters	287	426		
Number of restraints	0	0		
$\Delta \rho_{\text{max}} / \Delta \rho_{\text{min}}$ , e Å <sup>-3</sup>	0.46/-0.28	0.79/-2.76		

that the pyrrolyl rings and the substituted phenyl ring linking to imine groups lay trans to each other in both of complexes I and III.

Comparison of structure data of Ni(II) complexes and their free ligands [32–36] also highlights some structural differences. The first feature to note is that ligand bite angles portrayed by  $N_{imino}NiN_{pyrrole}$  are very acute (at 82.88° and 82.92° in I, 82.82° and 84.52° in III), this value is obtained decreases in the angles defined by N(1)C(1)C(5) (115.24°), N(2)C(5)C(1) (114.70°), N(4)C(14)C(18) (114.81°), and N(3)C(18)-C(14) (115.24°) for I, N(1)C(3)C(4) (117.16°), N(2)C(4)C(3) (115.13°), N(5)C(29)C(30) (117.13°) and N(6)C(30)C(29) (111.89°) for III, in relation to those observed in the free organic ligands L<sup>1</sup> and L<sup>3</sup>. In addition, angles at the pyrrolyl nitrogen  $CN_{pyrrole}C$  are decreased upon coordination, which is compensated by an increase of the angles at C atoms bound to pyrrolyl nitrogen. Besides, the bond lengths within pyrrole ring appear to be significantly affected, both C–C and C–N distances appear to increase in varying degrees as the ligand chelating with nickel. Meanwhile, the bond lengths in NCCN backbone of the ligand change upon coordination to nickel, the C– N<sub>pyrrole</sub> and C–N<sub>imine</sub> distances increase, whereas C–C distances decrease. All the imine C=N bonds only





Fig. 1. Molecular structure of I and III.

slightly increase upon coordination (C(5)–N(2) and N(2A)–C(5A) in I, C(4)–N(2) and N(4)–C(17) in III), indicating that  $\pi$ -back-donation from the nickel center to the imine fragment is not strong.

XRPD are used to characterize the purity of complexes I–III, the results are displayed in Fig. 2. From Figs. 2a and 2c, it is found that all the peaks in XRPD patterns are highly consistent with that simulated by SC-XRD, indicating good purity of the complexes of I and III. Using the similar procedures, two copies of the complex II were prepared and measured by XRPD for comparison, as shown in Fig. 2b. The position and height of all peaks in the powder diffraction patterns for two synthesized complexes **II** were consistent totally, so it was preliminarily determined that the synthesized complex **II** was of good purity.

C(10)

A series of MMA polymerization experiments were carried out to investigate the catalytic performance of mono(imino)pyrrole nickel complexes I-III. The influences of polymerization conditions were also studied, employing 22 µmol of nickel catalyst, 12 µmol

]	[	Ι	II
Bond	d, Å	Bond	d, Å
N(1)-C(1)	1.372(4)	N(3)-C(16)	1.421(17)
C(1)–C(5A)	1.412(5)	C(16)-C(17)	1.42(2)
C(5A)–C(6A)	1.499(5)	C(17)–C(18)	1.51(2)
N(2A)-C(5A)	1.309(4)	N(4)-C(17)	1.33(2)
N(2A)-C(7A)	1.451(4)	N(4)-C(19)	1.419(17)
Ni(1)-N(1)	1.907(3)	Ni(1)–N(3)	1.917(13)
Ni(1)-N(2A)	1.944(3)	Ni(1)–N(4)	1.929(10)
Ni(1)-N(1A)	1.907(3)	Ni(1)–N(1)	1.930(14)
Ni(1)-N(2)	1.944(3)	Ni(1)–N(2)	1.944(11)
C(1A)-N(1A)	1.372(4)	N(1)-C(3)	1.351(19)
C(1A)–C(5)	1.412(5)	C(3)–C(4)	1.39(2)
C(5)-C(6)	1.499(5)	C(4)–C(5)	1.495(18)
C(5)–N(2)	1.309(4)	N(2)-C(4)	1.349(19)
N(2)–C(7)	1.449(4)	N(2)–C(6)	1.404(18)
Angle	ω, deg	Angle	ω, deg
N(1)Ni(1)N(2A)	82.88(10)	N(1)Ni(1)N(2)	83.6(5)
N(1A)Ni(1)N(2)	82.88(10)	N(3)Ni(1)N(4)	84.5(5)
N(1)Ni(1)N(2)	97.12(10)	N(3)Ni(1)N(2)	95.4(5)
N(1A)Ni(1)N(2A)	97.12(10)	N(4)Ni(1)N(1)	96.9(5)

Table 2. Selected bond lengths (Å) and the selected bond lengths (Å) and the selected bond lengths (Å).	nd angles (deg) for I and III
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of AIBN as co-catalyst and 5 mL of toluene as solvent. The experimental data are listed in Table 3.

From the polymerization data shown in Table 3, it can be concluded that MMA cannot be polymerized without any main catalyst (nickel complex) or co-catalyst (AIBN), as illustrated in run 0. Run 1 shows that the main nickel catalyst cannot catalyze MMA polymerization alone. While the initiator AIBN alone can promote MMA polymerization to obtain very little PMMA, as illustrated in run 2. As run 2 and run 3 are compared, it could be found that the catalytic activity is enhanced from  $0.190 \times 10^4$  to  $4.791 \times 10^4$  g mol<sup>-1</sup> h<sup>-1</sup> by adding both of nickel catalyst and AIBN, the fact shows that these two reagents produce good synergistic catalysis effect, which greatly promotes the rate of MMA polymerization.

By comparing runs 3-5 in Table 3, a trend can be easily found that the activities  $(4.791 \times 10^4 \text{ to } 3.598 \times 10^4 \text{ g mol}^{-1} \text{ h}^{-1})$  and polymer dispersity index (PDI) (3.9877-2.8948) are decreased sequentially along with the order of catalysts **I**, **II**, **III**, indicating the methyl group in different position of benzene ring (*ortho, meta* and *para*) will influence the catalytic performance dramatically. The methyl group near C=N bond brings higher steric effects for the coordination catalysis process of MMA, which positively correlates with the polymerization activity and PDI. This intrinsic rule is in accordance with the rules observed in ethylene polymerization process by the similar nickel catalysts [19]. Catalyst I shows the highest catalytic activities so it is selected for further condition optimization.

Temperature significantly influences the catalytic activity for MMA polymerization. The runs 3 and 6–9 in Table 3 show that the activities of I are increased sequentially from  $1.321 \times 10^4$  to  $4.791 \times 10^4$  g  $mol^{-1} h^{-1}$ , as the temperature raise from 70 to  $100^{\circ}C$ , while the catalytic activities decrease slowly from  $4.791 \times 10^4$  to  $4.695 \times 10^4$  g mol<sup>-1</sup> h<sup>-1</sup>, as the temperature raise further to 110°C. Although  $M_n$  and PDI of PMMA indicate unregular correlation with polymerization temperature, both of which get the highest value at 100°C,  $65.873 \times 10^3$  g mol<sup>-1</sup> and 3.9877, respectively. At lower reaction temperature, molecules cannot get sufficient energy to form activated catalystmonomer complex and active center, so indicate relatively lower insertion rate of monomer and slower polymerization rate. At the higher temperature, the monomer has sufficient thermal energy to insert into the activation center and exacerbate chain propagation rate. Moreover, higher temperature will make viscosity of the system decrease, which is conducive to mass transfer and diffusion of monomers.

The runs 3 and 10–13 in Table 3 show that the activity of catalyst **I** increases sequentially from  $1.205 \times 10^4$  to  $4.791 \times 10^4$  g mol<sup>-1</sup> h<sup>-1</sup>, as the polymer-





**Fig. 2.** PXRD of I (a), II (b), III (c): experiment is shown in black, simulations are shown in red.

ization time prolongs from 4 to 10 h, while the catalytic activities decrease from  $4.791 \times 10^4$  to  $3.148 \times 10^4$  g mol<sup>-1</sup> h<sup>-1</sup> as the time raise further to 12 h. The molecular mass of **I** increases sequentially from  $55.202 \times 10^3$  to  $87.945 \times 10^3$  g mol<sup>-1</sup>, as the time raise from 4 to 8 h, while the molecular mass decrease slowly from  $87.945 \times 10^3$  to  $65.873 \times 10^3$  g mol<sup>-1</sup>, as the time prolongs further to 12 h. The molecular weight distribution is between 2.1467 and 3.9877. From above results, it could be concluded that at the optimum reaction conditions (polymerization temperature 100°C and time 10 h) the high activity can be obtained, while too high temperature or too long reaction time do not help for the production of active center.

The runs 3 and 14–17 in Table 3 show that the activities of I increase sequentially from  $2.183 \times 10^4$  to

 $4.791 \times 10^4$  g mol<sup>-1</sup> h<sup>-1</sup>, as the molar ratio of monomer and nickel catalyst (n(M)/n(C)) raise from 800 : 1 to 1200 : 1, while the activities decrease from  $4.791 \times 10^4$ to  $3.085 \times 10^4$  g mol<sup>-1</sup> h<sup>-1</sup>, as n(M)/n(C) increase further to 2400: 1. The molecular weight distribution is in the range of 2.5211 and 3.9877. The small n(M)/n(C)means relatively large concentration of catalyst active centers and low concentration of monomers, the separate active center easily leads to lower molecular mass  $(M_{\rm n} = 30.983 \times 10^3 \,\mathrm{g \ mol^{-1}})$  while the low concentration of monomer is inclined to result in a poor catalyst activity (2.183  $\times$  10<sup>4</sup> g mol<sup>-1</sup> h<sup>-1</sup>). While too much monomer doesn't make sure higher activity, for example, as n(M)/n(C) raise to 1400 : 1 to 2400 : 1, the concentration of the catalyst active centers is relatively low as compared with the monomer amount, which means low conversion rate. At the same time, too much monomer may raise the viscosity of polymerization system, which affect the diffusion of monomer to active center, and cause lower catalytic activity and molecular mass.

Thus, a series of mono(imino)pyrrole ligands  $(L^{1} L^{3}$ ) and the corresponding Ni(II) complexes (I–III) have been synthesized. Ligands were synthesized using microwave irradiation instead of a conventional liquid-phase reaction. Direct coordination strategy was adopted to generate the nickel(II) complexes. Both innovations bring several advantages to the preparation of the mono(imino)pyrrole nickel catalysts, such as cost and time savings, operation simplification. The crystal structures of I and III indicate similar molecular structure, in both of which Ni(II) are coordinated by two inverted N,N-bidentate mono(imino)pyrrole ligands using two imino and two pyrrolide N atoms to form a four-coordinate geometry. Ni(II) is located in a crystallographic inversion center with the pyrrolide rings and the imine groups trans to each other. As the nickel complexes are applied into MMA polymerization catalysis with the aids of co-catalyst AIBN, the results show that the relative molecular mass of PMMA is in the magnitude of  $10^4$ , PDI is between 1.5-4.0, and all catalysts have the medium activities in the range of  $4.791 \times 10^4 - 3.598 \times 10^4 \text{ g mol}^{-1} \text{ h}^{-1}$ . The ligand structure, monomer ratio, polymerization time and temperature all influence the catalytic performance to some extent. Experimental data show that the closer  $-CH_3$  on aniline ring to the imine group, the higher activity is likely obtained. As the molar ratio of monomer to catalyst I is of 1200: 1, the polymerization temperature of 100°C, time of 10 h, MMA polymerization provides the relatively higher activity  $(4.791 \times 10^4 \text{ g mol}^{-1} \text{ h}^{-1})$ , larger molecular weight  $(M_n = 65.873 \times 10^3 \text{ g mol}^{-1})$ , as well as the narrower molecular mass distribution (PDI = 3.9877).

Run	Catalyst	<i>T</i> , h	Temperature, °C	$n(\mathbf{M})$ : $n(\mathbf{C})^{\mathrm{b}}$	Activity <sup>c</sup>	$M_{\rm n}^{\rm d}$ (10 <sup>3</sup> g mol <sup>-1</sup> )	$\frac{\text{PDI}^{\text{e}}}{(M_{\text{w}}/M_{\text{n}})}$
0		10	100	No. catalyst and AIBN			
1	Ι	10	100	No. AIBN			
2		10	100	No catalyst	0.190	20.795	1.3644
3	Ι	10	100	1200 : 1	4.791	67.824	3.9877
4	II	10	100	1200 : 1	3.753	19.954	3.0307
5	III	10	100	1200 : 1	3.598	34.618	2.8948
6	Ι	10	70	1200 : 1	1.321	55.210	1.7541
7	Ι	10	80	1200 : 1	1.355	59.733	1.9814
8	Ι	10	90	1200 : 1	1.397	54.315	2.4463
9	Ι	10	110	1200 : 1	4.695	47.441	2.2305
10	Ι	4	100	1200 : 1	1.205	55.202	2.1467
11	Ι	6	100	1200 : 1	1.495	65.529	2.5627
12	Ι	8	100	1200 : 1	2.239	87.945	2.7784
13	Ι	12	100	1200 : 1	3.148	65.873	3.1268
14	Ι	10	100	800:1	2.183	30.983	2.5877
15	Ι	10	100	1600 : 1	4.381	72.599	2.9168
16	Ι	10	100	2000:1	3.619	101.814	2.6544
17	Ι	10	100	2400 : 1	3.085	15.120	2.5211

Table 3. MMA polymerization with nickel catalysts/AIBN<sup>a</sup>

<sup>a</sup> Reaction conditions: 22 µmol Ni catalyst, 5 mL toluene, 12 µmol AIBN.

<sup>b</sup>n(M) : n(C): molar ratio of MMA monomer to Ni catalyst.

<sup>c</sup> The catalytic activity  $(10^4 \text{ g mol}^{-1} \text{ h}^{-1})$ .

<sup>d</sup>  $M_{\rm n}$ : number average molecular weight of polymer PMMA.

<sup>e</sup> P $\ddot{\mathrm{DI}}\mathrm{I} = (M_{\mathrm{w}}/M_{\mathrm{n}}).$ 

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