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Polymerization of Methyl Methacrylate with Nickel(II) and Palladium(II) Iminopyridyl Mononuclear Bimetallic Complexes

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Abstract Methyl methacrylate polymerizations with a series of Pd(II) or Ni(II) bimetallic catalysts having general formula [(2-C_5H_4N)–C=N–(Z)–N=C–(2-C_5H_4N)] $[MX_2]_2$ {Z = (2,6-$C_6H_2R_2$)$_2$CH(4-C_6H_5); R = Me, *i*Pr, MX_2 = $PdCl_2$, $NiBr_2$} in combination with methylaluminoxane showed that bimetallic Pd(II) catalysts are much more active than their bimetallic Ni(II) nickel and monometallic analogs to give syndiorich poly(methyl methacrylate) with moderate molecular weight.

Keywords Bimetallic catalysts · Catalysis · Methyl methacrylate · Polymerization · Transition metal chemistry

1 Introduction

In order to achieve value added polymers by controlling the physical properties such as toughness, adhesion, barrier properties, surface properties, miscibility with other polymers and rheological properties, incorporating functional groups into nonpolar polyolefins is one of the hot issues. Late transition metal complexes, due to their less oxophillic nature relative to early transition metal complexes, can be utilized for the polymerization of polar monomers including methyl methacrylate (MMA) [1–6]. However, only a limited number of catalysts based on late transition metals have been used for homo- and copolymerization of MMA. Ni(acac)$_2$/methylaluminoxane (MAO) [7], Ni(II) complexes bearing *N*,*O*-chelate ligands activated with MAO [8–10], α-diimine Ni(II), and pyridyl bisimine Fe(II) and Co(II) complexes activated with MAO [11, 12] yielded poly(methyl methacrylate) (PMMA) with syndiorich microstructure.

Recently, bimetallic late transition metal complexes have been considered attractive candidates for inducing cooperative effects, which has attracted interest in both academic and industrial sectors [13, 14]. Cooperative effects were recently investigated for olefin polymerizations by using various bimetallic Ni(II), Pd(II), and Cu(II) complexes [15–21]. However, there have been a few examples of MMA polymerizations by using bimetallic nickel complexes [20, 22] and no reports by bimetallic Pd complexes, although Pd complexes is generally less oxophillic than Ni.

In this paper, we describe the polymerization of MMA by structurally modulated bimetallic Ni(II) or Pd(II) complexes of the general formula [(2-C_5H_4N)–C=N–(Z)–N=C–(2-C_5H_4N)] $[MX_2]_2$ {Z = (2,6-$C_6H_2R_2$)$_2$CH(4-C_6H_5); R = Me, *i*Pr, MX_2 = $PdCl_2$, $NiBr_2$} (Fig. 1) in combination with MAO.

2 Experimental

2.1 Materials and Equipment

All reactions were performed under a purified nitrogen atmosphere using standard glove box and Schlenk techniques. MMA and organic solvents were purified by known procedures and stored over molecular sieves (4 Å). All reagents used in this study were purchased from Aldrich Chemical Co. and used without further purification. MAO

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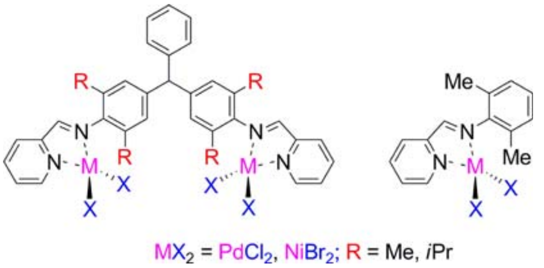
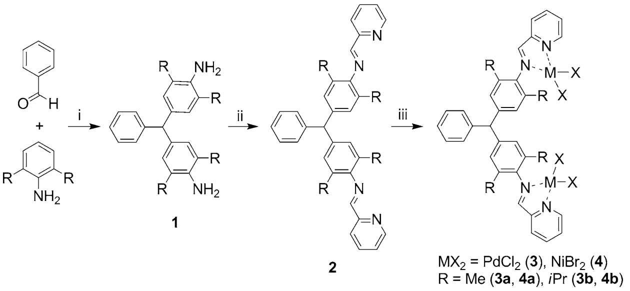


Fig. 1 Mono- and bimetallic iminopyridyl nickel(II) and palladium(II) complexes



Scheme 1 Synthesis of catalysts: (i) HCl; (ii) pyridine carboxaldehyde, MeOH; (iii) Pd(CH$_3$CN)$_2$Cl$_2$/(DME)NiBr$_2$

(8.4 wt% total Al solution in toluene) was obtained from Akzo Chemical and used as received.

The molecular weight (MW) and its distribution polydispersity (PDI) of PMMA were determined by gel permeation chromatography (GPC) using a Hewlett Packard Model 1100 series system in tetrahydrofuran (THF) at 25 °C as calibrated with polystyrene standards. Both ^{1}H NMR spectra (300 MHz) of compounds and ^{13}C NMR spectra (75 MHz) of the triad tacticity of PMMA were recorded on a Varian Unity Plus 300 spectrometer in CDCl$_3$, using tetramethylsilane as an internal reference. FT-IR spectra of the samples were recorded on KBr pellets by a Bruker IFS55 FT-IR spectrometer. Element analysis was carried out using Vario EL. Analytical thin layer chromatography (TLC) was conducted using Merck 0.25 mm silica gel 60F pre-coated aluminum plates with fluorescent indicator UV254. Purification of ligands was carried out with a Combi-Flash (Companion) auto-column machine. Elemental analysis was carried out using Vario EL analyzer and UV–visible spectra were recorded on a Shimadzu UV-1650PC UV–visible spectrophotometer. Mass spectra of catalysts were recorded using positive fast atom bombardment (FAB) methods on JEOL JMS-AX505WA, HP 5890 Series II spectrometer.

2.2 Synthesis of Ligands (**2a**,**2b**)

We have recently reported the synthetic procedure for ligand precursors (**1a**,**1b**) [23]. Ligands were synthesized according to the Scheme 1. To methanol solution of the corresponding ligand precursor, corresponding pyridine carboxaldehyde, and a catalytic amount of formic acid was added. It was stirred overnight at 30 °C and the product was purified.

(((Pyridin-2-yl)methyleneamino)-3,5-dimethylphenyl)((phenyl)methyl)-2,6-dimethyl-*N*-((pyridin-2-yl)methylene)benzenamine (**2a**). Yellow **2a** powder was obtained by reacting 2-pyridine carboxaldehyde (0.64 g, 6 mmol) with **1a** (0.99 g, 3 mmol) in 58% (0.89 g) yield. ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.14 (s, 12H, CH$_3^{\text{methyl}}$), 5.45 (s, 1H, CH), 6.74–6.88 (d, 2H, H$_{\text{arom}}$), 7.20–7.28 (m, 5H, H$_{\text{arom}}$), 7.31–7.39 (m, 2H, H$_{\text{arom}}$), 7.41–7.43 (m, 2H, H$_{\text{arom}}$), 7.83–7.88 (m, 2H, H$_{\text{arom}}$), 8.28 (t, 2H, H$_{\text{arom}}$) 8.38 (s, 2H, N=CH), 8.71 (d, 2H, H$_{\text{arom}}$); ^{13}C NMR (75 MHz, CDCl$_3$) δ 22.81, 55.76, 114.86, 126.32, 128.12, 131.15, 132.44, 135.64, 138.24, 141.15, 144.15, 147.54, 151.15, 157.14. Anal. Calcd for C$_{35}$H$_{32}$N$_4$: C, 82.64; H, 6.34; N, 11.01. Found: C, 82.61; H, 6.37; N, 10.99.

(((pyridin-2-yl)methyleneamino)-3,5-diisopropylphenyl)((phenyl)methyl)-2,6-diisopropyl-*N*-((pyridin-2-yl)methylene)benzenamine (**2b**). Brownish-yellow **2b** powder was obtained by reacting 2-pyridine carboxaldehyde (0.64 g, 6 mmol) with **1b** (1.33 g, 3 mmol) in 60% (1.13 g) yield. ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.25 (d, 24H, CH$_3^{\text{ipr}}$), 2.93 (sept, 4H, CH$^{\text{ipr}}$), 5.33 (s, 1H, CH), 6.88 (m, 4H, H$_{\text{arom}}$), 7.22–7.39 (m, 5H, H$_{\text{arom}}$), 7.40–7.43 (m, 2H, H$_{\text{arom}}$), 7.83–7.87 (m, 2H, H$_{\text{arom}}$), 8.29 (t, 2H, H$_{\text{arom}}$) 8.37 (s, 2H, N=CH), 8.69 (d, 2H, H$_{\text{arom}}$) ^{13}C NMR (75 MHz, CDCl$_3$) δ 22.18, 27.15, 55.88, 114.08, 121.14, 122.15, 123.15, 128.15, 131.16, 135.23, 136.75, 140.85, 142.57, 149.18, 152.01, 161.75. Anal. Calcd for C$_{43}$H$_{48}$N$_4$: C, 83.18; H, 7.79; N, 9.02. Found: C, 83.15; H, 7.82; N, 8.99.

2.3 Synthesis of Catalysts (**3a**,**b**) (Scheme 1)

To a CH$_2$Cl$_2$ solution of ligand 1:2 equivalent of metallating agent (Pd(CH$_3$CN)$_2$Cl$_2$ [24] or (DME)NiBr$_2$) was added and stirred overnight or up to complete dissolution of Pd(CH$_3$CN)$_2$Cl$_2$ or (DME)NiBr$_2$ at 30 °C. The complex, which precipitated in ether, was washed, filtered, and dried under vacuum at 60 °C. Note that the paramagnetic character of the Ni catalyst made its NMR analysis unfavorable [25–27].

3a. R = Methyl, Y = H: Yield = 88%. ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.23 (s, 12H, CH$_3^{\text{methyl}}$), 5.56 (s, 1H, CH), 6.85–6.91 (d, 2H, H$_{\text{arom}}$), 7.25–7.32 (m, 5H, H$_{\text{arom}}$), 7.98–8.03 (m, 2H, H$_{\text{arom}}$), 8.12–8.15 (m, 2H, H$_{\text{arom}}$), 8.39–8.41 (m, 2H, H$_{\text{arom}}$), 8.72 (t, 2H, H$_{\text{arom}}$) 8.88 (s, 2H, N=CH), 9.06 (d, 2H, H$_{\text{arom}}$); ^{13}C NMR (75 MHz, CDCl$_3$) δ 22.96, 56.23, 115.66, 123.42, 128.95, 132.35, 133.84, 136.84, 139.64, 143.65, 144.95, 148.84, 153.65, 161.54. Anal. Calcd for C$_{35}$H$_{32}$C$_{l4}$N$_4$Pd$_2$: C, 48.69; H, 3.74; N, 6.49. Found: C, 48.71; H, 3.78; N, 6.50. MS (FAB$^+$): $m/z = 827$ (M$^+$–Cl).

3b. R = isopropyl. Y = H: Yield = 89%. ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.20 (d, 12H, CH$_3^{ipr}$), 1.29 (d, 12H, CH$_3^{ipr}$), 3.13 (sept, 4H, CH^{ipr}), 5.39 (s, 1H, CH), 6.95 (m, 4H, H$_{arom}$), 7.26–7.42 (m, 5H, H$_{arom}$), 7.43–7.47 (m, 2H, H$_{arom}$), 7.89–7.93 (m, 2H, H$_{arom}$), 8.36 (t, 2H, H$_{arom}$) 8.56 (s, 2H, N=CH), 8.96 (d, 2H, H$_{arom}$); ^{13}C NMR (75 MHz, CDCl$_3$) δ 22.17, 23.07, 28.05, 55.96, 114.98, 121.44, 122.85, 123.75, 128.87, 132.12, 136.63, 137.65, 141.65, 143.77, 151.68, 154.61, 168.25. Anal. Calcd for $C_{43}H_{48}Cl_4N_4Pd_2$: C, 52.94; H, 4.96; N, 5.74. Found: C, 48.88; H, 4.63; N, 5.32. MS (FAB$^+$): $m/z = 940$ (M$^+$–Cl).

4a. R = Methyl, Y = H: Yield = 89%. Anal. Calcd for $C_{35}H_{32}Br_4N_4Ni_2$: C, 44.45; H, 3.41; N, 5.92. Found: C, 44.48; H, 3.50; N, 5.93. MS (FAB$^+$): $m/z = 865$ (M$^+$–Br).

4b. R = isopropyl. Y = H: Yield = 90%. Anal. Calcd for $C_{43}H_{48}Br_4N_4Ni_2$: C, 48.82; H, 4.57; N, 5.30. Found: C, 48.88; H, 4.63; N, 5.32. MS (FAB$^+$): $m/z = 977$ (M$^+$–Br).

Monometallic Pd(II) and Ni(II) complexes with the general formula [(2-C_5H_4N)–C=NAr][MX_2] {Ar = 2,6-$(Me)_2C_6H_3$, MX_2 = $PdCl_2$ (**5**), $NiBr_2$ (**6**)} were prepared according to the reported procedure [25–27].

2.4 Polymerization

Bulk polymerizations of MMA were carried out in a Schlenk tube (50 mL) with a connection to a vacuum system. In a typical example of bulk polymerization procedure, a prescribed amount of MAO dissolved in toluene was injected into the reactor and then toluene was removed under vacuum. Five milliliter of MMA (47.0 mmol) and 8 μmol of metal complex were then charged into the reactor in this order under nitrogen flow. The polymerization was carried out at constant temperature for a specific time. Resulting mixture was poured into a large amount of methanol to precipitate the polymer. The precipitated polymer was separated by filtration and washed with methanol before drying overnight at 60 °C under vacuum. Polymer yield was determined gravimetrically.

3 Results and Discussion

3.1 Catalyst Preparation

Recently we have reported Ni(II) α-diimine complexes derived from 2,6-disubstituted diamines which showed high activity towards ethylene polymerization [23]. Some of those diamines were utilized to synthesis the corresponding pyridylimine ligands as a potential candidate for bimetallic catalysts by condensation reaction with two equivalent of 2-pyridine carboxaldehyde as shown in Scheme 1. (DME)$NiBr_2$ was used as a metallating agent for Ni(II) iminopyridyl bimetallic catalysts while $Pd(CH_3CN)_2Cl_2$ [24] was utilized for the preparation of Pd(II) bimetallic catalysts. All the catalysts were synthesized in good yield.

3.2 MMA and PMMA Characterizations

Bulk polymerization results obtained by both Ni and Pd iminopyridyl bimetallic catalysts were summarized in Table 1. Taking the steric bulk of *ortho* substituents in ligands and the type and number of metal nucleus into consideration, it is observed that (i) increase in steric bulk of *ortho* substituents from methyl to isopropyl results in decreasing the catalytic activity for both Ni and Pd catalysts (run no. 1, 7, 11, and 12); (ii) Pd catalysts are much more active than Ni analogs for both mono- and bimetallic systems (run no. 1, 7, 13, and 14); and (iii) bimetallic catalysts are more effective than monometallic catalysts, especially for Pd catalysts (run no. 1, 13, 7, and 14). One reason for higher activity of Pd catalyst over Ni analog may be due to its less oxophillic nature and bigger size. Sun and coworkers have reported the MMA polymerizations by neutral Pd and Ni analogs in which the Pd system showed activity almost double of its Ni analog [28]. Similar observation was also reported for the homo- and copolymerization of norbornene and styrene with a binuclear Ni and Pd based diimine complexes [29]. It has also been reported that too high and low steric bulk leads to decrease the catalytic activity in MMA polymerization [30].

The increase in steric hindrance of complexes, **3a** vs. **3b** and **4a** vs. **4b**, reduces the catalytic activities by more than two times, indicating the N-substituents on the bridging fragment have considerable influence on the catalytic activity toward MMA polymerization. It is interesting to note that the bimetallic Pd and Ni complexes exhibit higher activities than the corresponding monometallic complexes **5** and **6** (run no. 1 vs. 13 and 7 vs. 14), $Ni(acac)_2$/MAO [31], Ni α-diimine/MAO and Fe/Co pyridyl bis(imine)/MAO systems [11, 12]. The similar results have been reported for MMA polymerization with a binuclear Ni and Cu acetylacetonato complexes/MAO systems [20].

The catalytic activity, microstructure, MW, and PDI were sensitive to experimental parameters such as temperature and Al to metal ratio (Table 1). Recently, Huang, and coworkers have reported that the catalytic activity of binuclear Cu and Ni complexes with bridging 2,5-diamino-1,4-benzoquinonediimines towards MMA polymerization first increased and then decreased with increasing temperature [20]. Similar trend is observed with bimetallic Pd catalyst (**3a**) albeit maximum activity is observed around 50 °C (Table 1). However, PMMA yield increases

Table 1 Bulk polymerization results of methyl methacrylate using monometallic Pd(II) (**5**) and Ni(II) (**6**), and bimetallic Pd(II) (**3**) and Ni(II) (**4**) iminopyridyl complexes combined with methylaluminoxane (MAO)

Run No.[a]	Cat.	Temp. (°C)	Al/Mt	Yield[b] (%)	R_p[c]	Triad fractions[d]			X_1^e	X_2^e	$M_n^f \times 10^{-4}$	PDI[f]
						mm	*mr*	*rr*				
1	**3a**	50	2,000	77.4	11.31	9.4	26.3	64.3	3.4	0.71	1.4	3.63
2	**3a**	50	1,000	43.5	6.38	8.4	25.5	66.1	3.4	0.67	1.4	3.42
3	**3a**	50	500	15.3	2.25	7.4	23.3	69.3	3.7	0.64	1.9	2.32
4	**3a**	30	2,000	0.3	0.03	15.8	27.9	56.3	4.5	1.13	1.7	3.21
5	**3a**	70	2,000	49.6	7.25	8.8	24.3	66.9	3.9	0.72	3.3	2.34
6	**4a**	50	200	2.4	0.34	5.9	28.2	65.9	1.9	0.42	3.9	1.29
7	**4a**	50	500	7.5	1.09	2.9	31.7	65.4	0.7	0.18	3.2	1.40
8	**4a**	50	1,000	3.4	0.50	11.1	31.9	57.0	2.4	0.70	3.0	1.89
9	**4a**	30	500	1.0	0.16	9.5	29.7	60.8	2.6	0.64	1.9	2.05
10	**4a**	70	500	8.9	1.31	7.5	30.3	62.2	2.0	0.50	1.6	2.01
11	**3b**	50	2,000	31	4.69	10.6	25.9	63.5	4.0	0.82	1.3	3.52
12	**4b**	50	500	3.5	0.53	5.9	30.2	63.9	1.6	0.40	2.7	1.35
13	**5**	50	2,000	18.6	2.72	8.0	25.4	66.6	3.3	0.63	1.2	2.11
14	**6**	70	500	6.7	0.97	4.3	34.2	61.5	0.9	0.25	3.6	1.33

[a] Polymerization conditions: MMA = 5 mL, catalyst = 8 μmol of metal, and time = 4 h

[b] Yield defined as the mass of dry polymer recovered/mass of monomer used

[c] Rate of polymerization in 10^4 g PMMA mol^{-1}-Ni h^{-1}

[d] Triad tacticity measured by ^1H and ^{13}C NMR

[e] $X_1 = 4[rr][mm]/[mr]^2$; $X_2 = 2[mm]/[mr]$

[f] Determined by GPC

monotonously from 1.0% at 30 °C to 8.9% at 70 °C for bimetallic Ni catalyst (**4a**).

The polymerization rate increases with Al/Pd ratio, resulting in maximum activity (1.131×10^5 g PMMA mol-Pd^{-1} h^{-1}) at Al/Pd = 2,000 (run no. 1). For Ni catalyst, maximum activity (1.31×10^4 g PMMA mol-Ni^{-1} h^{-1}) is observed around the Al/Ni ratio of 500 (run no. 10) and further increase of co-catalyst amount results in the decline of activity (run no. 8). The syndiotacticity of PMMA by **3a**/MAO catalyst increases from *rr* = 56.3% at 30 °C to 66.9% at 70 °C, however, no similar trend is observed for **4a**/MAO system. For both systems the syndiotacticity and MW decrease as Al to metal ratio increases.

The number average MW (M_n) values of PMMAs are in the range of 1.3–3.3 × 10^4 g mol^{-1} for **3a**/MAO and 1.6–3.9 × 10^4 g mol^{-1} for **4a**/MAO catalyst. The PDI values are in the range of 2.32–3.63 for **3a**/MAO system and 1.15–2.22 for **4a**/MAO system. Comparing M_n and PDI values of PMMA (run no. 1 vs. 11 and 7 vs. 12), the bulky aryl substituents have little effect on the chain transfer reactions. It is quite different from the generally observed phenomena in olefin polymerizations [2, 3], demonstrating the chain transfer reactions of MMA polymerization are different from those of olefin polymerization. The PDI values of PMMA obtained by bimetallic **3a** and **4a** complexes are higher than those of PMMA by their monometallic analogs **5** and **6** (run no. 1 vs. 13 and 7 vs. 14) and no bimodal distribution phenomena are observed for both bimetallic **3a** and **4a** complexes. It indicates that relatively higher PDI values of PMMAs obtained by the bimetallic complexes are most probably due to the cooperative interactions of the two adjacent metal centers in bimetallic complex systems. Since two metal centers are electronically coupled through the ligand bridge, the interaction between the two metals makes it possible to create more than one kind of active species during the polymerization [15], and the growing polymer chains from the two metal centers might induce some unexpected transfer reactions that are not expected in monometallic systems. Thermal characterizations revealed that glass transition temperatures of PMMAs produced by **3a**/MAO and **4a**/MAO are 126 and 128 °C, respectively, and are consistent with the characteristic of syndiorich atactic PMMA [32].

3.3 UV–Visible Analysis

UV–visible analysis for both Ni and Pd systems were carried out in toluene at 25 °C in the presence of MMA/MAO to get an insight into the active species formed during the polymerization. As shown in Fig. 2, absorption spectra of **3a** and **4a** bimetallic complexes and MMA showed no characteristic peaks between 350 and 600 nm. By combining **3a** and **4a** complexes with MAO and then with MMA, two new absorption peaks (409, 354 nm for **3a**/MAO/MMA system and 488, 449 nm for **4a**/MAO/MMA system) were observed. It is interesting to note that much stronger absorption peaks were observed for **3a**/MAO/MMA system at the same conditions and that this system showed much higher activity than **4a**/MAO/MMA system. Most probably, those newly appeared peaks are related to the formation of active sites. The position of absorption bands of transition metal complexes can be attributed to *d–d* transitions or to ligand to metal charge transfer band (LMCT), which can be varied depending on the metal geometry and therefore reflects the changes occurring in the coordination sphere of the metal [33].

3.4 Mechanistic Considerations

Recently, the possibility of free radical polymerization mechanism or coordination-insertion mechanism has been proposed for transition metal catalyzed polymerization of acrylates [34–38]. Novak and coworkers [34] have reported for neutral Pd catalysts in acrylate polymerization that an efficient radical inhibitor, galvinoxyl, can completely inhibit the process of polymerization, suggesting that the polymerization occurs via a radical mechanism. Li and et al. [37] reported that the syndiospecific polymerization of MMA catalyzed by the neutral nickel complexes bearing ketoamino ligands did not occur via a radical mechanism, as the adding galvinoxyl as a free radical inhibitor cannot inhibit the polymerization. Since MAO can react with galvinoxyl, this test is not reliable which may lead to wrong conclusion [38]. However, we evaluated the effect of radical inhibitor on the polymerization of MMA for both Ni and Pd bimetallic systems. Under standard conditions and adding five equivalent (per metal) of TEMPO as a free radical inhibitor, polymer yield, and catalyst productivity remained substantially the same, thus indicating that the polymerization of MMA may not occur via a radical mechanism. It was reported that the polymerization of MMA by Ni(acac)$_2$ [31] and salicylaldiminate nickel complexes [8–10] with MAO proceeds by a coordination-insertion mechanism.

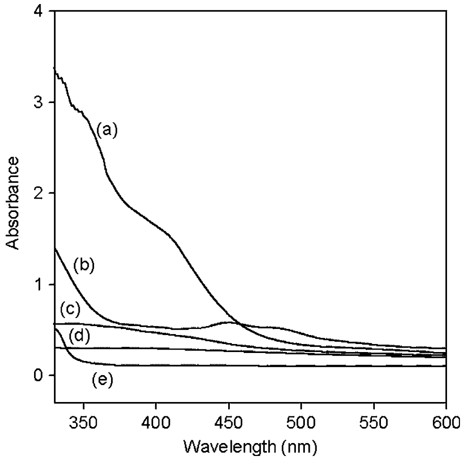
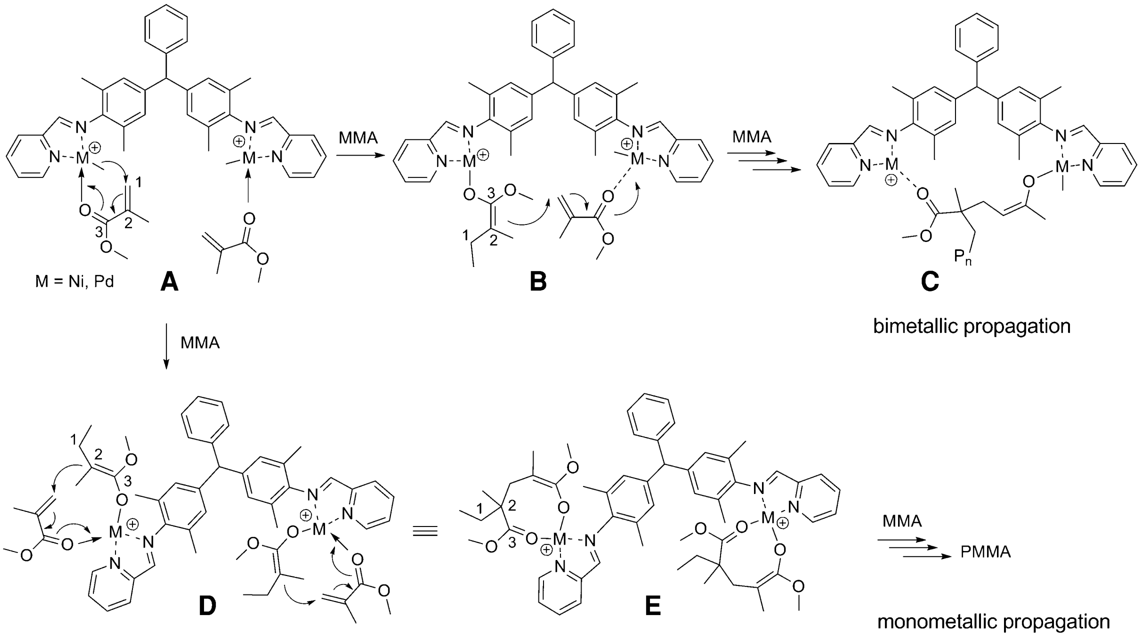


Fig. 2 UV–Vis absorption spectra of reaction mixtures of various catalyst precursors of the general formula: $[(2\text{-}C_5H_4N)\text{–}C{=}N\text{–}(Z)\text{–}N{=}C\text{–}(2\text{-}C_5H_4N)][MX_2]_2$ $\{Z = (2,6\text{-}C_6H_2Me_2)_2CH(4\text{-}C_6H_5);\ MX_2 = PdCl_2$ (**3a**), $NiBr_2$ (**4a**)$\}$: (a) **3a**/MAO/MMA (1/100/200), (b) **4a**/MAO/MMA (1/100/200), (c) **3a**, (d) **4a**, and (e) MMA in toluene at 25 °C

Triad testes may be a good clue to differentiate between enantiomorphic site control and chain end control. In the former case $2[mm]/[mr]$ should equal to one and in the latter, $4[rr][mm]/[mr]^2$ is theoretically unity [39]. The values based on these approximations are shown in Table 1. Although both values are quite far from unity, X_2 values are closer to one than X_1 values with a few exceptions. In addition both Pd(II) and Ni(II) catalysts yield syndiorich PMMA and Ni(II) catalysts showed high activity in ethylene oligomerizations [25–27] which can be considered as a support for coordination-insertion mechanism. These results suggest that the MMA polymerization proceeds via most probably with a metal coordination-insertion mechanism, although there are no other solid evidences to exclude a free radical mechanism.

The mechanism of chain growth in MMA polymerization involves displacement of a coordinated ester group of a growing chain by a coordinating MMA molecule, followed by MMA addition via an ester enolate intermediate, analogs to that proposed for MMA polymerization initiated by lanthanocenes [40] as shown in the Scheme 2 (monometallic propagation). During monometallic propagation a slow initiation step involves methyl transfer to the coordinated MMA leading to a cationic nickel/palladium enolate. The prochiral sp^2 carbon atom of MMA (carbon-2 in Scheme 2) remains prochiral after MMA addition, which is transformed into the prochiral sp^2 carbon atom (**B** in Scheme 2) of the ester enolate growing chain [41]. The double bond from 1,2 position is shifted to 2,3 position as shown in **B** (Scheme 2) and the repeating unit is added to this double bond. During MMA addition the prochiral sp^2 carbon of the ester enolate growing chain becomes a chiral sp^3 carbon atom (**C** in Scheme 2) which helps to determine the tacticity of the polymer. Thus in MMA polymerization sterioselectivity depend on the preferential approach of enatioface of the ester enolate growing chain to the adding monomer. But in α-olefin polymerization (e.g., propene) the prochiral sp^2 carbon of monomer becomes a chiral sp^3 carbon immediately after monomer insertion and the sterioselectivity depend on the preferential approach of monomer enatioface [41]. Subsequent events involves MMA binding to **D** in Scheme 2 and



Scheme 2 Plausible mechanistic pathway for methyl methacrylate polymerization by using bimetallic Pd(II) (**3**) and Ni(II) (**4**) iminopyridyl complexes combined with methylaluminoxane

repeated intramolecular Michael additions involved in propagation steps, produce PMMA via a monometallic propagation mechanism. Experimental mechanistic studies evidenced that the resting state is the eight membered ring **E** of Scheme 2 [41].

For bimetallic catalysts, a competition between the monometallic and bimetallic propagation mechanism can be expected [32, 42] and it will be more facile than monometallic catalysts since the two metals lie within a limited boundary. To get an insight into the propagation steps, molecular models of resting states **C** and **E** in Scheme 2 were built by using Hyperchem® software [23]. A series of geometry optimization and molecular mechanics (MM) calculations demonstrated that the energy of the resting state of monometallic propagation **E** with Pd bimetallic catalyst (79.30 kJ/mol) is higher than that (66.35 kJ/mol) of bimetallic propagation step **C**. It indicates that the resting state C is more favorable than **E**. Similar results were also observed with Ni complex. The growing polymer chain from one center may migrate to another adjacent center as shown in the bimetallic propagation step **C** in Scheme 2. Since Ni is more oxophillic than Pd, the resting state of Ni complex will be more intact, resulting in retarding further immediate insertion. This leads to low polymerization activity for Ni catalysts than their Pd analogs. Bimetallic propagation might induce some unexpected transfer reactions to enhance the polymerization activity mainly due to the effective spacial communication of the adjacent metals.

4 Conclusions

A series of structurally modulated iminopyridyl Pd(II) and Ni(II) mononuclear bimetallic catalysts were synthesized and screened for the bulk polymerizations of MMA in the presence of MAO as a co-catalyst. Pd(II)/MAO catalysts show much higher activity than Ni(II)/MAO catalysts bearing the same ligands. Due to the cooperative effects induced by two metal centers, bimetallic catalysts are more active than monometallic catalysts, especially for Pd(II) catalysts. The activity and polymer properties were sensitive to polymerization parameters such as temperature and MAO to metal ratio. The resulting PMMAs were characterized by moderate syndiotacticity (*rr* values ranged from 56 to 72%), moderate MW, and narrow PDI, depending upon the type and number of metal and polymerization parameters.

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References

1. Britovsek GJP, Gibson VC, Wass DF (1999) Angew Chem Int Ed 38:428
2. Ittel SD, Johnson LK, Brookhart M (2000) Chem Rev 100:1169
3. Gibson VC, Spitzmesser SK (2003) Chem Rev 103:283

4. Boffa LS, Novak BM (2000) Chem Rev 100:1479
5. Speiser F, Braunstein P, Saussine L (2005) Acc Chem Res 38:784
6. Zhang J, Wang X, Jin G-X (2006) Coord Chem Rev 250:95
7. Coutinho FMB, Costa MAS, Monteiro LF, Maria LC (1997) Polym Bull 38:303
8. Carlini C, Martinelli M, Galletti AMR, Sbrana G (2003) J Polym Sci A: Polym Chem 41:2117
9. Carlini C, Martinelli M, Passaglia E, Galletti AMR, Sbrana G (2001) Macromol Rapid Commun 22:664
10. Carlini C, Luise VD, Martinelli M, Galletti AMR, Sbrana G (2006) J Polym Sci A: Polym Chem 44:620
11. Kim I, Hwang JM, Lee JK, Ha CS, Woo SI (2003) Macromol Rapid Commun 24:508
12. Kim I, Kim JS, Han BH, Ha CS (2003) Macromol Res 11:514
13. Noe G, Rçder JC, Dechert S, Pritzkow H, Bolk L, Mecking S, Meyera F (2006) Adv Synth Catal 348:887
14. Li L, Metz MV, Li H, Chen MC, Marks TJ, Liable-Sands L, Rheingold AL (2002) J Am Chem Soc 124:12725
15. Zhang D, Jin G-X (2003) Organometallics 22:2851
16. Hu T, Tang L-M, Li X-F, Li Y-S, Hu N-H (2005) Organometallics 24:2628
17. Döhler T, Görls H, Walther D (2000) Chem Commun 11:945
18. Walther D, Döhler T, Theyssen N, Görls H (2001) Eur J Inorg Chem 8:2049
19. Taquet JP, Siri O, Braunstein P (2006) Inorg Chem 45:4668
20. Huang Y-B, Tang G-R, Jin G-Y, Jin G-X (2008) Organometallics 27:259
21. Jie S, Zhang D, Zhang T, Sun W, Chen J, Ren Q, Liu D, Zheng G, Chen W (2005) J Organomet Chem 690:1739
22. He X, Yao Y, Luo X, Zhang J, Liu Y, Zhang L, Wu Q (2003) Organometallics 22:4952
23. Bahuleyan BK, Son GW, Park DW, Ha CS, Kim I (2008) J Polym Sci A: Polym Chem 46:1066
24. Wayland BB, Schramm RF (1969) Inorg Chem 8:971
25. Laine TV, Piironen U, Lapalainen K, Klinga M, Aitola E, Leskela M (2000) J Organomet Chem 606:112
26. Laine TV, Lapalainen K, Liimatta J, Aitola E, Lofgren B, Leskela M (1999) Macromol Rapid Commun 20:487
27. Britovsek GJP, Baugh SPD, Hoarau O, Gibson VC, Wass DF, White AJP, Wiliams DJ (2003) Inorg Chem Acta 345:279
28. Sun H, Shen Q, Peng X, Yang M (2002) Catal Lett 80:11
29. Mi X, Ma Z, Wang L, Ke Y, Hu Y (2003) Macromol Chem Phys 204:868
30. Ihara E, Fujimura T, Yasuda H, Maruo T, Kanehisa N, Kai Y (2000) J Polym Sci A: Polym Chem 38:4764
31. Endo K, Inukai A (2000) Polym Int 49:110
32. Ning Y, Cooney MJ, Chen Y-X (2005) J Organomet Chem 690:6223
33. Coevoet D, Cramail H, Deffieux A (1998) Macromol Chem Phys 199:1451
34. Tian G, Boone HW, Novak BM (2001) Macromolecules 34:7656
35. Elia C, Sharon EB, Sen A (2002) Organometallics 21:4249
36. Albéniz AC, Espinet P, Raquel LF (2003) Organometallics 22:4206
37. Li X-F, Li Y-G, Li Y-S, Chen Y-X, Hu N-H (2005) Organometallics 24:2502
38. Nagel M, Paxton WF, Sen A, Zakharov L, Rheingold A (2004) Macromolecules 37:9305
39. Resconi L, Cavallo L, Fait A, Piemontesi F (2000) Chem Rev 100:1253
40. Yasuda H, Yamamoto H, Yokota K, Miyake S, Nakamura A (1992) J Am Chem Soc 114:4908
41. Caporaso L, Cavallo L (2008) Macromolecules 41:3439
42. Li Y, Ward DG, Reddy SS, Collins S (1997) Macromolecules 30:1875